UNIVERSITY OF CYPRUS
DEPARTMENT OF CHEMISTRY

Doctorate Thesis

Zwitterionic Biscyanines and Related Compounds

Theodosia Athinagora Ioannou

May 2013

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May 2013

EXPERIMENTAL PROCESSES ACCOMPLISHMENT STATEMENT

Except where noted below the work described within this thesis has been carried out exclusively by Theodosia A. Ioannou at the Organic Chemistry Research Laboratory, in the Department of Chemistry under the supervision of Dr. Panayiotis A. Koutentis, (January 2005 - January 2012).

The exceptions include: the single crystal X-ray crystallographic studies (performed by Dr. Anastasios J. Tasiopoulos of the Department of Chemistry, University of Cyprus); some theoretical calculations (performed by Prof. Michael Bendikov of Weizmann Institute of Science), some NMR spectroscopy (performed by Maria Koyioni, PhD student of University of Cyprus), the elemental analysis of all compounds (performed by Stephen Boyer of London Metropolitan University) and high resolution mass spectrometry (performed by John Barton of Imperial College London).

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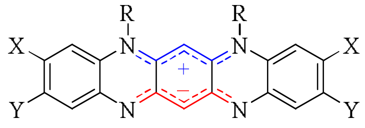

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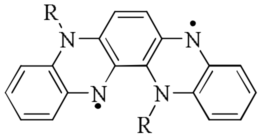

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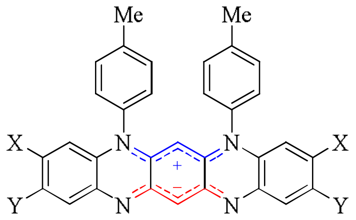

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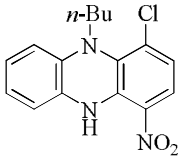

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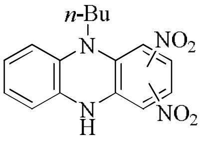

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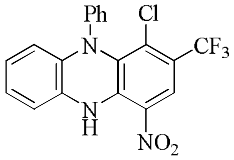

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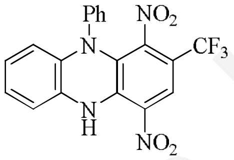

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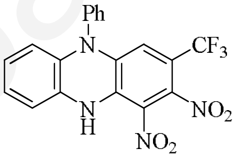

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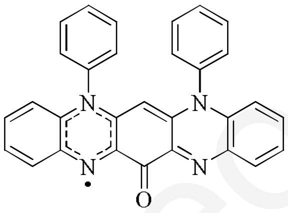

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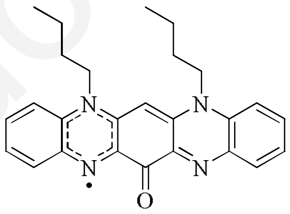

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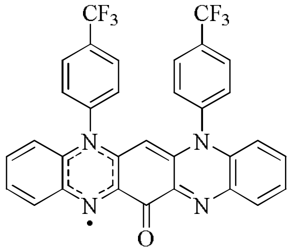

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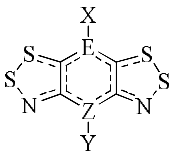

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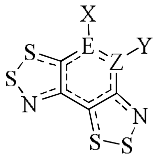
182 (E = CH, Z = N)
183 (E = N, Z = CH)
184 (E = Z = N)



181a (E = Z = CH)
185 (E = CH, Z = N)
186 (E = N, Z = CH)
187 (E = Z = N)

ABSTRACT

Linear and angular tetraazapentacenes are studied to ascertain their electronic structures. The research and discussion section (Chapters 2-5) follows an introduction on organic materials with semiconducting or magnetic properties (Chapter 1).

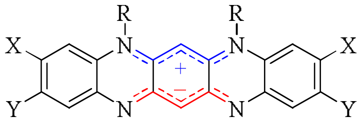
Chapter 2 focuses on linear tetraazapentacenes **51**, which prefer the zwitterionic singlet ground state instead of a triplet or singlet diradical state. On the contrary the angular **89** motif prefers a triplet ground state where the two free spins are located parallel to each other. With the linear tetraazapentacenes, various substitution patterns at strategic positions are shown to influence the energy gaps between the singlet-triplet states.

Chapters 3 describes the synthesis of linear tetraazapentacenes where a series of substituted linear tetraazapentacenes **91** (tolyl analogs of systems **51**) are synthesized in order to have spectroscopic data of these zwitterionic singlet ground state molecules that can be compared with the computational data. The agreement of the computational and spectroscopic data validates the computational method chosen.

Attempt to synthesize the angular tetraazapentacene **89** leads to the synthesis of a series of side products, phenazines **146**, **148**, **173**, **176**, **177**, and to an unexpected but important product, the linear radical **158**. This is covered in Chapter 4, where the mechanistic paths are analyzed as well as the alternative synthetic paths that were taken.

The related linear and angular arene-fused bis(1,2,3-dithiazoles) **180** and **181** were also studied towards their singlet-triplet energy gaps (Chapter 5). These systems are shown to be stabilized in the triplet or singlet diradical ground state but more towards the triplet ground states in the angular motif. The singlet and triplet states of the substituted benzo, pyrido **182** (X = CH, Y = N), **183** (X = N, Y = CH) and pyrazino **184** (X = Y = N) linear fused bis(1,2,3-dithiazoles) as well as their corresponding angular analogs **185-187** have been studied as well, showing singlet states for **182** and **184** while all the others are stabilized as triplet or singlet diradicals.

Chapter 6, the experiemental section, describes the synthetic procedures and spectroscopic characterization details for all synthesized products.



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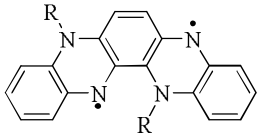

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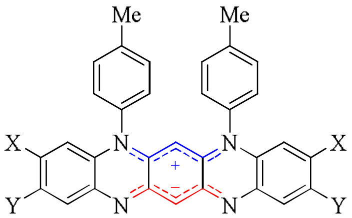

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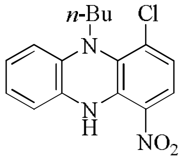

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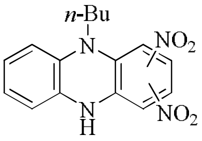

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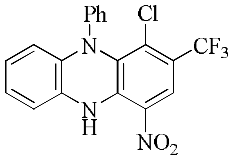

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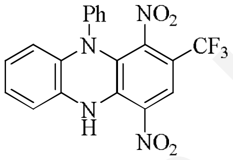

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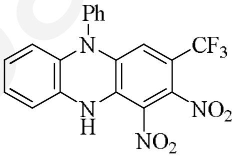

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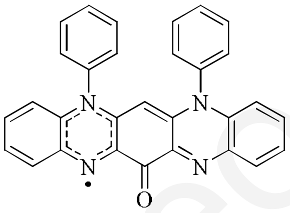

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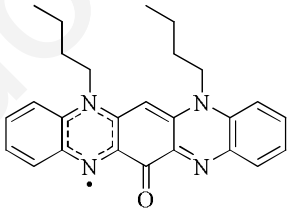

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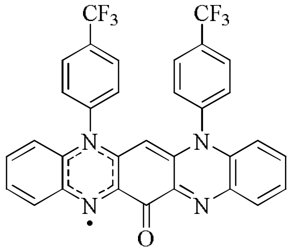

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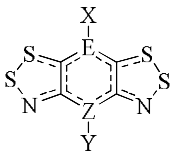

180a (E = Z = CH)
182 (E = CH, Z = N)
183 (E = N, Z = CH)
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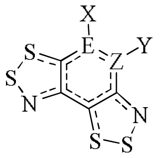

181a (E = Z = CH)
185 (E = CH, Z = N)
186 (E = N, Z = CH)
187 (E = Z = N)

ΠΕΡΙΛΗΨΗ

Γραμμικά και γωνιακά τετρααζαπεντακένια μελετούνται για την εξακρίβωση των ηλεκτρονιακών τους ιδιότητες. Η έρευνα και η συζήτηση (Κεφάλαια 2-5) παρατίθενται μετά από μια εισαγωγή περί οργανικών υλικών με ημιαγώγιμες και μαγνητικές ιδιότητες (Κεφάλαιο 1).

Το Κεφάλαιο 2 εστιάζεται στα γραμμικά τετρααζαπεντακένια **51**, που προτιμούν την αμφιπολική απλή θεμελιώδη κατάσταση αντί της τριπλής ή απλή κατάστασης δίριζας. Αντίθετα το γωνιακό σύστημα **89** προτιμά την τριπλή θεμελιώδη κατάσταση όπου τα μονήρη ηλεκτρόνια έχουν παράλληλη διευθέτηση. Στα γραμμικά συστήματα, διάφοροι υποκαταστάτες σε στρατηγικές θέσεις φαίνεται να επηρεάζουν την ενεργειακή διαφορά απλής-τριπλής κατάστασης.

Το Κεφάλαιο 3 περιγράφει τη σύνθεση των γραμμικών τετρααζαπεντακενίων όπου μια σειρά από υποκατεστημένα τετρααζαπεντακένια **91** (ανάλογα των συστημάτων **51** με *N*-τολυλ ομάδες) συντίθενται με σκοπό να συγκριθεί η φασματοσκοπία τους με τα δεδομένα που εξήχθησαν από την υπολογιστική μελέτη. Η συμφωνία μεταξύ τους πιστοποιεί την υπολογιστική μέθοδο που χρησιμοποιήθηκε.

Προσπάθεια σύνθεσης του γωνιακού τετρααζαπεντακενίου **89** οδηγά στη σύνθεση μιας σειράς παράπλευρων προϊόντων, των φαιναζινών **146**, **148**, **173**, **176**, **178**, και σε ένα απρόσμενο αλλά σημαντικό προϊόν, τη γραμμική ρίζα **158**. Αυτά καλύπτονται στο Κεφάλαιο 4, όπου αναλύεται ο μηχανισμός που οδήγησε στη σύνθεση της αλλά και η εναλλακτική πορεία που προτάθηκε.

Μελετήθηκαν επίσης τα ανάλογα γραμμικά και γωνιακά συστήματα 1,2,3-διθειαζολών **180** και **181** (Κεφάλαιο 5). Τα συστήματα αυτά φαίνεται να σταθεροποιούνται στην τριπλή ή απλή θεμελιώδη κατάσταση δίριζας ενώ περισσότερη σταθεροποίηση στην τριπλή κατάσταση παρουσιάζεται στα συστήματα με γωνιακή διαμόρφωση. Επιπρόσθετα μελετήθηκαν οι απλές και τριπλές κατάστάσεις των υποκατεστημένων βένζυλο, πυριδο **182** (X = CH, Y = N), **183** (X = N, Y = CH) και πυραζινο **184** (X = Y = N) γραμμικών συγχωνευμένων δις(1,2,3-διθειαζολών) καθώς και τα ανάλογα γωνιακά συστήματα **185-187** όπου παρουσιάστηκς η προτίμηση των συστημάτων **182** και **184** στην απλή θεμελιώδη κατάσταση ενώ όλα τα υπόλοιπα σταθεροποιούνται στην τριπλή ή απλή κατάσταση δίριζας.

Το Κεφάλαιο 6 καλύπτει τον χαρακτηρισμό των προϊόντων που συντέθηκαν.

ACKNOWLEDGEMENTS

I like to thank my supervisor Dr. P. A. Koutentis for providing the opportunity to work on the project described herein.

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I thank all past members of KRG group, particularly Irene, Haris, Sophia, George and Georgia for being so friendly and for their support and all the new members of the group especially Styliana, Maria, Georgia and Andreas for proof-reading my thesis. Also I would like to give many thanks and my appreciation to Maria Koyioni for her help on establishing the NMR spectroscopy on some synthesized systems and Christos Constantinides for his help and discussions on computational chemistry. Outside of the lab I thank my friends Natasa, Evi, Elena, Tina, Maria, Stella and Andreas for their friendship, patience and support and my friends and colleagues Nancy and Andreas for being in my life less than one year but asking everyday about my thesis progress.

Finally I would like to thank my family for their love, support and encouragement.

CONTENTS

Brief Contents

Detailed Contents

ABBREVIATIONS

Å	Ångströms
A	amperes
Ac	acetyl
aq.	aqueous
Ar	aryl
Bn	benzyl
BS	broken symmetry
Bz	benzoyl
ca.	approximately
cf.	compare
CI	configuration interactions
cm	centimetres
cm^{-1}	wavelength unit
d	doublet (NMR) or days
DCE	1,2-dichloroethane
DCM	dichloromethane
dd	double doublet
DEPT	distortionless enhancement by polarization transfer
DHTAP	dihydrotetraazapentacene
DFT	density functional theory
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
DMSO-d_6	deuterated dimethylsulfoxide
DPPH	*N*,*N*-diphenyl-*N*′-picrylhydrazyl
DSC	differential scanning calorimetry
DTQP	5,7-di-(*p*-tolyl)-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide
E^+	electrophile
EA	electron affinity
EDG	electron-donating group
e.g.	for example
EI	electron ionization

equiv.	equivalent
ESR	electron paramagnetic resonance
eV	electron volt unit
EWG	electron-withdrawing group
f(r)	function
FTIR	Fourier transform infrared
G	gas
GCMS	gas chromatography mass spectrometry
h	hour
Hal	halogen
HOMO	highest occupied molecular orbital
Hünig's base	*N*,*N*-diisopropylethylamine (i-Pr_2EtN)
Hz	Hertz unit
IE	ionization energy
inf.	inflection
I_p	ionization potential
IR	infrared
J	coupling constant
K_{ET}	electron-transfer rate
LG	leaving group
lit.	literature
LRMS	low resolution mass spectrometry
LUMO	lowest unoccupied molecular orbital
m	multiplet (NMR) or medium (IR) or metres
m/z	mass to charge ratio
M^+	molecular ion
2-MeTHF	2-methyltetrahydrofuran
MHz	megahertz unit
min	minutes
MO	molecular orbital
mp	melting point
MW	microwave
NBMO	nonbonding molecular orbital

NICS	nucleus independent chemical shift
nm	nanometer unit
NMR	nuclear magnetic resonance
Nuc	nucleophile
^{o}C	degrees Celsius
OLED	organic light-emitting diode
OFET	organic field-effect transistor
OSC	organic solar cell
ox	oxidation
p-NPNN	*p*-nitrophenyl nitronyl nitroxide
Ph	phenyl
PhCl	chlorobenzene
PhH	benzene
PhMe	toluene
ppm	parts per million
PTM	polychlorinated triphenylmethyl
q	quartet
rt	room temperature (*ca.* 20 ^{o}C)
s	singlet (NMR) or strong (IR)
S	Siemens
SOMO	singly occupied molecular orbital
SMM	single-molecule magnet
t	triplet
t	transfer integral
T	temperature
TAP	tetraazapentacene
T_c	Curie temperature
TCNQ	tetracyanoquinodimethane
TD	time-dependent
TEMPO	2,2,6,6-tetramethylpiperidine-*N*-oxyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TME	tetramethyleneethane

TMM	trimethylenemethane
Tol	tolyl
TPHA	tetraphenylhexaazaanthracene
TTF	tetrathiafulvalene
UV	ultra-violet
V	volts
vis	visible
w	weak (IR)
δ	chemical shift relative to a standard
Δ	heat (thermolysis)
ΔE_{HL}	energy difference between HOMO and LUMO
ΔE_{ST}	energy difference between the singlet and triplet states
λ_-	radical anion
λ_+	radical cation
λ_{max}	maximum wavelength
μ	mobility
Ω	Ohms

CHAPTER 1

Introduction

Sections **Page**

1.1 Organic Materials and Properties

Since the birth of electronic devices, life has become easier, and man’s work more efficient. Over the last decades, the amount of electronic devices used in our daily lives has increased. People now depend on them and demand that they become faster, smaller and “smarter”. To help achieve this, scientists search for and study new materials needed to develop new and improved devices that satisfy present and future needs.

The most important components in electronic devices are probably semiconductors. Owing to their advantages, semiconductor devices have replaced electron tubes in almost every application. For instance, semiconductor devices can function in hazardous environmental conditions since they are more rugged than electron tubes which are usually comprised of sealed glass or metal-ceramic enclosures. Due to their solid-state construction, semiconductors also eliminate the need for filaments or heater voltage and consequently no power input is required for operation, leading to instant, cooler and more efficient operation. The small size and the very low voltage ability operations are also advantages that semiconductor devices have. The ease to be damaged due to their sensitivity to temperature changes or inappropriate operating voltages are some of the disadvantages. Furthermore, the need for extremely high power in some applications, prohibits the entire replacement of electron tubes by semiconductor devices. These limitations however are being overcome as semiconductor technology develops. Some semiconductor devices are diodes (*e.g.*, light emitting diodes), transistors (*e.g.*, field effect transistors), solar cells and integrated circuits. By far, the most widely used material in such devices is silicon.[1]

Magnets are also widely found in devices used in our everyday life. They are used in the creation and distribution of electricity and are components in a plethora of electrical devices.[2] Their market is considered to be larger than that of semiconductors. Magnets have numerous applications such as (a) magnetomechanical applications *e.g.*, magnetic separators, (b) acoustic devices *e.g.*, loud-speakers and microphones; (c) electrical motors and generators; (d) information and telecommunication devices *e.g.*, fax machines and magnetic disks; and (e) magnetic shielding *e.g.*, high voltage electrical lines.[3] Electromagnets are made by a core, usually iron, and a wire coiled around it that concentrates the created magnetic field. Electromagnets, unlike permanent magnets, display magnetic properties only when electrical currents pass through them, either from a battery or another source of electricity and as such, they can be turned on and off.

Magnets and electricity have a complicated connection between them. Technically they both use the same particle: the electron. An electron moves and spins on its own axis at the same time. Whereas electricity is the result of its movement, the magnetic field is a result of its spin.

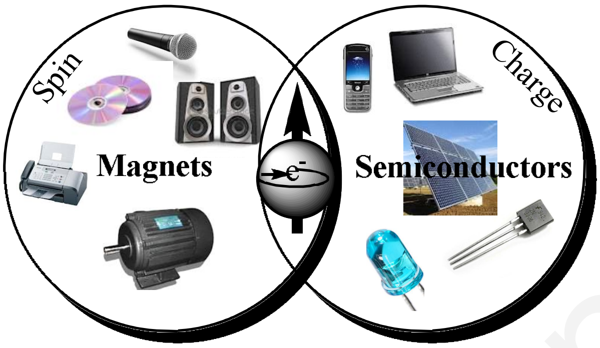


Figure 1. Different applications of magnets and semiconductors resulting by using the electrons' spins or charges.

Semiconductors use the transport of electron charge in integrated circuits for data processing, while magnets use the spins of electrons for data storage. As a consequence these basic components are used for different applications, however, a new class of devices called 'spintronic' or 'magnetoelectronic', require both properties by using conduction electrons' spins and not just their electrical charge in information circuits. A new generation of devices was born having the advantages of being smaller, more robust and having increased data processing speed, decreased electric power consumption and increased integration densities resulting in more capable and advanced electronic products.[4] The merging of electronics and magnetics promises new multifunctional devices but before this can become a reality, researchers need to find new materials that combine such properties *e.g.* ferromagnetic semiconductors and try to get a deeper understanding and control over spin related phenomena in magnetic and semiconductor materials.

The above electronic and magnetic properties are usually properties of inorganic elements. Organic compounds typically do not have such abilities. Only since the discovery of conductivity in polyethylene has the concept of using organics in electronic applications become accepted.[5] Organic systems that can easily process electron transport or organic systems with unpaired electrons, called open-shell, may have conductive and magnetic properties, respectively, giving rise to new applications. Organic semiconductors, organic magnets and even organic spintronics are now some of the top research areas being pursued for technology advancement. In the following sections brief discussions on organic semiconductors (Section 1.1.1) and organic magnets (Section 1.1.2) will be presented.

1.1.1 Electrical Conductivity and Organic Semiconductors

Conductors (and superconductors) and insulators are the two extremes of the ability to conduct charge, since the first class covers materials that include movable electric charges, while the second one covers materials that do not respond to an electric field and completely resist the flow of electricity. Semiconductors are a class of materials with intermediate electrical conductivity.

1.1.1.1 Electrical conductivity

The ability of a material to conduct charge is measured by its electrical conductivity σ and is measured in $\Omega^{-1}m^{-1}$. Electrical conductivity σ follows Ohm's law [$V = IR$, where V = Voltage drop in Volts (V), I = current in Amperes (A) and R = resistance in Ohms (Ω) or Siemens (S)]. This law can also be written as in the form $j = \sigma E$ where j is current density (current per unit area in A/m^2) and E is electric field or electrical potential gradient that comes out when the voltage drop is divided to the length of the material (L) $E = V/L$ measured in V/m.

Metals have large conductivities (> 10^5 $\Omega^{-1}m^{-1}$) that increase as temperature drops. By comparison, semiconductors have smaller conductivities and display different temperature dependence. This can be shown schematically in a spectrum of quantum excited states (Figure 2). Electrons on occupying frontier orbitals have a continuous range of energy levels in solids (band of quantum states). Quantum states of the electrons with low energy (closer to the nucleus) are full, up to a particular band called the valence band. The band immediately above the valence band is the conduction band where empty quantum states can accept electrons that can be excited from the valence band to the conduction band. The ease for this excitation depends on the energy gap between the two bands and this *band gap* distinguishes conductors, semiconductors and insulators. In fact, what distinguishes them is the size of the band gap between the Fermi level (or Fermi energy) and the conduction band. The Fermi energy of a substance is a result of the Pauli exclusion principle (stating that a maximum two electrons with opposite spins can be placed in each orbital) when the temperature of the material is lowered to absolute zero where all of the electrons in the solid attempt to get into the lowest available energy level. At absolute zero no electrons have enough energy to occupy any energy levels above the Fermi level. As the temperature of the material is raised above absolute zero the probability of electrons with energy greater than the Fermi energy increases and these electrons take part in electric conduction.

For metals, the Fermi energy level actually lies within the conduction band and it takes relatively little energy to bump these electrons into the band gap and that is why metals are typically good conductors. In case of semiconductors, the Fermi energy level lies between the valence band and conduction band, and more energy is required to excite the electrons sufficiently. For insulators, the Fermi level is considerably below the conduction band significantly reducing the movement of charges. In metals the highest energy occupied state and the least energy empty state do not differ much in energy, whereas in semiconductors or insulators they are separated by a significant energy gap. In semiconductors the energy gap is typically 0.5-3.0 eV while in insulators the gap is > 3 eV.[6]

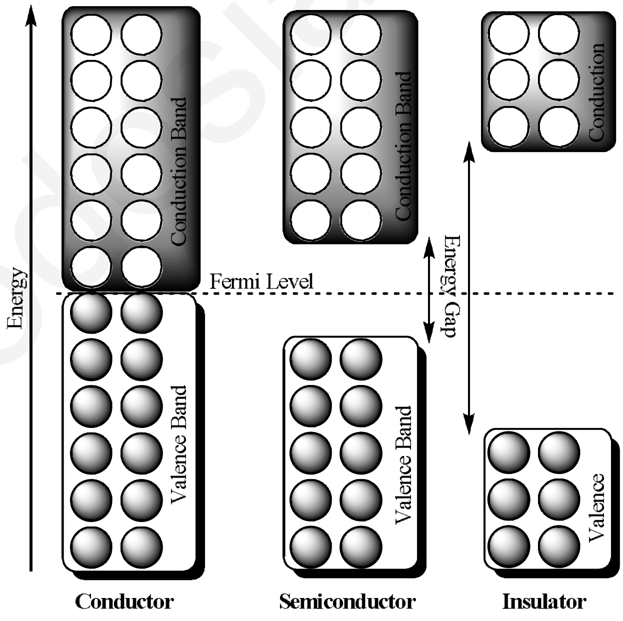


Figure 2. Schematic energy spectrum for metals, semiconductors and insulators. The valence and conduction bands are with filled and empty circles representing full and empty quantum states, respectively.

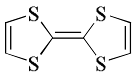
In both semiconductors and metals, the states that correspond to the frontier orbitals are mobile and thus electrons are permitted to travel from atom to atom while in insulators they are fairly immobile. Through covalent bonds, an electron moves by hopping to a neighboring bond. The Pauli exclusion principle requires the electron to be lifted into the higher antibonding state of that bond. For a net current to flow, more states for one direction than for the other direction must be occupied. Electrons excited to the conduction band also leave behind electron holes (unoccupied states in the valence band). Both the conduction band electrons and the valence band holes contribute to electrical conductivity. The holes themselves do not actually move, but a neighboring electron can move to fill the hole, leaving a hole at the place it had just come from, and in this way the holes appear to move, behaving as if they were actual positively charged particles.

Semiconductors are relatively poor conductors until they are "doped". The doping process inserts a small number of additional atoms into the crystal lattice of the original semiconductor. This in turn, provides additional levels, narrowing the band gap between the original valence and conduction bands. In this way its conductivity is greatly increased. This is usually achieved by adding elements like arsenic, phosphorous or boron. By doping with atoms that have more valence electrons than the host atoms in the existing semiconductor, then there are extra valence electrons between the two bands (n-type semiconductor) while by doping with atoms with less valence electrons then there are more "holes" (p-type semiconductor) facilitating the conduction.

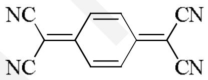
1.1.1.2 Organic semiconductors

Most organic solids are insulators for two main reasons: 1) There is a significant energy difference between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) and 2) the organic solids are usually molecular as they do not possess a system of covalent bonds extending over macroscopic distances. This results in small interactions between HOMOs of adjacent molecules forming a very narrow valence band and similarly a narrow conduction band arising from the small interactions between the LUMOs. Thus the band gap may be estimated as the HOMO-LUMO gap in a free molecule. To increase conductivity and access semiconductive properties in such systems, the HOMO-LUMO gap needs to be reduced. Extensive π-bonding or adding heteroatoms with lone pair electrons can give this result.

It was predicted in 1911 that certain organic solids may exhibit an electrical conductivity comparable to that of metals. This was confirmed in 1954 when Akamatu *et al.*,[7] reported a room temperature conductivity of around 10^{-1} S/cm for a bromine/perylene complex. Perylene itself is an insulator with a room temperature conductivity of around 10^{-15} - 10^{-17} S/cm. In this complex bromine acts as a donor/acceptor to give perylene an electron/hole enabling the flow of charge. Since then, considerable work has been carried out to prepare new conducting materials investigating properties of both donor and acceptor molecules. A major step was in 1972 when the acceptor molecule tetracyanoquinodimethane (TCNQ) and the donor molecule tetrathiafulvalene (TTF) were combined to form the charge transfer salt (TTF)(TCNQ) which was the first organic solid to show metallic conductivity over an extended temperature range.[8] Shortly afterwards, in 1977, Heeger, MacDiarmid and Shirakawa discovered metallic conductivity in iodine doped polyacetylene, the first conducting plastic.[5] For this discovery they received the Nobel Prize for Chemistry in 2000.



TTF



TCNQ

Why organic semiconductors? Organic semiconductors cannot compete with copper or silicon made devices on power but do display exciting properties, which enable new applications, that are not available to traditional semiconductors. They have the ability to be made in thin and flexible sheets, and thus can be used for displays on clothes or paper. Organic semiconductors are lighter, more flexible, and biodegradable compared to traditional semiconductors, furthermore, owing to advances in organic synthesis they can be manipulated and fine-tuned to provide tailored properties that fit specific applications at relatively low cost. *Applications.* Organic semiconductors have applications as optoelectronic materials and especially as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic solar cells (OSCs). OLEDs are based on electroluminescence instead of photoemission as in conventional LEDs and made possible the development of inexpensive and lightweight flat-panel displays. OFETs have been of great interest for applications, such as display drivers, identification tags and smart cards. Beside their advantages of low cost, flexibility and light weight, they can be processed at low temperatures compatible with plastic substrates, whereas higher temperatures are required for alternative Si-based FETs.[9-12] OFETs have led to a revolution in developing fast and inexpensive integrated circuits on plastic substrates based on organic semiconductor elements. When combined with the advantage of solution processability, organic materials allow for the use of a variety of printing techniques, such as inkjet printing and stamping, to fabricate large area devices at low cost. OSCs have reached quantum efficiencies that make them attractive for delivering cheap solar power.[13,14] Studies on OSCs have attracted particular attention due to the application of them in renewable green energy strategy.

1.1.2 Magnetism and Organic Magnets

Magnetism was first discovered by ancient Greeks when they noticed certain rocks called lodestones were naturally magnetized, and this was later exploited by Chinese workers who invented the compass.[15] The name comes from Magnesia, a district in Greece. Magnets can be "hard" (permanent) or "soft" (non-permanent). Permanent magnets produce an external magnetic field on other magnets or on an electric current, while non-permanent magnets guide or deflect magnetic fields and have large magnetic moments in response to small electric currents.

1.1.2.1 Magnetism

A typical magnetic material is attracted or repulsed to another magnet. This behavior arises from the intrinsic spin of an electron which, because it is negatively charged, has a magnetic dipole moment in the opposite direction to the moment of the spin. If a molecule has at least one orbital with an unpaired electron then there can be a net spin on a material composed of such molecules. Magnets are materials with ordered spins (parallel spins). If in the way that the molecules are ordered, the spins of the unpaired electrons are cancelled (opposite spins resulting from antiparallel alignment), then no magnetic behavior can be observed. Magnetism is usually not a molecular property but a macroscopic one and the total sum of all the individual spin magnetic moments must not be equal to zero. The vector sum when normalized to unit volume of the material is called magnetization (M).[16,17]

There are four main types of magnetic behavior: paramagnetism, ferromagnetism, ferrimagnetism and antiferromagnetism depending on the alignment of the spins in the solid state (Figure 3).[3,16,17]

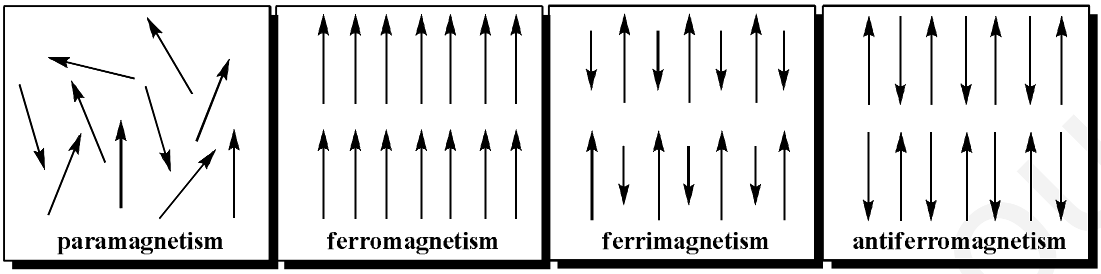


Figure 3. Spin alignment representations for the four main types of magnetism.

Paramagnetism: This is the most common behavior of organic molecules with one unpaired electron. In the solid state, independent uncoupled spins are separated in such a way that their spin coupling energy is much smaller than the thermal energy, leading to no interaction among them (no coupling). The distribution of the spins is random and there is a weak form of magnetism. Spins in a paramagnetic material are aligned with the application of an external magnetic field. If an external magnetic field of intensity H is applied and the field within the substance is B, such that $B > H$, the material is paramagnetic. With the removal of the external field on a paramagnetic material, the alignment of the spins breaks again.

Ferromagnetism: The most classic ferromagnet is iron. When the distances between neighboring molecules are such that the coupling energy is larger than the thermal energy, then there is alignment of the spins. In ferromagnetism, this alignment is parallel resulting in a net magnetic moment. In ferromagnets a percentage of the internal field B remains in the absence of an external magnetic field even after several years.

Ferrimagnetism: It is a kind of ferromagnetism and comes out from antiferromagnetism since the neighboring spins again are aligned antiparallel. The difference here is that spins have different magnetic moments and thus they do not cancel each other. As a result macroscopically there is a net moment and the material acts like a ferromagnet.

Antiferromagnetism: In this case, the coupling energy is again larger than the thermal energy but the magnetic spins are aligned antiparallel and such spins cancel each other. Thus there is no net magnetic moment. Since the antiparallel alignment of the spins is a process analogous to bond formation, this behavior is the most favorable.

Ferro-, and ferrimagnets are actually composed of small domains where the magnetic moments are aligned (Figure 4). The related direction of the magnetic moment in adjacent domains is not parallel. This phenomenon lowers the total energy of the magnet because if all the spins are parallel then there is a large energy stored in the magnetic field, however, in the domains the energy stored is small due to the fact that the magnetic moments point in various directions. By placing the material in a strong external magnetic field or by passing electrical current through it, some or all the magnetic domains become aligned. The more domains aligned, the stronger the magnetic field in the material.

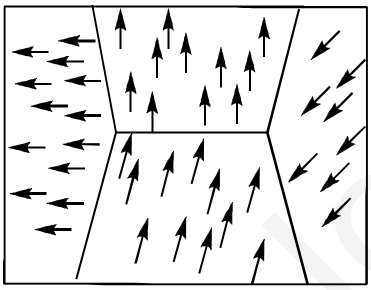


Figure 4. Spin alignment representations for domains within a ferromagnet.

All these types of magnets involve two-dimensional magnetic behavior. To achieve long range magnetic order and bulk ferromagnetic behavior, three dimensional interactions are typically necessary. Depending on the exchange interaction J, which is the type and degree of coupling between neighboring spins, the magnetic material can be ferromagnetic ($J > 0$) or antiferromagnetic ($J < 0$). There are three main ways to describe magnetic interactions:

Ferromagnetic exchange resulting from orthogonal orbitals: This happens when there are lone electrons in orthogonal orbitals which are located in the same spatial region. The antibonding space electron wavefunction is lower in energy than the bonding space electron wavefunction and the high spin state is stabilized. Examples are carbene (methylene)[18] and trimethylmethane.[19]

Interactions between spin containing species in different regions: Here the spins that interact are in different regions and the type of interaction (ferromagnetic or antiferromagnetic) is calculated by the total wavefunction of the system. If the spins are in the same molecule the unpaired electron in the SOMO (Singly Occupied Molecular Orbital) polarizes the paired electron spins in an orthogonal bond connecting it to another moiety containing an unpaired electron (spin polarization). If the spins are in different molecules the type of interaction is calculated by configuration interactions (CI) as the two molecules that contain spins approach each other.

Dipole-dipole exchange interactions: These interactions are performed between spins through space, and are independent of the orbitals overlap. These interactions are very weak and are created due to the magnetic fields from each molecule that contains spin. They can lead to the alignment of spins (ferromagnetic or antiferromagnetic) at very low temperatures (< 1 K). As such, they are important only at very low temperatures and can cooperate with the other two types of magnetic interactions leading to spin alignment.

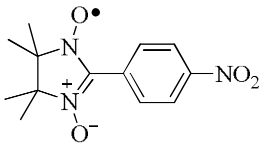
Dependence of magnetism: The manner in which spins couple (ferromagnetic *vs* antiferromagnetic) can be ascertained in a number of ways, with two of the more common being variable temperature ESR experiments and magnetic susceptibility experiments. Magnets are characterized by their response to the approach to another magnet. If the spins of a magnet do not interact, a net magnetic moment M, is induced in the magnet when exposed to an applied magnetic field, H. In this case M is proportional to H since $M = \chi H$, where χ, the proportionality constant, is defined as the molar magnetic susceptibility. The constant χ depends on temperature and is characterized by the Curie expression: $\chi = C/T$, where C is the Curie constant.

1.1.2.2 Organic magnets

Unpaired electrons are needed to have a potential magnet. In molecular organic magnets the unpaired electron is delocalized over the various atoms that constitute the molecule while in traditional inorganic magnets, the unpaired electron spin is largely confined to the metal ion center. Obtaining magnetic materials that are totally composed of organic molecules is challenging owing to the difficulty of having unpaired and aligned spins in organic molecules. Organic molecules with unpaired electrons are called radicals and are open-shell molecules since they have unfilled shells due to the unpaired electrons.

The control of the radical stability and reactivity in a single molecule and the prevention of cancellation of the spin in the three dimensions of the crystal structure are not readily achieved. As such, there are only a few known examples of organic radicals that display bulk ferromagnetism such as some nitroxy nitronyl[20] *e.g.*, *p*-nitrophenyl-nitronyl nitroxide (*p*-NPNN) **1** ($T_c = 0.65$ K)[21,22] and some verdazyl radicals.[20] However, these radicals only show ferromagnetism at temperatures below 1 K which is too low to be useful.[23] The fullerene-based charge transfer-salt [tetrakis(dimethylamino)ethylene]C_{60} exhibits ferromagnetism at higher temperature (T_c = 16.1 K) but still is too low.[24]

2,5,8-Tri-*tert*-butyl-phenalenyl **2**,[25] perchloro-2,5,8-triazaphenalenyl radical **3**[26] and 1-(4-chlorophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazinyl **4**[27] are some examples of organic radicals that exhibit antiferromagnetic behavior.



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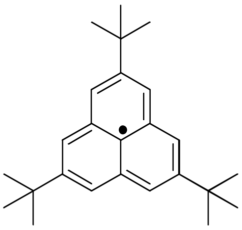

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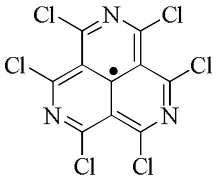

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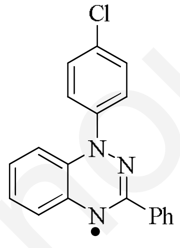

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Why organic magnets? While organic magnets do not possess the magnetic properties of their inorganic counterparts, they have several important advantages, making them worthy of study. These advantages include the high strength, mechanical flexibility, solubility, low temperature processability, low density, biocompatibility, transparency, high magnetizations and magnetic susceptibilities. Due to their structure, they may also have additional semiconducting properties, while their properties may be easily modulated by means of organic chemistry.[3]

Applications. A variety of applications of organic radicals were reported. For instance, polymers with magnetic properties like polythiophene with a nitroxide radical attached on each monomeric unit and polyethylene with verdazyl radical attached to each monomer were considered as magnetic inks.[28] Nitroxyl, verdazyl, hydrazinyl and aminotriazinyl radicals have found applications in batteries.[29] Hydrazinyls, verdazyls, pyridinyls, aryloxides and ionic radicals have been applied in photosensitive devices.[30] Verdazyl radical was also applied in electrochromic devices,[31] while nitroxide and benzodithiazolyl radicals found applications in spin probes.[32]

1.2 Electrons and Principles

To understand how electrons can provide magnetic or conductive properties in an organic system we need to understand the principles that describe their behavior. The energy of an electron is quantized, that is, limited to certain values and allowed energy states (orbitals). Orbitals are descriptions of the wave properties of electrons in atoms and molecules and show the region of space in which the electrons can be found. Using quantum mechanics (the theory that describes electrons behavior), Erwin Schrödinger expressed the picture of an orbital to be simplistic and inaccurate by showing regions of electron density with the location and route of the electron described as probabilities. Electron density is a measure of the probability of finding an electron in an orbital. Quantum mechanics describe orbitals by the mathematical wavefunction ψ. The sign of the wavefunction for an electron can be positive (+) for wave peak or negative (-) for a wave trough. The wavefunction is zero at a node, indicating zero probability for finding an electron.

Electrons in orbitals are characterized by quantum numbers which, for atoms, are n, l, m, and s. The principal quantum number n ($n = 1, 2, 3, \ldots$) describes the energy and size of an orbital (orbitals of higher n have higher energy); the angular momentum quantum number l (depends on n and takes any integer value from 0 to $n - 1$) describes the shape of an orbital [*e.g.*, $l = 0$ (s orbitals) are spheres]; the magnetic quantum number m (depends on l and takes values between -l and +l) describes the orientation of an orbital and the spin quantum number s assumes a value of +1/2 or -1/2. A number of principles are known that define the way electrons are placed in orbitals:

Heisenberg's uncertainty principle: the exact position and velocity of an electron cannot be specified but only the probability that it occupies a certain region of space can be specified.

Pauli's exclusion principle: a maximum of two electrons may be placed in any one atomic orbital, and these electrons must have opposite spins that are generally indicated by showing the electrons as arrows pointing up (↑) or down (↓).

Hund's rule: when electrons are distributed among identical orbitals of equal energy, single electrons are placed into separate orbitals before the orbitals are filled, and the spins of these unpaired electrons are the same.

Aufbau principle: to determine the electronic configuration of an atom, electrons are placed one by one into orbitals of the lowest possible energy in a manner consistent with the Pauli exclusion principle and Hund's rules and continues through the higher-energy shells, until the appropriate number of orbitals is filled for each atom. "Aufbau" means "building up" in German.

Chemical bonding can be an energetically favorable process. When atoms combine into a molecule, the electrons of each atom are no longer localized on individual atoms but belong and can be delocalized to the entire molecule. The combination of n atomic orbitals gives n molecular orbitals. Bonding molecular orbitals are formed when individual atomic orbitals constructively overlap, *i.e.* they arise through in phase interactions. The energy of an electron in the bonding molecular orbital is lower than that of an electron in an atomic orbital. When out of phase interactions take place between atomic orbitals, then antibonding molecular orbitals are formed and the energy of electrons in these are higher than in the atomic orbitals.

Molecular orbitals have different energies and are arranged in order of increasing energy, then populated with electrons according to the Pauli and Aufbau principles and Hund's rules. The electrons occupy the bonding molecular orbitals before occupying the antibonding orbitals. The most common bonding situations occur when bonding molecular orbitals contain electron pairs and antibonding molecular orbitals are empty. The above rules are valid both for atomic orbitals in an element *e.g.*, carbon (Figure 5a) and molecular orbitals in a molecule *e.g.*, ethyne (Figure 5b).

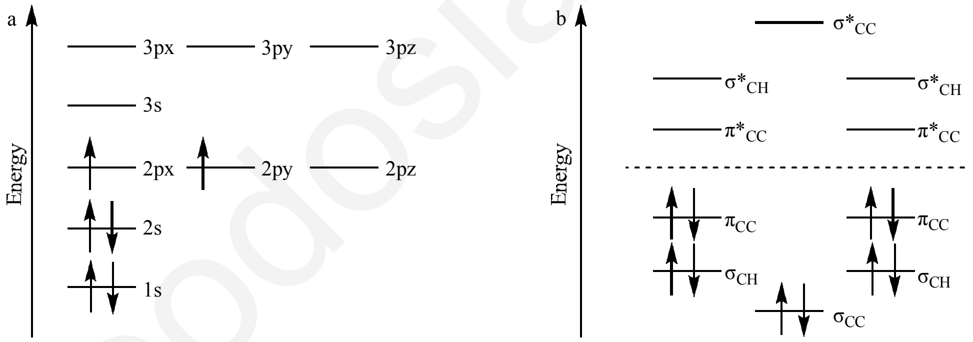


Figure 5. Filling a) the atomic orbitals of carbon atom and b) the molecular orbitals in ethyne.

The "octet rule" is a bonding theory according to which each atom will share, gain, or lose electrons in order to fill outer electron shells with eight electrons. There are many exceptions to the octet rule and can be separated in three classes: i) electron deficient molecules where some elements in these molecules have not enough electrons to form an octet *e.g.*, boron; ii) expanded octets where elements in periods greater than period 3 on the periodic table are included and due to *d* orbitals can expand their valence shells to accommodate more than eight electrons *e.g.*, sulfur; and iii) free radicals where the valence electrons contain an odd number of electrons in the valence shell.

While the first two classes of exceptions can be considered stable due to the pairing of electrons despite having less or more than eight electrons in the outer shell, the third class where unpaired electrons exist is a different story. The existence of unpaired electrons can change the chemistry and the properties of the system since due to violation of the octet rule upon pairing of electrons that stabilizes each atom, unpaired electrons are highly reactive and try to form bonds. Molecular oxygen for example is a molecule with two unpaired parallel electrons in its outer shell placed in two degenerate orbitals (orbitals of equal energy) (Figure 6). It can be often represented as •O-O• and is considered as a stable diradical (triplet state, see Section 1.3.3). Due to the unpaired electrons though, molecular oxygen does not react directly with many other systems that have only pairs of electrons in their electronic configuration (singlet state) but easily reacts with other radicals with an unpaired electron (doublet state) and thus is susceptible to radical formation giving reactive oxygen species (ROS•) like the superoxide anion ($O_2{\bullet}^-$), hydroperoxide radical ($HO_2\bullet$) and hydroxyl radical (•OH).

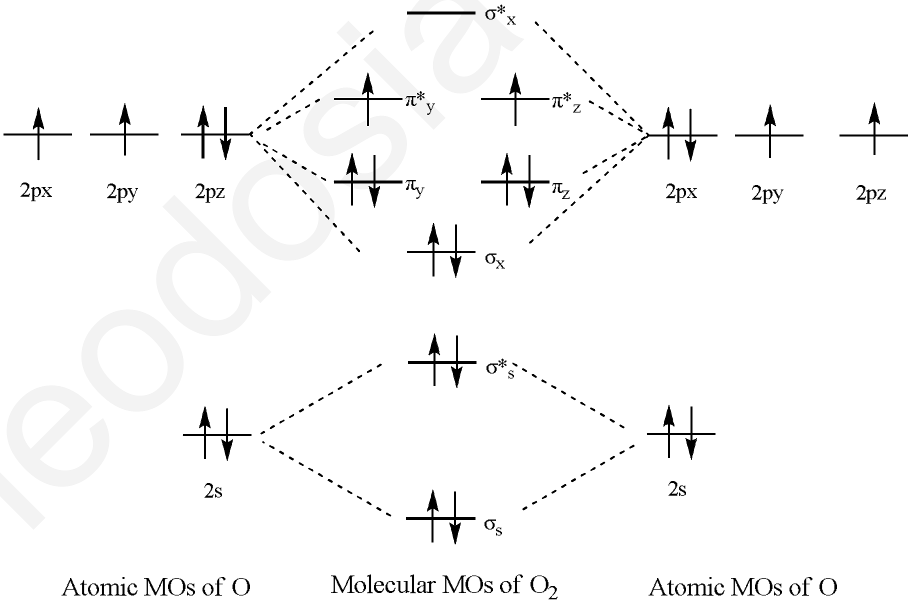


Figure 6. Filling up the molecular orbitals (MOs) in oxygen molecule (O_2).

Organic radicals may afford organic high spin systems in the solid state and therefore gain magnetic behavior as discussed in the previous section.

1.3 Organic Radicals and Polyradicals

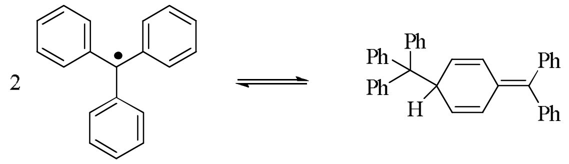
According to the Pauli's exclusion principle, Hund's rule and the octet rule (Section 1.2) it is rare to find unpaired electrons in an organic molecule. There are, however, exceptions where unpaired electrons can exist in such molecules which are called radicals. Molecular orbitals that host only one electron are known as Singly Occupied Molecular Orbitals (SOMOs). If a molecule has many unpaired electrons that occupy an analogous number of SOMOs, then the molecule is a polyradical. Radicals based on simple valency considerations have less bonds than expected and thus are highly reactive. In general, due to the presence of unpaired electrons organic radicals can easily take part in reactions, such as hydrogen abstraction, dimerization, oxidation, disproportionation or recombination, and as a result they can easily achieve a closed-shell character. In many cases, steric hindrance built around the atoms hosting the greatest spin density can prevent undesireable reactions.[33-37] As such, the synthesis of stable radicals and polyradicals is a challenging task in organic synthesis.

1.3.1 Hydrocarbon-Based Radicals

Important examples of hydrocarbon based radicals are the triphenylmethyl and phenalenyl radicals. They have been extensively studied and many derivatives and analogs are known.

1.3.1.1 Triphenylmethyl radicals

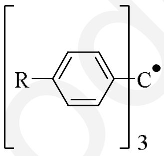
Triphenylmethyl radical **5**, synthesized by Gomberg, marked the beginning of organic free radical chemistry.[38] Under anaerobic conditions, radical **5** is relatively stable due to the steric protection of the central carbon, where the bulk of the radical spin density exists. The three phenyl groups adopt a propeller conformation, with the rings twisted by ~30° with respect to the plane containing the central carbon and the three *ipso* phenyl carbons.[39-41] Triphenylmethyl **5** and its derivatives are best described as persistent rather than stable radicals since in dilute and deoxygenated solution, radical **5** cannot be isolated and is in equilibrium with its σ dimer **6** (Scheme 1).[42]



5 **6**

Scheme 1. Triphenylmethyl radical **5** in equilibrium with its σ dimer **6**.

Substitution on the phenyl rings decreased the tendency for dimerization. *Para* substitution on all three phenyl rings like system **7**[40,41,43-46] or even better by chloro-substitution as in systems **8-10** gave them excellent chemical stability.[47-52] Radical **10** is the prototype of what has become a large number of polychlorinated triphenylmethyl (PTM) radicals that display outstanding stability.[53] Work on these chlorinated radicals showed that not all the chlorines are necessary for this stability but the six chlorines in the *ortho* positions are. This is demonstrated by the relative stabilities of perchlorinated tris(thienyl)methyl radicals **11** and **12**,[54] since the 2-thienyl derivative **11** which has only three *ortho*-chlorine groups is not particularly persistent and decomposes within minutes whereas compound **12**, with six *ortho*-chlorines, is comparably stable to **10**. Heteroaromatic analogs of **5** in which one or more of the phenyl groups is replaced by, *e.g.*, pyridyl,[55] thienyl,[56,57] or benzotriazolyl[58,59] do not show dramatically different stability from the parent compound.



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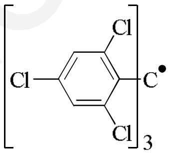

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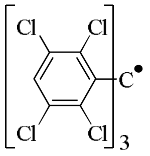

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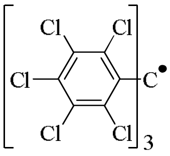

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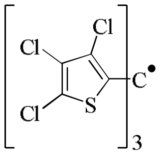

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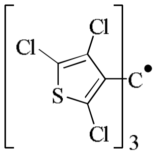

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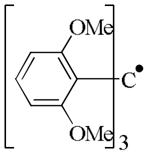

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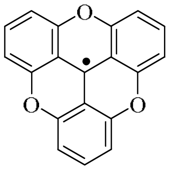

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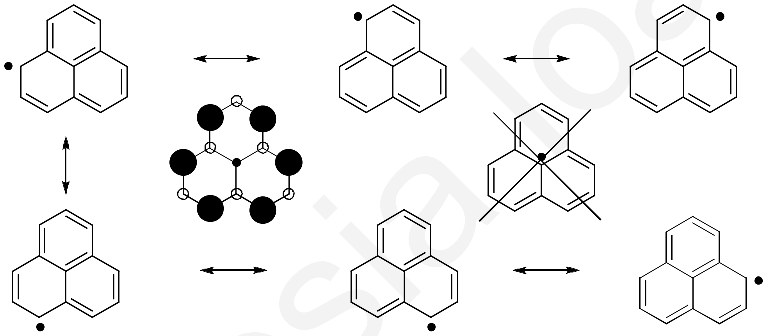
Ortho substituents other than chlorine, can also reduce the reactivity of triarylmethyls like in tris(2,6-dimethoxyphenyl)methyl radical **13**.[60] Its fused analog **14**, the sesquixanthydryl radical, is not monomeric.[61] Compound **14** gained resonance delocalization due to its planar orientation of the phenyl groups but lost the steric barrier to radical dimerization giving a σ dimer of unknown structure since its poor solubility made its characterization difficult.

1.3.1.2 Phenalenyl radicals

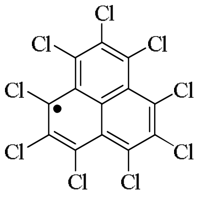
The phenalenyl radical **15** (Scheme 2) was prepared by Reid[62] and independently by Calvin[63] after phenalene oxidation. A number of simple derivatives have been generated[64,65] and the older literature has been reviewed.[66] The spin density in radical **15** is predominantly on the six *peri* carbon atoms. The spin density at the three peripheral (β) carbons is much smaller and it arises from spin polarization effects. It also suggests no spin density on the central carbon.[67] Such a resonance structure would consist of a methyl type radical inside an antiaromatic periphery and thus would not be appropriate.[37]



Scheme 2. Resonance structures and spin density distribution of phenalenyl **15**.

Most simple phenalenyls weakly and reversibly dimerize *via* σ bond formation.[65,66,68] Placement of *t*-butyl groups at the three β carbons effectively shuts down the σ dimerization pathway, resulting in an alternative dimeric structure, that of a π dimer where the two radicals are stacked face-to-face and antiparallel to minimize steric interactions between R groups. The first phenalenyl π dimer structure was reported by Nakasuji[25,69] and has been subsequently studied in some detail by Kochi.[68,70-72]

Other substituents on the phenalenyl periphery such as chlorine in **16**,[73] sulfur in **17**[74,75] or oxygen in **18**[67,76,77] render stable phenalenyl radicals. Nakasuji has prepared a series of ‘oxophenalenoxyl’ radicals like **18** which can be considered hybrids of phenalenyls and phenoxyl radicals.[78-80] These radicals appear to be qualitatively somewhat less stable than the phenalenyl radicals.



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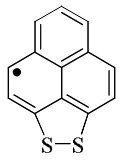

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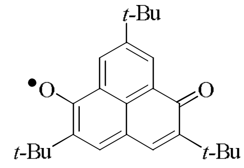

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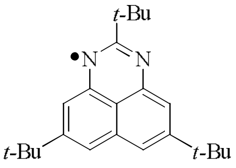

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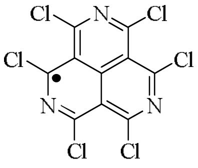


3

The phenalenyl skeleton has been subjected to heteroatom perturbation as well. Examples are 2,5,8-tri-(*t*-butyl)-1,3-diazaphenalenyl **19** which was prepared by Nakasuji and decomposed significantly slower in air than its hydrocarbon analog,[81] and the triaza-version of **16**, the triazaphenalenyl **3** which is stable and monomeric.[26]

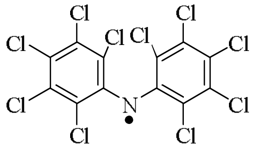
1.3.2 Heterocyclic Radicals Based on Nitrogen

Many of the most stable organic radicals have a substantial portion of spin density on nitrogen. Examples are the aminyl and hydrazyl radicals.

1.3.2.1 Aminyl radicals

Most simple aminyl radicals [R_2N•] are short-lived species that rapidly dimerize to hydrazines or undergoing other radical reaction pathways.[82,83] To be isolated, steric shielding is required *e.g.*, the perchlorodiphenylaminyl radical [$(C_6Cl_5)_2N$•] **20**.[84]

Aminyl radicals incorporated into a cyclic, *p*-conjugated framework exhibit enhanced stability. There are several examples of isolable phenazinyl radicals **21**.[85-88] In all of these cases R ≠ H otherwise they give the corresponding closed shell phenazine. The aromatic groups also have electron withdrawing (C≡N, NO_2) and/or bulky substituents. Most stable phenazinyls are predominantly monomeric in solution at room temperature but associate upon cooling, most likely *via* π dimer formation. Crystal structures of several derivatives show the radicals forming π dimers or π-stacked structures in the solid state. The related phenoxazinyls and phenothiazinyls (obtained by replacement of the NR group by O or S, respectively) are generally quite short-lived species except for some derivatives that are stabilized due to steric factors.[82,89]



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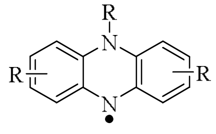

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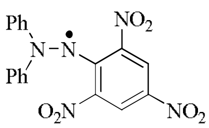
1.3.2.2 Hydrazyl radicals

Acyclic hydrazyl radicals [$R_2NNR\bullet$] are in general only persistent and often not very long-lived, in solution. The most stable example is *N*,*N*-diphenyl-*N'*-picrylhydrazyl (DPPH) **22** which has been known for decades and is used as an EPR reference compound.[82] A number of stable radical families contain the hydrazyl moiety built into a cyclic and/or delocalized skeleton. For example, radicals **23** are generally stable enough to be isolated (R' substituents are aromatic residues and R ≠ H). A few derivatives have been crystallographically characterized and all were monomeric in the solid state.[90,91] The spin distribution in radicals **23** suggests that these are still mainly hydrazyl-like radicals, but with non-negligible spin density also on the imine nitrogen. Similarly, the benzotriazinyl radicals **26** have substantial spin density on all three nitrogen atoms as well as appreciable spin on the annelated benzene ring.[92,93]



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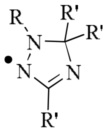

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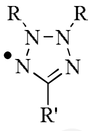

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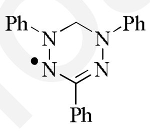

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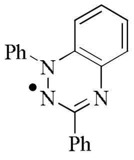

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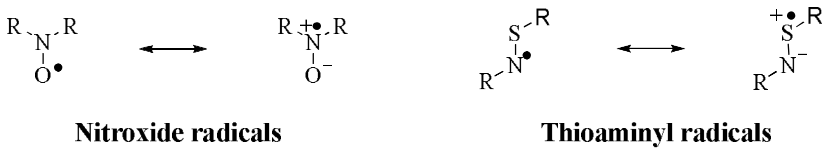
Other examples of resonance-delocalized hydrazyls are the tetrazolinyl radicals **24**[94-96] where their stability is improved by introducing electron withdrawing substituents on the nitrogen atoms[96] and verdazyl radicals of general structure **25**. Verdazyls are relatively stable and were discovered accidentally in 1963 by Kuhn and Trischmann.[97,98] Many derivatives with various aromatic or non aromatic substituents have been prepared.[92,97-101]

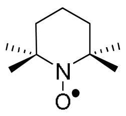
This spin delocalization upon nitrogens helps the radical stabilization. Such a stability is also achieved by other heteroatom radicals as well such as radicals containing N along with O, S, Se or P. For instance nitroxides [$R_2NO\bullet$] are the most well-known class of stable radicals with respect to air, water, dimerization and other radical-based reactions. They have substantial spin density on both N and O since they can be represented by two resonance structures. Similar resonance structures can be observed in other heteroatom radicals that contain nitrogen for instance in thioaminyl radicals (Scheme 3).



Scheme 3. Resonance structures of nitroxide and thioaminyl radicals.

Particularly stable are nitroxides with two quaternary carbon-based substituents like 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) **27** as well as "imino nitroxides" **28** or nitronyl nitroxides like *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN) **1**.[20,22,102-104] The latter are resonance-delocalized nitroxides and they can be considered as the most stable examples of nitroxides. They were first reported by Ullmann 40 years ago.[22]

Other monomeric examples of heteroatom nitrogen containing radicals are some 1,3,2- and 1,2,3-dithiazolyl radicals like **29** (X = CH or N)[105] and **30**, respectively.[106] The "dithiazolodithiazolyl" radical **31** (R' = H, Me, Et, Pr and R'' = H, Me, Cl, Ph) are other examples of stable resonance-delocalized systems.[107-110]



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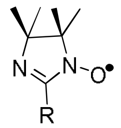

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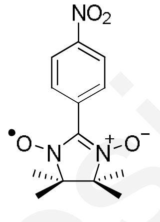

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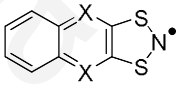

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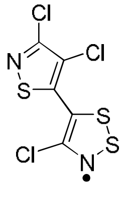

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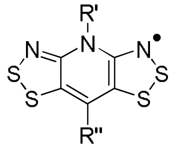

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1.3.3 Diradicals and Polyradicals

To achieve high spin in the solid state, it is better to have polyradicals with their spin already aligned in parallel rather than by using monomeric radicals (more spins per unit volume, higher magnetization). The solid state packing can always cancel or enhance the high spin character, but before tackling this problem, it is good to first achieve high spin character in a single molecule as in a diradical or a polyradical.

This can be achieved in coordination chemistry where polynuclear metal complexes containing several transition-metal ions where the spins can be localized, can exhibit magnetic properties. These systems are called single-molecule magnets (SMMs) and they were first discovered in 1993 when a Mn complex $[Mn_{12}O_{12}(OAc)\cdot 16(H_2O)_4]\cdot 4H_2O\cdot 2AcOH$ was synthesized having a large spin ground state.[111-113] SMM have several advantages over traditional magnets like solubility, crystallizability and stability due to the shell of the organic groups that protect the magnetic cores.[114] High spin purely organic materials, however, remain big challenges.

The simplest way to describe the pair of odd electrons in a diradical is to assign each one to a localized orbital *e.g.*, Φ_A and Φ_B, respectively. These orbitals can interact through a weak one-electron overlap integral (S_{AB}), or two-electron exchange integral (K_{AB}). If the overlap integral S becomes too large (bond formation) or if the energy difference between Φ_A and Φ_B is too large (electrons are localized as a pair in the lower orbital, Hund's rule), then the diradical character is lost. As long as these interactions are weak, the diradical character remains, but we can still have either a singlet or a triplet state. Both states describe the diradical but they differ in the manner in which the electron spins couple. For a pair of electrons, their total spin (S) can be either $S = 1$ ("parallel spins") or $S = 0$ ("antiparallel spins") and in terms of spin multiplicity, ($2S + 1$,) these spin values correspond to triplet and singlet, respectively. The singlet state, however, may be either a single configuration with the same spatial occupation or a mixture of configurations.[115] Singlet diradicals for instance are open-shell systems characterized by two unpaired electrons occupying a different part of space with a small sharing region. The triplet state is the desired multiplicity state regarding developing high spin systems with potential magnetic behavior where spins are parallel (Figure 7). The energy difference between the singlet and triplet states (ΔE_{ST}) measures the strength of the spin coupling. Spin-orbit coupling effects are neglected. $\Delta E_{ST} = E_S - E_T$ and since energies are negative, a positive ΔE_{ST} results when triplet is lower in energy and thus the ground state is triplet and a negative ΔE_{ST} results when the ground state is singlet.

		Spin S	**Multiplicity 2S+1**
Ferromagnetic coupling	↑ ↑	1	Triplet
Antiferromagnetic coupling	↑ ↓	0	Singlet

Figure 7. Spin alignment in singlet and triplet state.

1.3.3.1 Hydrocarbon diradicals as ferromagnetic coupling units

A few organic moieties have triplet ground states and many molecules have been designed based on them. Two of these moieties are trimethylenemethane (TMM), first detected by Dowed in 1966,[19,116-118] and *m*-xylylene.[119-121] Their ΔE_{ST} was *ca.* +15 kcal/mol for TMM[19,116,120,122-124] and +9.6 kcal/mol for xylylene[121,125,126] with the triplet state lying below singlet as denoted from the positive values. These motifs are used as ferromagnetic coupling units in an effort to develop high spin organic molecules. The origin of the triplet state preference on these non-Kekulé systems[127] (fully conjugated but at least two atoms are not π-bonded) can be expressed *via* molecular orbital or valence bond theory.[128]

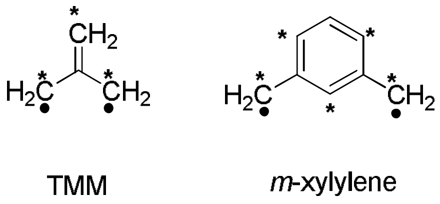
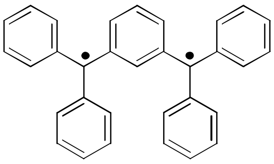


Figure 8. TMM and *m*-xylylene diradicals. Starred and unstarred carbons are shown.

In 1950 Longuet-Higgins proved that, in a non-Kekulé hydrocarbon that contains no 4*n*-membered rings, the number of atoms that cannot be assigned to π bonds is equal both to the number of a nonbonding molecular orbitals (NBMOs) and to the number of electrons that must be accommodated in them.[127] Thus, each of TMM and *m*-xylylene, has two π NBMOs, which contain a total of two electrons as a diradical. On the basis of Hund's rule[129] Longuet-Higgins predicted that the ground state of a non-Kekulé hydrocarbon with n electrons in n π NBMOs would have a spin quantum number of $S = \mathrm{n}/2$[127] and thus each of these diradicals should have a triplet ground state ($S = 1$), in which the two nonbonding electrons occupy different NBMOs and have parallel spins. If after these assumptions, such a molecule had a singlet state instead, then this is addressed as "a violation of Hund's rule in non-Kekulé hydrocarbons".[130]

By using valence bond approach and the */non* rule for planar π systems, again TMM and *m*-xylylene keep the triplet ground state. Using this rule, atoms are * or non* alternately and if $N^* = N$ then the π NBMOs are disjoint (have no atoms in common and are localized on two seperated subparts) and if $N^* \neq N$ then they are non-disjoint (have atoms in common). Disjoint NBMOs such as in tetramethyleneethane (TME) without having electron density at the same atom result in small destabilization factor by the Coulomb repulsion compared to non-disjoint type. Non-disjoint NBMOs such as TMM have electron density at the same atom and according to Hund's rule, each orbital is filled with one electron with parallel spin, avoiding the Coulomb repulsion by filling one orbital with two electrons. Therefore, such molecules with non-disjoint NBMOs are expected to prefer a triplet ground state while in disjoint NBMOs, singlet and triplet states will have nearly equal relative stability or even reversed. Ovchinnikov derived the formula $S = (N^*-N)/2$[131] which in case of $N^* = N$ predicts $S = 0$ and a singlet ground state while when $N^*-N = 2$ as in case of TMM and *m*-xylylene, then $S = 1$ and the triplet state is favored (Figure 8). This */non* topology has been applied in many diradicals to predict their ground state preference and even studied for charged polyradicals.[132]

Examples of hydrocarbon diradicals having the *m*-xylylene coupling unit are *m*-quinonoid diradicals like the Schlenk hydrocarbon **32**,[133,134] which was the first synthesized diradical of this family and was based on triphenylmethyl radical. Diradical **32** could be easily oligomerized in ambient temperature and the ESR spectrum and Curie studies of its oligomerized sample suggest that a minor species gave a triplet ground state.[135,136] Steric protection was required then in *para* positions to the triarylmethyl sites like diradicals **33** and **34** which show triplet ESR spectra.



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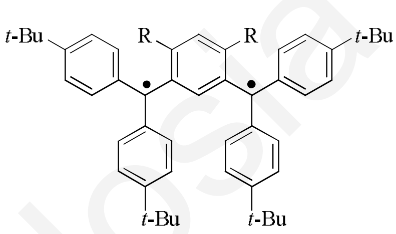

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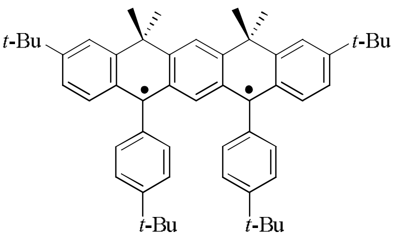

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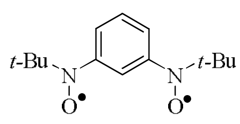
1.3.3.2 Diradicals containing heteroatoms

Many stable diradicals contain heteroatoms by having heteroatom-containing spin sites attached to a strong ferromagnetic coupling unit like TMM and *m*-xylylene. An example is the nitroxyl diradical **35**[137] having *m*-xylylene as a coupling unit and stabilized in the triplet state. Unlike system **35**, its alkyl substituted analogs **36**[138] and **37**[139] are suggested to have the singlet ground state as an exception to the expected result. The contribution of resonance structures **39** and **40** was considered as the reason for the singlet state preference but rejected since the systems are not planar and herein X-ray did not show any shortening of the N-C(Ph) or O-C(Ph) bonds. The twisted radical sites with predicted torsion angles about 70-90°[140,141] might cause the singlet ground state of the last two examples due to the lower spin polarization, since the nitroxide groups are not coplanar with the phenyl ring, and the possible antiferromagnetic through-space interaction between the spins. Surprisingly the bis-trifluoromethyl derivative **38** after rapid cooling that leads to a singlet state was slowly converted in low temperatures to its triplet ground state.[142]



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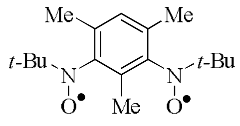

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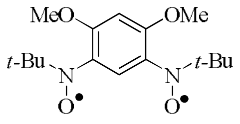

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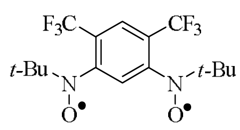

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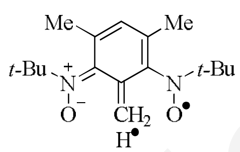

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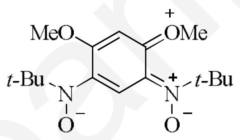

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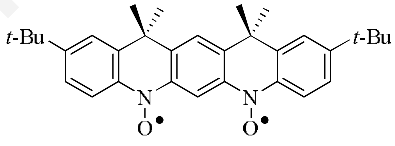
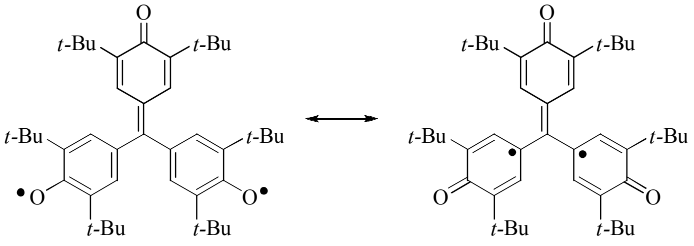
Another triplet ground state diradical is the nitroxide diradical **41** which is a derivative of diazapentacene.[143,144] Diradical **41** is stable at room temperature and retains strong ferromagnetic coupling. It illustrates both the high spin character and the properties of the azaacene backbone (discussed in Section 1.5).



41

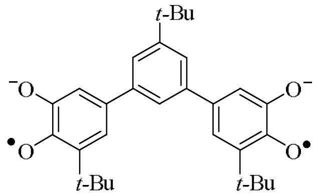
"Yang's biradical" **42**,[145] is a stable triplet diradical. The three benzenoid rings of this molecule are twisted by ~34° in a propeller-like arrangement,[146] similar to the structures of simple triarylmethyl radicals. Nearly 50% of the total spin density lies on the three carbons directly adjacent to the central carbon.[146] Thus although **42** is represented and often described as a phenoxyl-based diradical, resonance structure **42b**, which is a more accurate representation of the spin density, suggests that Yang's biradical could alternatively be categorized as a delocalized version of TMM (Scheme 4).



42a **42b**

Scheme 4. Resonance structures of “Yang’s biradical” **42**.

A series of *m*-xylylene and TMM-based bis(semiquinones) like **43** and **44**, respectively have been synthesized by Shultz and coworkers.[147] These compounds gave triplet ground states while a fluorenyl linked system **45** being synthesized for comparative purposes exhibits antiferromagnetic character in a singlet ground state.



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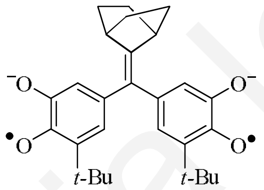

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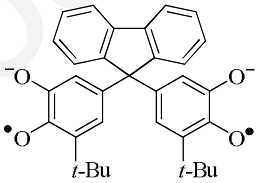

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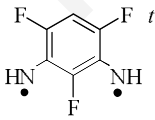
1.3.3.3 Aminyl diradicals

To the best of our knowledge there are only a few examples of triplet aminyl diradicals: The Platz diradical **46**[148] and Rajca’s diradical **47**[149,149] were both shown to be persistent triplets in solution at low temperatures, -195 °C and -140 °C, respectively in 2-MeTHF. Rajca *et al.*, later prepared two aminyl diradicals, **48**[150] and **49**,[151] that were persistent at room temperature.



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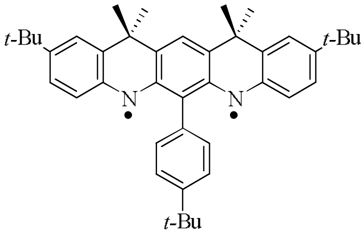

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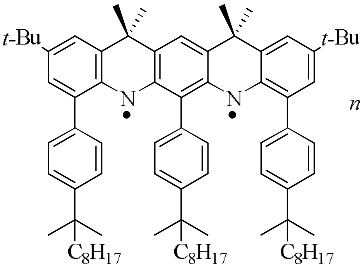

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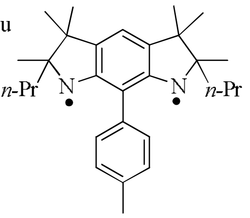

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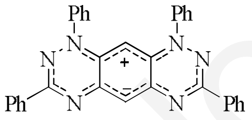
The structures above are based on the *m*-phenylene moiety and the nitrogen spin carriers seem to render the stable diradical character in a triplet ground state. But that was not always achieved. Similar compounds like compounds **50**-**55** (discussed in Section 1.4) failed to afford a triplet ground state but instead gave closed shell zwitterionic biscyanines. In the latter systems, apart from the nitrogen spin carriers, there are additional electronegative heteroatoms in the system *e.g.*, nitrogens. This subsequently affects the electronic properties and possibly the ground multiplicity state preference. As will be discussed later, the zwitterionic character is preferred in these systems to avoid their potential antiaromaticity after a single $\pi \rightarrow \pi^*$ excitation.

1.4 Zwitterionic Azaacenes

Tetraphenylhexaazaanthracene (TPHA) **50**,[152] an analog of stable Blatter's radical **24**,[153] and diphenyltetraazapentacene **51** (R = Ph)[154,155] exist as singlet ground states with a zwitterionic "double-barreled" biscyanine motif. Analogous biscyanine zwitterions that have since appeared in the literature are the pyridine-bridged bis-1,2,3-dithiazole **52**[156] and the monocyclic 1,2,4,5-tetrasubstituted benzene **55**.[157-159] Furthermore, compounds **53**[160] and **54**[161] that are aza analogs of **50** and **51**, respectively were also recently reported.



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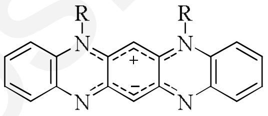

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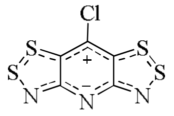

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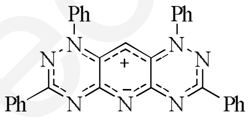

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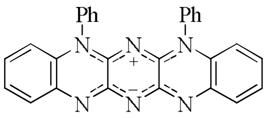

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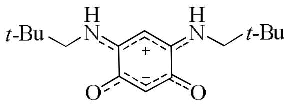
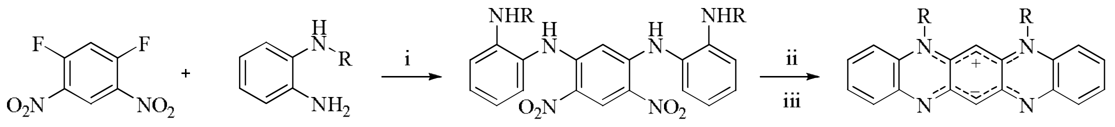


55

Koutentis[155] developed a strategy for the synthesis of zwitterionic tetraazapentacenes, including **51**. The preparation involved a double nucleophilic aromatic substitution of 1,5-difluoro-2,4-dinitrobenzene **56** with *N*-substituted-1,2-benzenediamines **57** to give 2,4-dinitrobenzene-1,5-diamines **58** in good yield.

Hydrogenation of compounds **58** followed by heating in ethanol in air gave the zwitterionic tetraazapentacenes **51** (Scheme 5).



56 **57** **58** **51**

Scheme 5. Synthesis of zwitterionic tetraazapentacenes. *Reagents and conditions:* i) *i*-Pr_2EtN (2 equiv.), EtOH, 80 °C, 24 h, 83-91%; ii) H_2, Pd/C, EtOH, rt, 3 h; iii) air, EtOH, 80 °C, 77-85%.[155]

Their optical properties were examined, and upon attachment of long alkyl chains (instead of phenyl groups), compound **51** becomes liquid crystalline.[162] The combination of optical and liquid crystalline properties makes derivatives of **51** potentially interesting in thin film devices. The zwitterionic structure **51** (R = Ph) displays an absorption maximum λ_{max} of 744 nm (EtOH), which upon protonation is blue-shifted to 660 nm (monoprotonated) and 639 nm (diprotonated).[154] Furthermore, in a correlation between solvent polarity ET(30) and the maximium π-π* absorption, compound **51** displays negative solvatochromic behavior, typical of zwitterionic compounds.

Braunstein *et al.*,[157] described this family of zwitterionic biscyanine compounds as “potentially antiaromatic” due to the fact that a single $\pi \rightarrow \pi^*$ excitation would restore π delocalization and antiaromaticity. To avoid this “potential antiaromaticity” and hence a triplet ground state, the molecules prefer to partition their overall electronic system into two charge conjugated π subsystems (cyanines) which are structurally connected by σ bonds but not electronically conjugated. Haas and Zilberg[163] indicated that these molecules can be envisioned as the union of two odd electron radicals. These zwitterions are the result of an electron transfer from the donor to the acceptor radical subunit. This transfer will only take place if the donor and acceptor radicals have a low ionization potential and a high electron affinity, respectively.

Calculations, performed on these systems,[152,154-159,163] showed that the lowest triplet states of the heterocyclic members of this family are energetically close to the singlet zwitterionic ground states. This close energetic competition can be manipulated by substitution. Many theoretical and experimental studies on *m*-phenylene diradicals and also on carbenes indicated that substituents can influence their singlet-triplet energy gaps (ΔE_{ST}) and hence their ground state multiplicities.[164-169] A computational study on the effect of the substitution and the structural motif on the ground state multiplicity of tetraazapentacenes and related systems indicated that angular systems preferred the triplet ground state while the linear analogs are stabilized in the singlet.[170]

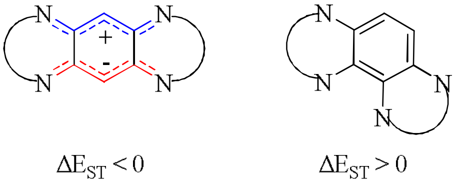


Figure 9. Linear structures prefer singlet ground state ($\Delta E_{\mathrm{ST}} < 0$) and angular structures triplet state ($\Delta E_{\mathrm{ST}} > 0$) according to DFT computational studies.[170]

The zwitterionic nature provides unique properties. Some zwitterionic compounds have exceptional optical properties like high fluorescence quantum yields and strong solvatochromic behavior. Furthermore, studies using quantum mechanical modeling on zwitterionic systems composed of C, H, N have shown strong magnetic character and thus triplet ground state. An example is the zwitterionic betaine system (Figure 10) where the pyridine moiety acts as acceptor and the imidazole moiety acts as a donor that are linked with a π bridge by alternating C=C bonds.[171] In this system the exchange interactions between electron spin are relatively strong and local and independent of the length of the bridge.

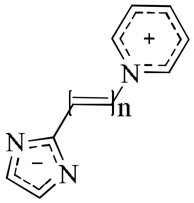


Figure 10. Zwitterionic betaine molecule with a pyridine acceptor and an imidazole donor linked by alternating C=C bridge.

Compared to Kekulé-type nitrogen-rich acenes, non-Kekulé structures show considerable narrowing of their singlet-triplet energy separations, thereby making these types of π conjugated fused heterocycles fascinating candidates for the design of organic electronics and molecule-based magnetic substances. Π Conjugation permits effective intra- and intermolecular delocalization and charge transport and thus this feature is essential for a system to act as a semiconductor. In addition, because of the π conjugation, high-energy occupied and low-energy vacant molecular orbitals facilitate injection of holes or electrons from the source electrode into the semiconductor and the following extraction at the drain electrode.[172] The polyacene backbone, which is responsible for this high π conjugation resulting in interesting electronic properties, will be further discussed in Section 1.5 with emphasis on pentacenes and azapentacenes.

1.5 Pentacene and Azapentacenes

Polyacenes are polycyclic aromatic hydrocarbons consisting of fused benzene rings (Figure 11). Due to their extended πconjugation these compounds are attractive as building blocks in the design of organic electronic materials.[11,160,173-175] Large polyacenes were predicted to behave as one-dimensional organic conductors with a zero band gap.[176,177] Recently, it was proposed that linear polyacenes would behave as two polyacetylene chains with a triplet ground state and a vanishing band gap.[178] They have been studied widely from both theoretical and experimental scientists but the thorough understanding of electronic properties in large oligoacenes ends with pentacene since homologues higher than hexacene remain to be fully characterized. In addition, oligoacenes larger than anthracene are unstable towards oxidation as well as dimerization and are poorly soluble.[179,180]

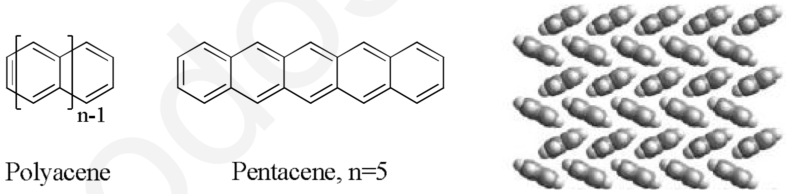
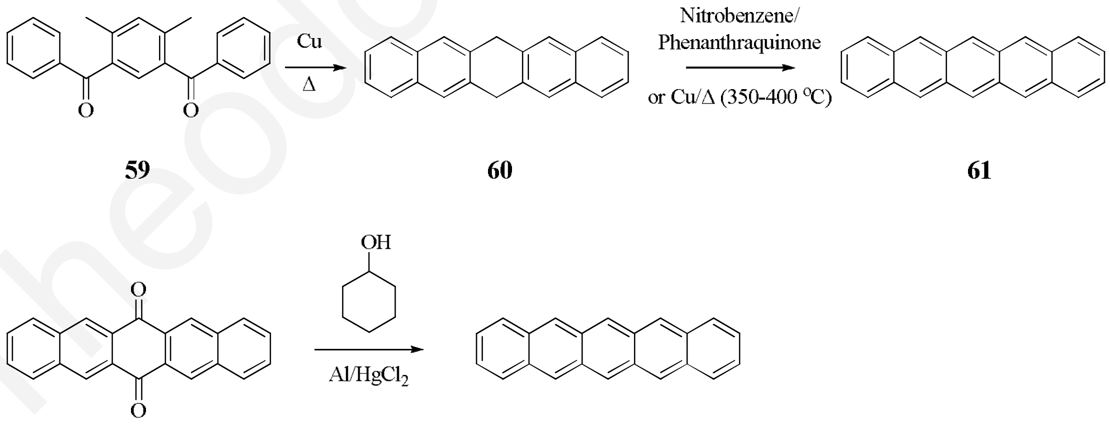


Figure 11. Structure of polyacenes and pentacene and crystal packing of pentacene in a herringbone motif.[181]

1.5.1 Pentacene

Pentacene has received much attention as a semiconductor in field-effect transistors (FETs) because of its unusually high charge-carrier mobility. Pentacene’s facile and reversible oxidation to its radical cation in the solid state enables its use as a hole-transporting semiconductor. The observed high hole mobility is a result of its good transfer integral (t) and correct nodal overlap of the highest occupied molecular orbitals (HOMOs) of adjacent molecules, as well as a small reorganization energy of the radical cation (λ_+) when going from the neutral molecule to the radical cation.[182] High-quality FET devices made from thin films of pentacene typically show mobilities greater than 1.5 cm^2/Vs,[183] with mobilities up to 35 cm^2/Vs,[184] while ambipolar charge transport has been observed in pentacene thin films (although electron mobilities were very low and n-type behavior was only observed under vacuum).[185] Pentacene has also been used as the p-type material in organic solar cells (with C_{60} as the n-type material), yielding power conversion efficiencies as high as 2.7%.[186,187]

Pentacene melts above 300 °C and sublimes at 372 °C. It was first synthesized by Clar and John starting from *m*-xylophenone (Scheme 6).[188-190] A vigorous Friedel-Crafts reaction yielded 40% of 4,6-dibenzoyl-1,3-dimethylbenzene **59** which was converted into dihydropentacene **60** in an unstated yield after heating with copper. Dehydrogenation of **60** to pentacene **61** was accomplished by boiling the dihydro derivative in nitrobenzene with phenanthraquinone or by passing over copper at 350-400 °C. More recently, pentacene has been easily synthesized in 54% yield by reduction of pentacenequinone **62** (prepared by condensation of cyclohexane-1,4-dione with *o*-phthalaldehyde) using an aluminum-cyclohexanol mixture.[191] Before the above short synthesis, it had been shown that pentacene could be synthesized by a three-step procedure in an overall yield of 30% starting from 1,2-dimethylenecyclohexane and benzoquinone.[192]



59 **60** **61**

62 **61**

Scheme 6. Synthesis of pentacene.

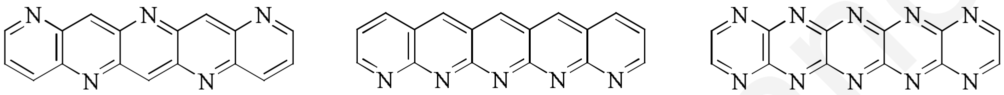
Similar to its lower homologues, pentacene and its derivatives pack in a herringbone motif[193] that allows for excellent π-π overlap in the solid state (Figure 11), although it can potentially adopt any of a number of polymorphs.[194] This polymorphic nature complicates device studies, since band structure calculations have shown significant electronic differences between polymorphic forms.[195] Other drawbacks of pentacene beside polymorphs is its environmental instability, low thermal stability and photooxidation.[196-198] In addition pentacene's insolubility in organic solvents at room temperature requires costly vacuum evaporation techniques for its deposition.[199,200]

Due to the problems mentioned above on handling pentacene, analogs and derivatives were considered. Substituted oligoacenes have received considerable attention,[201-205] while acenes incorporating heteroatoms only came into focus over the past decade.[172,187,206] Nitrogen containing acenes (azaacenes) are known to be more stable than their parent hydrocarbons against photooxidation and dimerization.[172,207] The stability of the aza analogs of pentacene is relevant to the breaking of the conjugation in the pentacene skeleton *via* entering the amino groups.[198] This functionality gives different properties such as better solubility and even easier synthesis and derivatization.

1.5.2 Azaacenes and Azapentacene

Azaacenes, due to the nitrogen heteroatoms are considered as n-type semiconductors where the charge carriers are electrons, in contrast to acenes which are considered as p-type semiconductors having holes as the charge carriers. Winkler and Houk studied computationally Kekulé-type azaacenes to examine their n-type potentials.[172] Tetraazatetracenes and larger analogs showed larger singlet-triplet energy separations (ΔE_{ST}) than their corresponding hydrocarbons. They estimated reorganization energies, singlet-triplet energy splitting between ground state singlet and lowest triplet and singlet [$\Delta E_{(\mathrm{S0\text{-}T1})}$ and $\Delta E_{(\mathrm{S0\text{-}S1})}$, respectively], ionization energy (IE) and electron affinity (EA). The authors compared pentacene with a series of azapentacenes as in the structural models of **63**-**65** and concluded, to obtain good electron-transporting properties, that the proposed azapentacenes should carry at least seven nitrogen atoms in their perimeter and/or electronegative substituents such as nitriles, which allow for a graphite-like packing.

Critical parameters are the reorganization energy of the radical anion (λ_{-}) in combination with a high electron affinity. Enforcement of a suitable supramolecular arrangement of these materials should maximize the transfer integral t, as the mobility μ should be related to the electron-transfer rate (K_{ET}) between two molecules, a function of the term that contains the transfer integral t and λ_{-}. If the absolute temperature T is close to zero, K_{ET} would largely depend on the size of t. If λ_{-} is very small, K_{ET} and therefore μ would also only be dependent upon t, which is defined by the magnitude and phase of the overlap of the lowest unoccupied molecular orbitals (LUMOs) of neighboring, interacting molecules, as discussed by Brédas *et al.*[182] A pentacene with at least seven nitrogen atoms reached both the minimum required levels for the electron affinity (EA ~3.0 eV) and reorganization energies for electron transport (λ_{-} ~0.20 eV) to be useful for applications in molecular electronics.

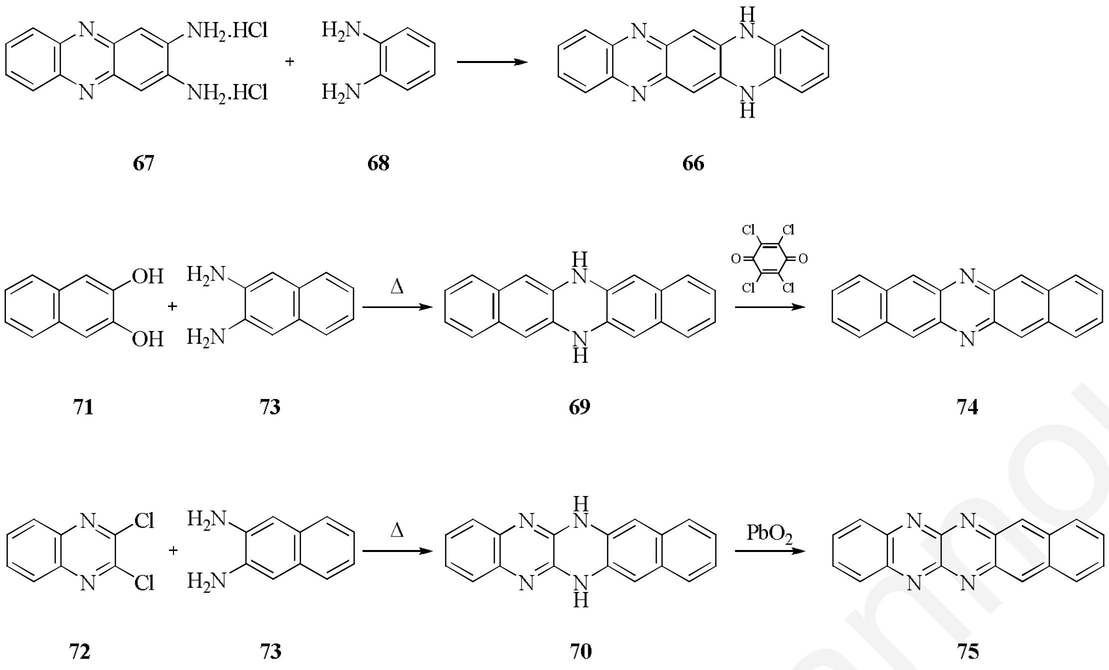


63 **64** **65**

	63	64	65
ΔE_{HL}	2.576	2.615	2.320
$\Delta E_{(\mathrm{S0\text{-}T1}),\mathrm{vert}}$	1.320	1.403	1.276
$\Delta E_{(\mathrm{S0\text{-}S1}),\mathrm{vert}}$	2.308	2.409	1.383
$\mathrm{IE}_{\mathrm{vert}}$	7.340	7.384	8.439
$\mathrm{EA}_{\mathrm{vert}}$	1.977	2.010	3.164
λ_{+}	0.115	0.128	0.356
λ_{-}	0.151	0.165	0.203

Figure 12. Selected data [B3LYP/6--31G(d)] in eV for systems **63-65**. For comparison the analogous data for pentacene are: $\Delta E_{\mathrm{HL}} = 2.211$ eV, $\Delta E_{(\mathrm{S0\text{-}T1}),\mathrm{vert}} = 0.994$ eV, $\Delta E_{(\mathrm{S0\text{-}S1}),\mathrm{vert}} = 1.994$ eV, $\mathrm{IE}_{\mathrm{vert}} = 5.935$ eV, $\mathrm{EA}_{\mathrm{vert}} = 1.056$ eV, $\lambda_{+} = 0.093$ eV, $\lambda_{-} = 0.132$ eV.[172]

Hepp and Fischer[208-211] gave the first report on pyrazine-containing acenes referring to the synthesis of dihydrotetraazapentacene (DHTAP) **66** by condensing 2,3-diaminophenazine hydrochloride **67** with 1,2-benzenediamine **68**. Later Hinsberg[212] investigated *N*-heterocyclic homologues such as **69** and DHTAP **70** that were synthesized by melting dihydroxynaphthalene **71** or dichloroquinoxaline **72** with 2,3-diaminonaphthalene **73**, respectively (Scheme 7).

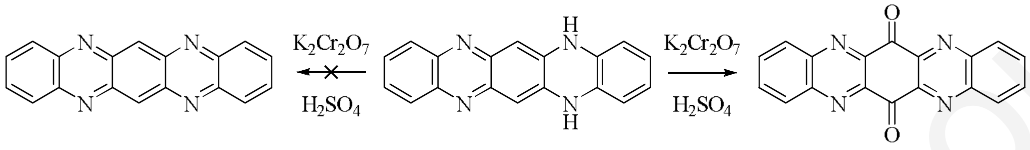


Scheme 7. Early synthesis of azapentacenes.

Nuckolls investigated the heteroacene **69** and several of its derivatives for organic electronics applications.[198] The single-crystal structure of **69** (from benzophenone) is similar to that of pentacene, but the molecules are slipped with respect to each other, thereby avoiding the overlap of the dihydropyrazine rings in the solid state. The molecules of **69** are planar in the solid state, despite the formally antiaromatic, central dihydropyrazine ring. The heteroacene **69** (reinvestigated by Miao *et al.*,[213]) forms three different polymorphs in the solid state and in thin films, of which one has a comparatively high field effect mobility (0.45 $cm^2V^{-1}s^{-1}$), making it a contender with pentacene, particularly as **69** is stable and does not undergo oxidative degradation. The high charge-carrier mobility of **69** is explained by the correct packing that allows facile charge transport according to the models of Brédas *et al.*[214]

Attempts to oxidize dihydrodiazapentacene **69** and dihydrotetraazapentacene **70** by chromate to afford the diazapentacene **74** and tetraazapentacene (TAP) **75**, respectively failed while it worked well with their tetracene analogs. Only in 1967 Kummer and Zimmermann[215] reported azapentacenes *via* oxidation of **69** by *p*-chloranil, and of **70** by lead dioxide. The azahexacene analog of **69** could not be oxidized either with *p*-chloranil or lead dioxide indicating that might be too unstable or/and too insoluble.[216]

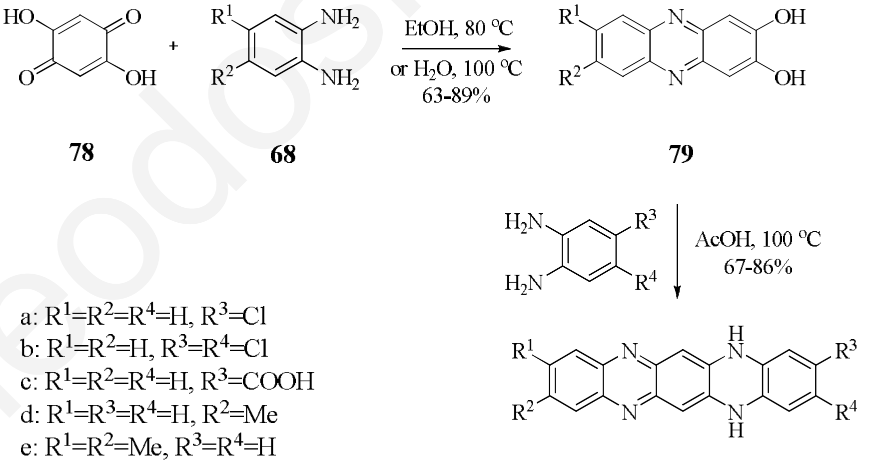
Badger and Pettit also published the synthesis of DHTAP **66** by condensing 2,3-diaminophenazine with *o*-benzoquinone in benzyl alcohol, or by heating 1,2-benzenediamine or its hydrochloride salt in naphthalene under a stream of O_2.[217] They also demonstrated that the oxidation of homofluorindine **66** with acidic dichromate led to the quinone **76** and not to the tetraazapentacene **77** (Scheme 8).



77 **66** **76**

Scheme 8. Oxidation of DHTAP **66** leads to quinone **76**.

Siri *et al.*,[216] reported the synthesis of a series of substituted tetraazapentacenes **66** using an alternative route involving condensation of 1,2-benzenediamines **68** with 2,5-dihydroxy-*p*-benzoquinone **78** in alcohol or water to afford high yields of substituted 2,3-dihydroxyphenazines **79** that are then reacted individually with excesses of substituted 1,2-benzenediamines in the presence of glacial acetic acid (Scheme 9).



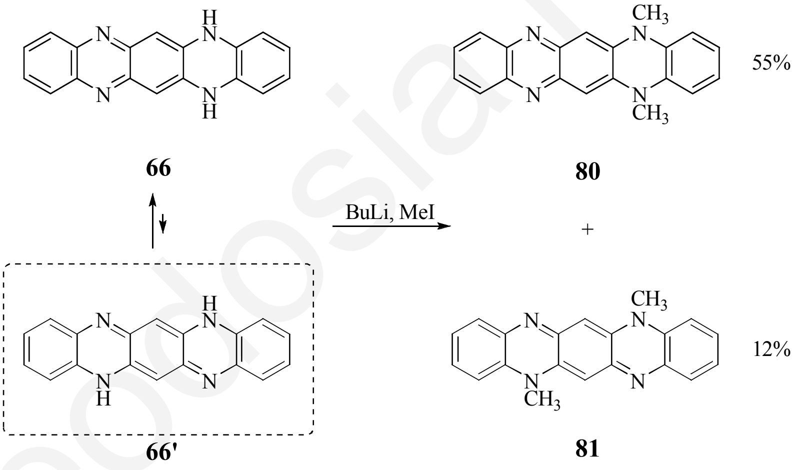
78 **68** **79** **66**

a: R^1=R^2=R^4=H, R^3=Cl
b: R^1=R^2=H, R^3=R^4=Cl
c: R^1=R^2=R^4=H, R^3=COOH
d: R^1=R^3=R^4=H, R^2=Me
e: R^1=R^2=Me, R^3=R^4=H
f: R^1=R^2=Me, R^3=COOH, R^4=H

Scheme 9. Synthesis of substituted TAPs **66** by Siri *et al.*[216]

Studying their electrochemical properties, the DHTAPs exhibit one poorly reversible oxidative step and multi reductive steps which indicate chemical evolution of the oxidized and reduced species.[218] Compared with the unsubstituted parent system **66**, molecules **66b** and **66c** are more difficult to oxidize due to the presence of electron-withdrawing groups (EWGs) while stronger influence was observed in the case of **66c** owing to a mesomeric effect. As expected, molecules **66d** and **66e**, bearing electron-donating groups (EDGs), were easier to oxidize than the parent **66**.[216]

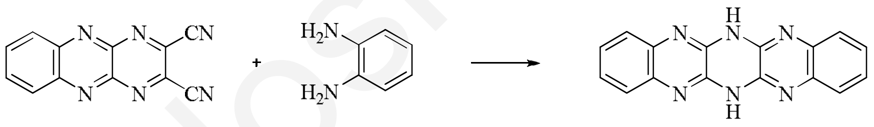
The *N*,*N'*-dihydro heteroacenes are formally antiaromatic, but the heteroacenes (*e.g.*, **74** and **75**) should be aromatic like the linear acenes. Homofluorindine **66** displays a structural distinction: The *N*-H motif can either be arranged to give an (antiaromatic) dihydropyrazine or a quinoid structure where the two NHs are in different rings and opposite positions as in **66'**. Using NMR and quantum-chemical calculations, it has been shown that the "antiaromatic" form, **66** is the prevalent one (estimated to be 4.2 kcal/mol more stable), and the quinoidal **66'** form must be there in low or vanishing concentrations.[218-220] Tang and Miao[221] methylated **66** and obtained a mixture of **80** (55%) and **81** (12%), separated by chromatography and characterized by X-ray crystallography (Scheme 10). While quinoid compound **81** is planar in the solid state and has the smaller bandgap, compound **80** is nonplanar as a consequence of the steric hindrance of the methyl groups when compared to **66**.



Scheme 10. Methylation of **66** gives derivatives **80** and **81** in 55 and 12% yields, respectively.

The redox behavior of acene compounds containing the pyrazine unit is unusual. As mentioned above, as the length of the pyrazinacene is increased the fully oxidized form becomes even less favored and as the number of fused pyrazine rings increases, the reduced form is increasingly favored. This is exemplified by DHTAP **66** which cannot be oxidized to the tetraazapentacene **77**. The somewhat unusual stability of the "antiaromatic" compounds compared to their fully aromatic counterparts was investigated using computational techniques by Bunz and Schleyer.[222] Nucleus Independent Chemical Shift (NICS) calculations,[223] even though they have been criticized for their reliability as aromaticity indicators,[224,225] were used to estimate the aromatic and antiaromatic contributions for each six-membered ring in two model compounds of diazatetracene and the reduced derivative dihydrodiazatetracene[226,227] showing that each of the rings were diatropic (diamagnetic) in case of the fully oxidized compound while for the reduced compound showed that despite containing 4n π electrons, it was weakly aromatic. The reduced pyrazine ring was locally paratropic (paramagnetic) and the remaining rings locally diatropic. However, the remote π contributions for each of the rings were distinctly paratropic. In other words, the reduced form can be viewed as globally aromatic, yet the central dihydropyrazine ring is strongly (locally) antiaromatic.

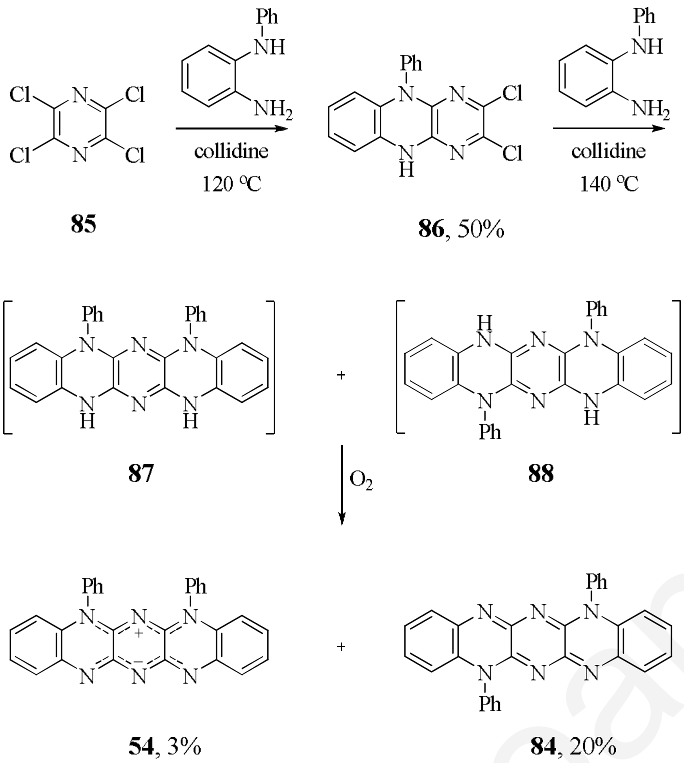
Other reported synthesis of *N*-heterocyclic acenes like 6,13-dihydro-5,6,7,12,13,14-hexaazapentacenes **82** include the nucleophilic aromatic substitution of 2,3-dicyano-1,4,5,10-tetraazaanthracenes **83** by benzenediamines **68** (Scheme 11).[228] Interestingly, historically, it was discovered as a condensation product of dichloroquinoxaline and diaminoquinoxaline in 1903,[229] and several patents claim its derivatives for applications as dyes.[230-232]



83 **68** **82**

Scheme 11. Synthesis of 6,13-dihydro-5,6,7,12,13,14-hexaazapentacenes **82**.

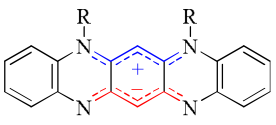
Recently, Fleischhauer *et al.*,[161] extended the hexaazapentacene family with the synthesis of the quinoidal fluorubine **84**, which was formed as the main product (20%) together with the zwitterionic compound **54** (3%) after tetrachloropyrazine **85** was condensed with 2,3-dichloro-5-phenyl-5,10-dihydropyrazino[2,3-*b*]quinoxaline **86** and the resultant regioisomeric mixture **87** and **88** was further oxidized (Scheme 12).



Scheme 12. Synthesis of quinoidal fluorubine **84** with its zwitterionic analog **54**.

1.6 Target of Project

In an effort to investigate new organic materials with interesting electronic properties, tetraazapentacene system **51** was studied. A preliminary computational study investigated the effect of EDGs and EWGs in strategic positions and determined substitution patterns that moderated the singlet-triplet energy gap (ΔE_{ST}). Our objective was to complete this computational study and validate it with experimental data by preparing several derivatives. The decrease or increase of ΔE_{ST} upon substitution on **51** can afford a useful tool for the design of high spin systems and at the same time candidates that may avoid zwitterionic character and be stabilized in the triplet ground state and therefore provide materials for magnetic or spintronic applications. The effect of the substitution as well as the conformation on analogous linear and angular dithiazoles was also investigated computationally.



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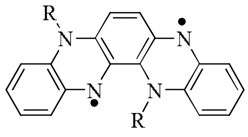


89

The promising candidate for electronic properties, angular analog **89**, which theoretically is stabilized in the triplet ground state is an additional synthetic target to study.

CHAPTER 2

Computational Study on Linear Tetraazapentacenes

2.1 Introduction

Tetraazapentacenes were investigated as potential diradicals due to the *m*-phenylene ferromagnetic coupling unit that could support two unpaired electrons located on the unsubstituted nitrogens (Figure 13).

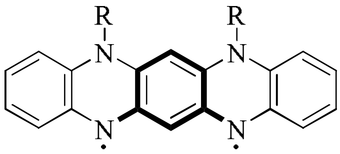
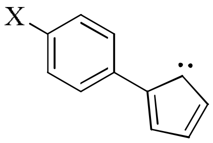


Figure 13. General structure of linear 5,7-disubstituted tetraazapentacenediyls.

The synthesis, characterization[154,155] and computational[233] study of 5,7-disubstituted tetraazapentacenes, however, proved that the compounds exist in the singlet and not the triplet ground state with an energy gap between the two states $\Delta E_{ST} = -10.05$ kcal/mol in favor of the singlet. The compounds exist as zwitterions (Figure 14), sporting both negative and positive cyanines, which is achieved by sacrificing the aromaticity of the central arene.[157] It is a challenge to investigate the electronic properties of such a system and also to modify its structure to enable diradical character.

Singlet-triplet gaps (ΔE_{ST}) have been modified upon substitution *e.g.*, in carbenes.[234-237] π Donors or acceptors on CX_2 species influence the ground state preference and ΔE_{ST} dramatically. For instance $C(C{\equiv}N)_2$ is stabilized in triplet state ($\Delta E_{ST} =$ 79.5 kcal/mol) while $C(NH_2)_2$ is stabilized in singlet state ($\Delta E_{ST} = -26.3$ kcal/mol).[235] Systems CX_2 and CXY have been studied computationally by various methods in an effort to provide accurate correlations with experimental data.[238] Similarly computational studies (B3LYP/6-311++G**) on aryl substituted cyclopentadienylidenes **90** showed that electron donating substituents at the phenyl group increase (more positive) ΔE_{ST} while electron withdrawing substituents decrease it.[239] HOMO-LUMO gaps support and explain the ΔE_{ST} screening,[240,241] since HOMO-LUMO gaps are increased upon EWG substitution and in contrast, they are decreased upon EDG substitution at the phenyl ring.



X = $-NH_2$, $-OH$, $-CH_3$, -F, -Cl, -Br, -H, $-CF_3$ and $-NO_2$

90

With the linear 5,7-disubstituted tetraazapentacenes we can assume that the negative and positive cyanines are major components of the HOMO and LUMO frontier orbitals, respectively. Furthermore, the substitution on strategic positions on the tetraazapentacene system can influence electronically the negative and positive cyanines and therefore the relative energies of the HOMO and LUMO orbitals. For example, the introduction of substituents that donate electron density either inductively or mesomerically to the negative cyanine would be expected to raise the HOMO energy level while by the introduction of substituents that withdraw electron density from the positive cyanine would be expected to lower the energy of the LUMO (Figure 14). Careful selection of substituents can therefore provide low band gap materials and if the HOMO-LUMO gap is sufficiently reduced (*i.e.*, $\Delta E_{\text{HOMO-LUMO}} < 1.5$ eV)[242] then the system should prefer the triplet over the singlet ground state.

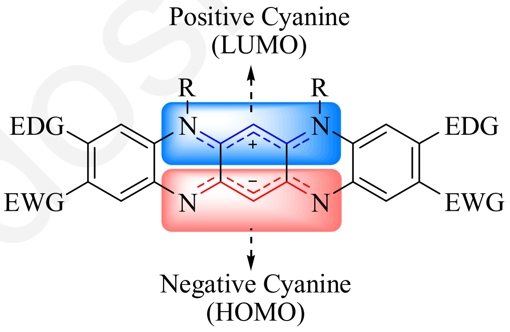


Figure 14. Substitution on tetraazapentacene to affect the HOMO-LUMO gap.

Tetraazapentacenes substituted on either positions X, Y, E or Z with a variety of EDGs and EWGs were studied computationally to understand the influence of the specific substitution (Figure 15). Analogs of several of these compounds were also synthesized (see Chapter 3) to validate the computational results. Furthermore, combinations of EDG and EWG's were studied computationally in an attempt to reach a theoretical triplet state structure. The energetic gap between the singlet and triplet state was estimated computationally as well as other electronic features such as the

HOMO-LUMO energetic difference, the band gap, the dipole moment, the spin electronic density and the geometric data.

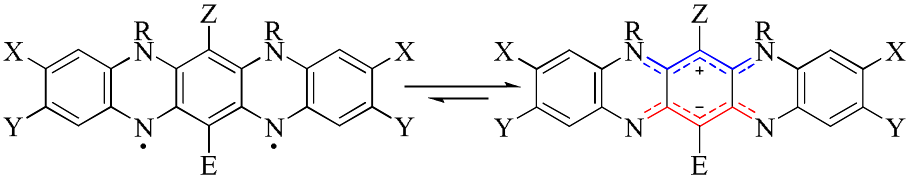
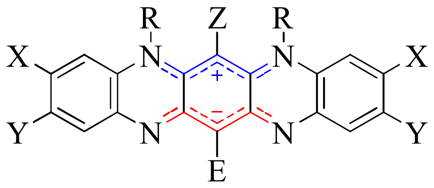


Figure 15. Triplet and singlet state of linear 5,7-disubstituted tetraazapentacenes.

2.2 Target Molecules

The systems studied were tetraazapenacenes substituted on the X, Y, E and Z positions. The substitution involved electron donating groups (EDGs) (NH_2, OMe and Me) and electron withdrawing groups (EWGs) (NO_2, C≡N, CF_3, F and Br). The substituents can have mesomerical (NH_2, OMe, NO_2, C≡N) or inductive (Me, CF_3, F, Br) effect. Table 1 shows the range of the substituted systems studied arranged in series of decreasing singlet-triplet gap (see Section 2.3). Hammett constants σ_{meta} and σ_{para}, which show the effectiveness of EDG or EWG substituents to donate or remove electron density to or from the biscyanine, respectively, are listed in Table 1 and provide information about the inductive or mesomeric influence of each substituent.[243,244]

Table 1. List of substituted TAPs studied computationally.



TAP	X	Y	E	Z	$\sigma_{meta}{}^{a}$	$\sigma_{para}{}^{a}$
51a	NO_2	NH_2	H	NH_2		
51b	H	H	CN	H	0.56	0.66
51c	NO_2	NH_2	H	H		
51d	H	H	H	NO_2	0.71	0.78
51e	H	NH_2	H	NH_2	-0.16	-0.66
51f	NO_2	H	H	H	0.71	0.78
51g	CN	OMe	H	H		
51h	H	NH_2	H	H	-0.16	-0.66
51i	CF_3	H	H	H	0.43	0.54
51j	CN	H	H	H	0.56	0.66
51k	H	F	H	H	0.34	0.06
51l	H	OMe	H	H	0.12	-0.27
51m	H	H	H	NH_2	-0.16	-0.66
51n	H	Br	H	H	0.39	0.23
51o	H	Me	H	H	-0.07	-0.17
51p	H	H	H	H	0.00	0.00
51q	H	H	H	CN	0.56	0.66
51r	H	CF_3	H	H	0.43	0.54
51s	Br	H	H	H	0.39	0.23
51t	H	CN	H	H	0.56	0.66
51u	Me	H	H	H	-0.07	-0.17
51v	H	NO_2	H	H	0.71	0.78
51w	F	H	H	H	0.34	0.06
51x[b]	NH_2	NO_2	H	H		
51y	OMe	H	H	H	0.12	-0.27
51z	NH_2	H	H	H	-0.16	-0.66
51aa	OMe	CN	H	H		
51ab	H	H	NH_2	H	-0.16	-0.66
51ac	NH_2	H	NH_2	H	-0.16	-0.66
51ad	NH_2	NO_2	H	H		
51ae	NH_2	NO_2	NH_2	H		

[a] Hammet constants are included for better understanding of substitution affect on HOMO-LUMO energy levels.

[b] Asymmetrical system: Substitution on one X and one Y position.

2.3 Methodology

For the computational study, density functional theory (DFT) with the spin polarized Becke's three parameter hybrid (U)B3LYP method[245,246] was employed using Gaussian 2003 or 2009[247] on Linux work stations. The geometries of the studied systems were fully optimized at the UB3LYP/6-31G(d) level of theory, both on singlet and triplet states. The optimization calculations of the singlets were followed by stability calculations that used the broken symmetry (BS) application[248-257] in case of internal instability. The analytical second derivatives were computed using vibrational analysis to confirm each stationary point as a minimum by giving zero imaginary frequencies. The stability and frequency calculations were performed at the same level of theory as the optimization calculations and where the BS approach was required, the optimization, stability and frequency calculations were repeated using the BS method at B3LYP/6-31G(d). The zero point energy was derived *via* the frequency calculations and scaled by 0.981 to correct the energy taken by the optimization calculation of each state.[258]

Using the above method, the structures ground state, singlet-triplet energy difference (ΔE_{ST}) and the spin-coupling constant J, which describes the effective exchange interaction between spin-carrier sites, were computed. The sign and value of J establishes the magnetic behavior of the structure. A positive J indicates triplet ground state and ferromagnetic coupling between the two spins while a negative J designates singlet ground state with antiferromagnetic coupling between the spins. There are three spin-projected methods that estimate J by equations that differ in their application ability depending on the overlap degree between the magnetic orbitals (SOMOs). The first one ($J_{ab}^{(1)}$) developed by Ginzberg,[259] Noodleman[260] and Davidson[261] (GND) is applied when the overlap of the SOMOs is small, the second one ($J_{ab}^{(2)}$) proposed by GND, Bencini[262] and Ruiz[263] is used when the overlap is large and the third one ($J_{ab}^{(3)}$) derived by Yamaguchi and Houk[264,265] leads to the first and second one in weak and strong overlap, respectively:

$$J_{ab}^{(1)} = \frac{{}^{BS}E_{DFT} - {}^{T}E_{DFT}}{S_{\max}^{2}} \qquad J_{ab}^{(2)} = \frac{{}^{BS}E_{DFT} - {}^{T}E_{DFT}}{S_{\max}\left(S_{\max}+1\right)} \qquad J_{ab}^{(3)} = \frac{{}^{BS}E_{DFT} - {}^{T}E_{DFT}}{{}^{T}\left\langle S^{2}\right\rangle - {}^{BS}\left\langle S^{2}\right\rangle}$$

Where: ${}^{BS}E_{DFT}$: total scaled energy for the singlet BS state

${}^{T}E_{DFT}$: total scaled energy for the triplet state

${}^{T}\langle S^2 \rangle$: total spin angular momentum for the triplet state

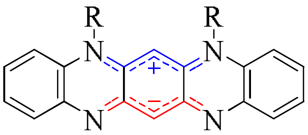
${}^{BS}\langle S^2 \rangle$: total spin angular momentum for the BS state

S_{max} : spin size of the triplet. Calculation formula: ${}^{T}\langle S^2 \rangle = S_{max}(S_{max} + 1)$

$J_{ab}{}^{(3)}$ is close to $J_{ab}{}^{(1)}$ when ${}^{T}\langle S^2 \rangle \cong S_{max}(S_{max} + 1)$ and ${}^{BS}\langle S^2 \rangle \cong S_{max}$ where S_{max} is the spin size for the triplet state, E_{DFT} is the total energy and S^2 is the total angular momentum for BS or triplet state. $J_{ab}{}^{(3)}$ is equal to $J_{ab}{}^{(2)}$ on strong overlap region where ${}^{BS}\langle S^2 \rangle \cong 0$. The energetic gap between singlet and triplet state can be estimated by the equation $\Delta E_{ST} = {}^{T}\langle S^2 \rangle J_{ab}$ given by Ginzberg where $\Delta E_{ST} = E_S - E_T$. Since both energies are negative, a positive sign of ΔE_{ST} denotes that the triplet state is the most stable while a negative ΔE_{ST} indicates that the singlet state is the lowest one.

While hydrogens were used as the substituents on the 5,7-nitrogens (positive cyanine) to facilitate the calculations, we nevertheless, ensured the lack of substituents did not dramatically affect the geometric or electronic properties calculated, by computationally investigating the influence of the 5,7-substituent *N*-Me (C_{sp^3}), *N*-Et (C_{sp^3}), *N*-vinyl (C_{sp^2}), *N*-aryl (C_{sp^2}) and *N*-C≡CH (C_{sp}) on the parent system (Table 2). Interestingly, the geometric data of the three center rings were nearly identical but the dipole moment of each structure differed significantly when the aryl substituent was introduced.

Table 2. Dipole moments of R-substituted systems.



R	Dipole Moment (Debye)	σ_{meta}	σ_{para}
H	7.41	0.00	0.00
Me	8.23	-0.07	-0.17
Et	8.42	-0.07	-0.15
vinyl	8.46	0.05	-0.02
p-Tol	10.81		-0.50
C≡CH	6.74	0.21	0.23

Methyl, ethyl and vinyl substituents give similar dipole moments to the system (8.23-8.46 D) but the C≡CH group significantly decreased the dipole moment (6.74 D). What was notable was the important increase of the dipole moment (10.81 D) in the case of *p*-tolyl. The increase of the dipole moment from an *sp*^{2} aliphatic substituent to an *sp*^{2} aromatic substituent could be explained by the ability of the aromatic ring to attract electron density ($\sigma_{para} = -0.50$) maximizing the positive charge on the positive cyanine. As can be seen from the optimized structure (Figure 16) the aryl substituent is orthogonal (dihedral angel 89.72°) and therefore no π-overlap is expected. The same is true for the vinyl substituent but to a lesser degree (dihedral angel 72.87°).

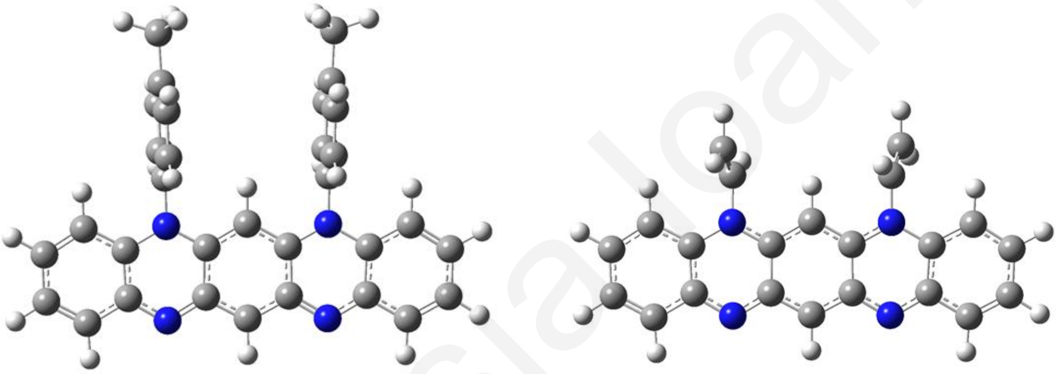


Figure 16. Optimized *N*-tolyl and *N*-vinyl substituted TAPs show that the tolyl and vinyl substituents are orthogonal to the azaacene structure.

Since the dipole moment is an important electron property of the system and the above results show that it depends from the *N*-substituent, the use of *N*-tolyl substituent on the systems is necessary for the calculations, at least for the ones that were synthesized having *N*-tolyl substituents, to compare more accurately the computational and experimental results. The computational cost though is increased when *N*-tolyl substituents are used instead of just *N*-H. Thus *N*-H substituents were used for the calculation of the substituted tetraazapentacenes while the parent and the substituted systems that were synthesized were also calculated with *N*-tolyl substituents.

What was expected from the computational study on these systems was the determination of the system's ground state, the energetic difference between singlet and triplet state (ΔE_{ST}) and any other properties that could be estimated and related to the substitution. Thus, beside optimization followed by frequency calculations, other calculations such as Time Dependence (TD) and Nucleus-Independent Chemical Shifts (NICS) calculations were applied. TD calculations provide the energetic difference of the ground and the first excited state (Band Gap) and thus they are a valuable tool for screening the substitution effect on the system. It can also be used for a good comparison with the experimental UV/*vis* data of the synthesized compounds and therefore can be used to validate the overall computational data. NICS calculations can be used to estimate the ring current of each ring and thus help describe how the aromaticity of each ring is affected by substitution. The central ring for example is more aromatic in the triplet state but sacrifices its aromaticity in the singlet state.

2.4 Computational Results

2.4.1 Spin Coupling and Singlet-Triplet Gap

Table 3 summarizes the computational data of the substituted tetraazapentacenes that were studied. Energies are in Hartrees (1 Hartree = 627.5095 kcal/mol). ΔE_{ST} and J are in kcal/mol. The data include the energies of singlet and triplet states (E_{S}, E_{T}) corrected by the zero point energy corrections ZPE, the total angular momentum $\left\langle S^2 \right\rangle$ of the triplet and singlet broken symmetry state, the spin coupling constants $J_{ab}^{(1)}$, $J_{ab}^{(2)}$ and $J_{ab}^{(3)}$ (shown also as J^1, J^2, J^3 respectively) and the energetic difference ΔE_{ST} for each J_{ab} as well as the energetic gap of singlet and triplet state by the abstraction $\Delta E_{\mathrm{ST}} = E_{\mathrm{S}} - E_{\mathrm{T}}$.

The ranking of structures in Table 3 is in order of most the stable singlet (top) to the least stable singlet (down) structures. Structure **51ae**, has the lowest $\Delta E^{\mathrm{U}}_{\mathrm{ST}}$ (1.61 eV) which indicates a potential triplet ground state. All the systems above the parent molecule are substituted contrarily to the way that should reduce the energetic gap of the singlet and triplet state. EDGs are placed *para* to the positive cyanine and EWGs are placed *para* to the negative cyanine and thus ΔE_{ST} is increased and the singlet ground state is more stabilized. The systems below the parent system demonstrate a reduction of ΔE_{ST} reaching even a positive value indicating stabilization of the triplet state. For instance, the amino group (NH_2) which act as EDG and is placed *para* to the negative cyanine on molecule **51z** reduced ΔE_{ST} at about 3.5 kcal/mol reaching -6.53 kcal/mol in referenced to the parent compound **51p** ($\Delta E^{\mathrm{U}}_{\mathrm{ST}}$ = -10.06 kcal/mol).

Table 3. Total energies (E_S, E_T) in hartrees, spin angular momentum ($\langle S^2 \rangle$) for singlet and triplet state, spin coupling constants J^1, J^2 and J^3, the energetic difference ΔE_{ST} for each J and ΔE^U_{ST} by abstracting E_S-E_T.

TAP	E_S ($\langle S^2 \rangle$)	E_T ($\langle S^2 \rangle$)	J^1	ΔE^1_{ST}	J^2	ΔE^2_{ST}	J^3	ΔE^3_{ST}	ΔE^U_{ST}
51a	-1486.919 (0.00)	-1486.885 (2.05)	-14.55	-29.80	-7.33	-15.02	-7.33	-15.02	-15.02
51b	-1004.145 (0.00)	-1004.124 (2.05)	-13.16	-26.93	-6.63	-13.57	-6.63	-13.57	-13.57
51c	-1431.587 (0.00)	-1431.566 (2.05)	-12.34	-25.27	-6.22	-12.74	-6.22	-12.74	-12.74
51d	-1116.411 (0.00)	-1116.391 (2.05)	-12.16	-24.89	-6.13	-12.54	-6.13	-12.54	-12.54
51e	-1077.882 (0.00)	-1077.862 (2.05)	-11.90	-24.35	-5.99	-12.27	-5.99	-12.27	-12.27
51f	-1320.903 (0.00)	-1320.884 (2.05)	-11.51	-23.58	-5.80	-11.89	-5.80	-11.89	-11.89
51g	-1325.360 (0.00)	-1325.341 (2.05)	-11.43	-23.46	-5.77	-11.83	-5.77	-11.83	-11.83
51h	-1022.568 (0.00)	-1022.550 (2.05)	-11.30	-23.13	-5.69	-11.65	-5.69	-11.65	-11.65
51i	-1585.967 (0.00)	-1585.949 (2.05)	-10.79	-22.12	-5.44	-11.15	-5.44	-11.15	-11.15
51j	-1096.392 (0.00)	-1096.374 (2.05)	-10.76	-22.08	-5.43	-11.13	-5.43	-11.13	-11.13
51k	-1110.380 (0.00)	-1110.363 (2.05)	-10.78	-22.08	-5.43	-11.12	-5.43	-11.12	-11.12
51l	-1140.876 (0.00)	-1140.859 (2.05)	-10.66	-21.84	-5.38	-11.01	-5.38	-11.01	-11.01
51m	-967.233 (0.00)	-967.216 (2.05)	-10.55	-21.60	-5.32	-10.88	-5.32	-10.88	-10.88
51n	-6054.127 (0.00)	-6054.110 (2.05)	-10.20	-20.90	-5.14	-10.53	-5.14	-10.53	-10.53
51o	-990.480 (0.00)	-990.464 (2.05)	-9.78	-20.04	-4.93	-10.10	-4.93	-10.10	-10.10
51p	-911.898 (0.00)	-911.882 (2.05)	-9.74	-19.96	-4.91	-10.06	-4.91	-10.06	-10.06
51q	-1004.148 (0.00)	-1004.132 (2.05)	-9.58	-19.63	-4.83	-9.90	-4.83	-9.90	-9.90
51r	-1585.964 (0.00)	-1585.949 (2.05)	-9.57	-19.61	-4.83	-9.88	-4.83	-9.88	-9.88
51s	-6054.127 (0.00)	-6054.112 (2.05)	-9.25	-18.95	-4.66	-9.55	-4.66	-9.55	-9.55
51t	-1096.387 (0.00)	-1096.372 (2.05)	-9.21	-18.87	-4.64	-9.51	-4.64	-9.51	-9.51
51u	-990.480 (0.00)	-990.465 (2.05)	-8.79	-18.00	-4.63	-9.07	-4.63	-9.07	-9.07
51v	-1320.896 (0.00)	-1320.882 (2.05)	-8.41	-17.22	-4.24	-8.68	-4.24	-8.68	-8.68
51w	-1110.378 (0.00)	-1110.365 (2.05)	-8.16	-16.70	-4.11	-8.42	-4.11	-8.42	-8.42
51x	-1171.735 (0.01)	-1171.723 (2.04)	-7.71	-15.75	-3.88	-7.93	-3.90	-7.98	-7.93
51y	-1140.877 (0.00)	-1140.865 (2.05)	-7.05	-14.42	-3.55	-7.27	-3.55	-7.27	-7.27
51z	-1022.570 (0.00)	-1022.559 (2.04)	-6.34	-12.96	-3.19	-6.53	-3.19	-6.52	-6.53
51aa	-1325.357 (0.21)	-1325.346 (2.05)	-6.16	-12.61	-3.10	-6.35	-3.46	-7.08	-6.35
51ab	-967.236 (0.53)	-967.236 (2.04)	-2.75	-5.60	-1.38	-2.82	-1.86	-3.80	-2.82
51ac	-1077.909 (0.66)	-1077.910 (2.04)	-1.52	-3.09	-0.76	-1.55	-1.13	-2.30	-1.55
51ad	-1431.575 (0.00)	-1431.573 (2.04)	-1.14	-2.34	-0.58	-1.18	-0.58	-1.18	-1.18
51ae	-1486.915 (0.90)	-1486.927 (2.04)	1.57	3.20	0.79	1.61	1.41	2.88	1.61

EDGs on positions X and EWGs on positions Y indeed decrease ΔE_{ST}. NH_2 and C≡N substituents that have similar donating and withdrawing ability respectively [$\sigma_{para}(NH_2) = -0.66$ and $\sigma_{para}(C{\equiv}N) = 0.66$] help us compare the effect of EDG and EWG substitution on each position. Thus by comparing -NH_2 and -C≡N substituted systems it seems that EDGs at position X (compound **51z**, ΔE^U_{ST} = -6.53 kcal/mol, decreasing parent's ΔE_{ST} at about 3.53 kcal/mol) have bigger influence on decreasing ΔE_{ST} than EWGs at positions Y (compound **51t**, ΔE^U_{ST} = -9.51 kcal/mol, decreasing parent's ΔE_{ST} at only 0.54 kcal/mol). Still EDGs placed *para* to the negative cyanine and EWGs placed *para* to the positive cyanine, decrease ΔE_{ST} while EDGs placed *para* to the positive cyanine and EWGs placed *para* to the negative cyanine, increase it.

Halogens F and Br are exceptions to the above resulting conclusion. They act mainly as EWGs but they can also act as EDGs mesomerically due to their lone electrons.

They may be placed in the "correct" positions but they predominantly influence the negative cyanine which is *meta* to them. This is explained from the corresponding Hammett values [$\sigma_{meta\text{(F)}} > \sigma_{para\text{(F)}}$ and $\sigma_{meta\text{(Br)}} > \sigma_{para\text{(Br)}}$]. Especially in the case of F [$\sigma_{meta\text{(F)}} = 0.34$, $\sigma_{para\text{(F)}} = 0.06$], where Hammett values support a weak mesomeric effect but a strong inductive effect. As a result, ΔE_{ST} is not reduced as expected but is increased instead. In the case of F substituent, molecule **51k**, ΔE_{ST} is increased at -11.12 kcal/mol. On the contrary, when they are placed on the X positions, ΔE_{ST} is reduced significantly *e.g.*, molecule **51w** where F is on X position ($\Delta E^{\text{U}}_{\text{ST}}$ = -8.42 kcal/mol). In the case of Br [$\sigma_{meta\text{(Br)}} = 0.39$, $\sigma_{para\text{(Br)}} = 0.23$], molecule **51s** where Br is on X position ($\Delta E^{\text{U}}_{\text{ST}}$ = -9.55 kcal/mol) shows more reduction of ΔE_{ST} compared to molecule **51n**, ($\Delta E^{\text{U}}_{\text{ST}}$ = -10.53 kcal/mol) where Br is on Y position.

The direct substitution on the positive cyanine (position Z) with the strongly electron withdrawing cyano group ($\sigma_{para} = 0.66$, $\sigma_{meta} = 0.56$), gave structure **51q** ($\Delta E^{\text{U}}_{\text{ST}}$ = -9.90 kcal/mol) which had a negligible effect on ΔE_{ST} compared to the parent **51p** ($\Delta E^{\text{U}}_{\text{ST}}$ = -10.06 kcal/mol). In contrast, direct substitution on the negative cyanine with the strongly donating amino group ($\sigma_{para} = 0.66$, $\sigma_{meta} = 0.16$) gave structure **51ab** ($\Delta E^{\text{U}}_{\text{ST}}$ = -2.82 kcal/mol) indicating a significant reduction of ΔE_{ST}. This result indicated that the negative cyanine was more important for the determination of the ground state of the molecule. The picture of the HOMO molecular orbital explains this since there is relatively little orbital density on the positive cyanine at C_6 (Z position) while there is considerable orbital density C_{13} (E position) on the negative cyanine (Figure 17), as such substituent effects at C_{13} (E) were greater than those at C_6 (Z). The direct substitution on the negative cyanine (position E) seem to have the largest effect on ΔE_{ST} not only if it is compared with direct substitution on the positive cyanine (position Z) but also with positions X and Y. For instance NH_2 substitution on X position (compound **51z**) gave $\Delta E^{\text{U}}_{\text{ST}}$ = -6.53 kcal/mol while on E position (compound **51ab**) gave $\Delta E^{\text{U}}_{\text{ST}}$ = -2.82 kcal/mol.

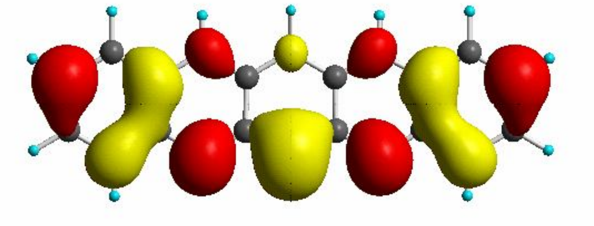


Figure 17. HOMO of the parent system.

The coexisting combination of substituents on the outer rings and directly on the cyanines gave a positive ΔE_{ST} which indicated destabilization of the singlet state. The stronger EDGs and EWGs of the studied substituents were NH_2 (σ_{para} = -0.66, σ_{meta} = -0.16) and NO_2 (σ_{para} = 0.78, σ_{meta} = 0.71), respectively. By controlling the combination of the substituents and adding two EDG substituents (NH_2) *para* to the negative cyanine and two EWG substituents (NO_2) *para* to the positive cyanine (molecule **30**), the reduction of ΔE_{ST} reached -1.18 kcal/mol. An additional substitution of NH_2 (molecule **31**) directly on the negative cyanine gave further reduction of ΔE_{ST} reaching the positive difference +1.61 kcal/mol which favored the triplet state.

To summarize, the direct substitution on the negative cyanine (position E) seem to have the largest effect on ΔE_{ST} compared with the rest strategic positions while halogens and especially F affect on their *meta* positions than the *para* as is also indicated from their Hammett values ($\sigma_{meta} > \sigma_{para}$). The general outcome is that indeed EDG substituents placed *para* to the negative cyanine and EWG substituents placed *para* to the positive cyanine, decrease the singlet-triplet energy gap ΔE_{ST}, destabilizing the singlet ground state and favoring the triplet.

The ability of a substituent to increase or decrease the energy of HOMO or LUMO can be seen in Table 4. The energies of HOMO and LUMO orbitals are in a.u. while their energetic difference ΔE_{HL} is in eV. ΔE_{HH} and ΔE_{LL} are the differences in eV of the HOMO and LUMO, respectively of each substituted molecule with the parent system according to the equations:

$\Delta E_{HL} = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$

$\Delta E_{HH} = E_{\mathrm{HOMO}} - {}^{51\mathrm{p}}E_{\mathrm{HOMO}}$

$\Delta E_{LL} = E_{\mathrm{LUMO}} - {}^{51\mathrm{p}}E_{\mathrm{LUMO}}$

Positive and negative values of ΔE_{HH} and ΔE_{LL} indicate increase and decrease of the substituted molecule's orbital energy level with respect to that of the parent molecule. Increment and decrement of the HOMO and LUMO orbital energies, respectively (positive ΔE_{HH} and negative ΔE_{LL}) are required to achieve a reduction of the HOMO-LUMO energy gap of the parent system. This was achieved, both in increasing ΔE_{HH} and decreasing ΔE_{LL}, on molecule **51ae**. In all other substituted systems, it was observed that HOMO and LUMO were both increased or decreased in energy to different degrees. The decrease of the HOMO-LUMO gap became clearer on molecules **51y** - **51ae** reaching a gap under 1.5 eV. According to Hoffmann, where the gap is less than 1.5 eV, the two nonbonding electrons on a diradical, will prefer to occupy degenerate orbitals having their spins parallel leading to a triplet ground state.[242] According to our calculations, the triplet ground state is achieved when this energy gap is less than 1 eV which is the case of molecule **51ae**. These data agree with the previous conclusions from the ΔE_{ST} data where molecules substituted on the correct strategic positions with NH_2 and NO_2 substituents, gave the best results compared with substituted molecules with other EDGs or EWGs.

Table 4. Frontier orbitals' energies and differences.

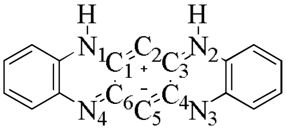
TAP	E_{HOMO} (au)	E_{LUMO} (au)	ΔE_{HH} (eV)	ΔE_{LL} (eV)	ΔE_{HL} (eV)
51a	-0.18273	-0.11873	-0.84	-0.90	1.74
51b	-0.16839	-0.09854	-0.45	-0.35	1.90
51c	-0.18441	-0.12133	-0.89	-0.97	1.72
51d	-0.16791	-0.09865	-0.44	-0.35	1.88
51e	-0.14130	-0.07241	0.28	0.36	1.87
51f	-0.19228	-0.12839	-1.10	-1.16	1.74
51g	-0.18243	-0.11695	-0.83	-0.85	1.78
51h	-0.14280	-0.07521	0.24	0.28	1.84
51i	-0.17279	-0.10563	-0.57	-0.54	1.83
51j	-0.18351	-0.11843	-0.86	-0.89	1.77
51k	-0.16122	-0.09379	-0.26	-0.22	1.83
51l	-0.14906	-0.08230	0.07	0.09	1.82
51m	-0.15005	-0.08257	0.05	0.08	1.84
51n	-0.16527	-0.09879	-0.37	-0.36	1.81
51o	-0.14848	-0.08205	0.09	0.10	1.81
51p	-0.15175	-0.08568	0.00	0.00	1.80
51q	-0.16484	-0.09929	-0.36	-0.37	1.78
51r	-0.16937	-0.10366	-0.48	-0.49	1.79
51s	-0.16260	-0.09840	-0.30	-0.35	1.75
51t	-0.17909	-0.11404	-0.74	-0.77	1.77
51u	-0.14657	-0.08165	0.14	0.11	1.77
51v	-0.18209	-0.11980	-0.83	-0.93	1.70
51w	-0.15498	-0.09198	-0.09	-0.17	1.71
51x	-0.15570	-0.09606	-0.11	-0.28	1.62
51y	-0.13955	-0.07976	0.33	0.16	1.63
51z	-0.13074	-0.07279	0.57	0.35	1.58
51aa	-0.17247	-0.11133	-0.56	-0.70	1.66
51ab	-0.13563	-0.08480	0.44	0.02	1.38
51ac	-0.11763	-0.07222	0.93	0.37	1.24
51ad	-0.15821	-0.11209	-0.18	-0.72	1.26
51ae	-0.14337	-0.11104	0.23	-0.69	0.88

On close inspection of the monosubstituted systems, it can be seen that of the EDG groups examined the amino group (-NH_2, σ_{para} = -0.66, σ_{meta} = -0.16) was the most effective at increasing the HOMO energy level (*e.g.*, on structure **51z**, Δ_{HH} = 0.57 eV) while of the EWG groups the nitro (-NO_2, σ_{para} = 0.78, σ_{meta} = 0.71) was the most efficient at reducing the LUMO energy level (*e.g.*, on structure **51f**, Δ_{LL} = -1.16 eV). Hammett values indicate these substituents are strongly *para* directing, presumably owing to their ability to contribute in a mesomeric manner. In contrast, the halogens, in particular the F groups have Hammett values (σ_{meta} = 0.34, σ_{para} = 0.06) that support stronger *meta* directing effects (*i.e.*, greater inductive contributions). As such the X = F analog (structure **51w**) affects not the HOMO but the LUMO since it is *meta* directing and not *para*, resulting in decreasing the LUMO energy level (Δ_{LL} = -0.17 eV) in a small degree and even less decreases the HOMO energy level (Δ_{HH} = -0.09eV). Furthermore, when F is placed on Y position, due to its *meta* directing effect, it reduces the HOMO energy level (Δ_{HH} = -0.26 eV) together with the LUMO energy level (Δ_{LL} = -0.22 eV). Me (σ_{meta} = -0.07, σ_{para} = -0.17) and CF_3 (σ_{meta} = 0.43, σ_{para} = 0.54) on the other hand, even though they act inductively, they affect the *para* position mostly but not in a tremendous difference. As such, in systems **51u** and **51o**, methyl achieves increase of both HOMO and LUMO energies while in systems **51r** and **51i**, CF_3 achieves reduction of both HOMO and LUMO energies, independently if they are placed in the “right” or “wrong” position since there was little difference. OMe substituent for example which is an EDG substituent with different inductive and mesomeric affect (σ_{meta} = 0.12, σ_{para} = -0.27) gives much different influence on HOMO and LUMO energy levels if is placed on “right” (structure **51y**, Δ_{HH} = 0.33 eV, Δ_{LL} = 0.16 eV) or “wrong” position (structure **51l**, Δ_{HH} = 0.07 eV, Δ_{LL} = 0.09 eV).

2.4.2 Geometric Data

Analysis of the geometric data for singlet and triplet state for the parent system **51p** (R = H) shows the difference between the two states and supports the zwitterionic character of the singlet state.

Table 5. Selected bond lengths (Å) and angles (°) of the parent system (R=H) on singlet and triplet state.



	C_1-C_2	C_2-C_3	C_4-C_5	C_5-C_6	C_1-C_6	C_3-C_4	N_1-C_1	N_2-C_3	C_4-N_3	C_6-N_4
Singlet	1.3948	1.3947	1.4033	1.4033	1.4646	1.4647	1.3535	1.3535	1.3449	1.3449
Triplet	1.3953	1.3953	1.4079	1.4079	1.4319	1.4319	1.3879	1.3879	1.3661	1.3661

	$C_1C_2C_3$	$C_4C_5C_6$	$C_2C_3C_4$	$C_2C_1C_6$	$C_3C_4C_5$	$C_1C_6C_5$	$N_1C_1C_6$	$N_2C_3C_4$	$C_1C_6N_4$	$C_3C_4N_3$
Singlet	119.46	123.33	121.47	121.30	117.13	117.13	116.99	116.98	121.30	121.30
Triplet	119.95	122.46	121.07	121.07	117.73	117.73	116.90	116.90	123.33	123.32

On going from the triplet to the singlet state of the parent system, no significant change in the cyanine C-C bond lengths (1.3953 *vs* 1.3948 Å, respectively) was observed while the C-N bond lengths decrease (1.3661/1.3879 *vs* 1.3449/1.3535 Å, respectively) and the lateral C-C bond lengths that connect the two cyanines (C_1-C_6 and C_3-C_4) increase (1.4319 *vs* 1.4647 Å). The longer lateral C-C bonds in the singlet state support their single bond character and lack of conjugation between the two cyanine π subsystems. This disproportion of the bond lengths in the central arene shows that the system avoids its overall antiaromaticity by sacrificing the aromaticity of the central arene for the creation of the two independent cyanines. This observation was also explained by Braunstein *et al.*,[266] describing such systems as "potentially antiaromatic" that in order to avoid antiaromaticity prefer to divide their electronic systems into two charged subunits connected by σ bonds. The only significant difference between the bond angles of the singlet and triplet states is the slightly larger angle of the $C_1C_6N_4$ bond angles of the negative cyanine (123.33° on triplet *vs* 121.30° on singlet).

The tendency of the substituted molecules to have longer bond lengths on the C-C bonds that connect the two cyanines could be an indication of their preference for the singlet ground state. As such, by comparing the geometric data of the theoretical studied substituted systems with the parent molecule, their ability to reduce or increase the singlet-triplet gap may be correlated with the length of the lateral cyanine C-C bonds. The geometric data, selected bond lengths (Å) and bond angles (°) of the singlet state substituted molecules are listed in Tables 6 and 7, respectively, while selected bond lengths of *N*-R substituted systems where R = Me, Et, vinyl, aryl and ethynyl are listed (Table 8).

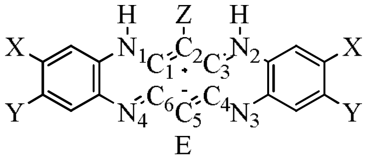


Table 6. Selected bond lenghts (Å) of the parent and the substituted systems on singlet state.

TAP	C_1-C_2	C_2-C_3	C_4-C_5	C_5-C_6	C_1-C_6	C_3-C_4	N_1-C_1	N_2-C_3	C_4-N_3	C_6-N_4
51a	1.4040	1.3983	1.4021	1.4013	1.4645	1.4709	1.3430	1.3506	1.3434	1.3439
51b	1.3942	1.3942	1.4235	1.4235	1.4616	1.4616	1.3538	1.3538	1.3331	1.3331
51c	1.3940	1.3940	1.4014	1.4014	1.4699	1.4699	1.3506	1.3506	1.3433	1.3433
51d	1.4372	1.4372	1.3991	1.3991	1.4613	1.4613	1.3386	1.3386	1.3489	1.3489
51e	1.4045	1.3992	1.4043	1.4033	1.4605	1.4668	1.3454	1.3529	1.3445	1.3455
51f	1.3940	1.3940	1.4011	1.4011	1.4656	1.4656	1.3528	1.3528	1.3457	1.3457
51g	1.3943	1.3943	1.4014	1.4014	1.4654	1.4655	1.3530	1.3530	1.3456	1.3457
51h	1.3950	1.3950	1.4036	1.4036	1.4656	1.4656	1.3529	1.3529	1.3447	1.3447
51i	1.3944	1.3944	1.4020	1.4020	1.4654	1.4654	1.3532	1.3532	1.3451	1.3451
51j	1.3943	1.3943	1.4015	1.4015	1.4647	1.4647	1.3535	1.3535	1.3459	1.3459
51k	1.3947	1.3947	1.4027	1.4027	1.4653	1.4653	1.3529	1.3529	1.3448	1.3448
51l	1.3948	1.3948	1.4033	1.4033	1.4666	1.4666	1.3524	1.3524	1.3439	1.3439
51m	1.4046	1.3989	1.4038	1.4031	1.4598	1.4660	1.3459	1.3535	1.3447	1.3455
51n	1.3947	1.3947	1.4025	1.4025	1.4647	1.4647	1.3537	1.3537	1.3451	1.3451
51o	1.3948	1.3949	1.4034	1.4034	1.4647	1.4647	1.3536	1.3536	1.3452	1.3453
51p	1.3948	1.3947	1.4033	1.4033	1.4646	1.4647	1.3535	1.3535	1.3449	1.3449
51q	1.4143	1.4143	1.4045	1.4045	1.4578	1.4578	1.3448	1.3448	1.3457	1.3457
51r	1.3943	1.3943	1.4026	1.4026	1.4645	1.4645	1.3542	1.3542	1.3451	1.3451
51s	1.3944	1.3944	1.4027	1.4027	1.4640	1.4640	1.3545	1.3545	1.3456	1.3456
51t	1.3940	1.3940	1.4022	1.4022	1.4648	1.4648	1.3547	1.3547	1.3446	1.3446
51u	1.3949	1.3948	1.4036	1.4036	1.4638	1.4638	1.3543	1.3543	1.3456	1.3457
51v	1.3940	1.3940	1.4021	1.4021	1.4643	1.4643	1.3552	1.3552	1.3449	1.3449
51w	1.3946	1.3946	1.4034	1.4034	1.4629	1.4629	1.3554	1.3554	1.3453	1.3453
51x	1.3963	1.3928	1.3995	1.4070	1.4587	1.4630	1.3562	1.3583	1.3492	1.3444
51y	1.3947	1.3947	1.4041	1.4041	1.4603	1.4603	1.3574	1.3574	1.3475	1.3475
51z	1.3941	1.3941	1.4026	1.4026	1.4634	1.4634	1.3562	1.3562	1.3453	1.3453
51aa	1.3950	1.3950	1.4045	1.4046	1.4601	1.4600	1.3574	1.3573	1.3473	1.3471
51ab	1.3959	1.3959	1.4113	1.4112	1.4485	1.4485	1.3592	1.3592	1.3543	1.3543
51ac	1.3939	1.3939	1.4035	1.4035	1.4597	1.4597	1.3599	1.3599	1.3465	1.3465
51ad	1.3956	1.3955	1.4112	1.4111	1.4528	1.4528	1.3554	1.3554	1.3517	1.3517
51ae	1.3953	1.3953	1.4118	1.4119	1.4471	1.4471	1.3620	1.3620	1.3538	1.3538

All the substituted systems as well as the parent have almost equivalent bond lengths on the C-C bonds of the cyanines (C_1-C_2, C_2-C_3, C_4-C_5 and C_5-C_6) and longer bond lengths on the C-C bonds that connect the two cyanines (C_1-C_6 and C_3-C_4). These two latter bond lengths though have not much difference among the substituted molecules to reflect any significant deviation from the singlet ground state of the parent system. Only on structures **51ab**-**51ae**, with the smallest ΔE_{ST} values, do the bond lengths C_1-C_6

and C_3-C_4 noticeably shorten (1.447-1.459 Å). By plotting the lateral C-C bond lengths (C_1-C_6) *vs* ΔE_{ST} this can be seen more clearly: graphs in Figure 18 plot the TAP systems with *N*-H substituent and the X and Y substituted with *N*-*p*-tolyl substituent, respectively. The first and last points are labeled with the structure's number to show that indeed there is tendency for shorter C_1-C_6 as the ΔE_{ST} reduces in favor of the triplet state.

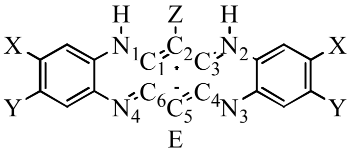


Table 7. Selected angles (°) of the parent and the substituted systems on singlet state.

TAP	$C_1C_2C_3$	$C_4C_5C_6$	$C_2C_3C_4$	$C_2C_1C_6$	$C_3C_4C_5$	$C_1C_6C_5$	$N_1C_1C_6$	$N_2C_3C_4$	$C_1C_6N_4$	$C_3C_4N_3$
51a	118.15	122.80	121.75	122.34	117.68	117.28	117.65	116.89	121.24	121.51
51b	119.53	122.37	121.91	121.91	117.14	117.14	116.67	116.67	121.50	121.50
51c	119.41	123.15	121.42	121.42	117.30	117.30	116.72	116.72	121.76	121.76
51d	118.57	123.20	120.53	120.53	118.59	118.59	116.91	116.91	120.86	120.86
51e	118.40	123.11	121.74	122.22	117.40	117.12	117.73	116.98	120.97	121.29
51f	119.31	122.93	121.44	121.44	117.44	117.44	116.85	116.85	121.49	121.49
51g	119.34	123.05	121.44	121.44	117.36	117.36	116.87	116.87	121.49	121.49
51h	119.53	123.44	121.44	121.44	117.07	117.07	116.82	116.82	121.51	121.51
51i	119.38	123.17	121.46	121.46	117.27	117.27	116.94	116.94	121.37	121.37
51j	119.32	123.02	121.45	121.45	117.38	117.38	116.93	116.93	121.39	121.39
51k	119.43	123.26	121.46	121.46	117.20	117.20	116.91	116.91	121.39	121.39
51l	119.49	123.42	121.46	121.46	117.08	117.08	116.89	116.89	121.47	121.47
51m	118.29	123.00	117.47	122.27	117.47	117.18	117.90	117.13	120.76	121.07
51n	119.36	123.18	121.48	121.48	117.25	117.25	116.99	116.99	121.31	121.31
51o	119.49	123.37	121.46	121.46	117.11	117.12	116.95	116.95	121.36	121.36
51p	119.46	123.33	121.47	121.30	117.13	117.13	116.99	116.98	121.30	121.30
51q	119.38	123.61	120.97	120.97	117.53	117.53	117.75	117.75	120.85	120.85
51r	119.36	123.20	121.50	121.50	117.22	117.22	117.01	117.01	121.28	121.28
51s	119.39	123.22	121.49	121.49	117.21	117.21	117.05	117.05	121.29	121.29
51t	119.30	123.15	121.53	121.53	117.25	117.25	117.02	117.02	121.27	121.27
51u	119.49	123.35	121.46	121.46	117.12	117.12	117.03	117.03	121.28	121.28
51v	119.23	123.08	121.56	121.56	117.29	117.29	117.07	117.07	121.23	121.23
51w	119.40	123.28	121.51	121.51	117.15	117.15	117.11	117.11	121.21	121.21
51x	119.36	123.20	121.75	121.28	117.00	117.40	117.21	117.03	121.03	121.38
51y	119.51	123.35	121.47	121.47	117.10	117.10	117.22	117.22	121.30	121.30
51z	119.30	123.17	121.55	121.55	117.22	117.22	117.14	117.14	121.21	121.21
51aa	119.50	123.38	121.48	121.49	117.08	117.07	117.21	117.21	121.13	121.13
51ab	118.20	121.35	122.19	122.19	118.01	118.00	116.58	116.58	122.14	122.14
51ac	119.25	123.21	121.64	121.64	117.13	117.13	117.39	117.39	121.07	121.07
51ad	118.16	121.19	122.19	122.19	118.11	118.11	116.37	116.37	122.25	122.25
51ae	117.79	121.03	122.46	122.46	118.10	118.10	116.70	116.70	122.12	122.12

Regarding the bond angles, a common characteristic can be observed on all substituted systems and that is the larger central angle ($C_4C_5C_6$) and CCN angles ($C_1C_6N_4$ and $C_3C_4N_3$) of the negative cyanine compared to the opposite angles ($C_1C_2C_3$, $N_1C_1C_6$

and $N_2C_3C_4$) of the positive cyanine. In contrast, the other CCC angles ($C_1C_6C_5$ and $C_3C_4C_5$) of the negative cyanine are smaller compared to the opposite angles ($C_2C_1C_6$ and $C_2C_3C_4$) of the positive cyanine.

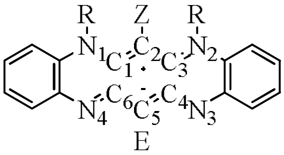


Table 8. Selected bond lenghts (**Å**) of *N*-R substituted systems on singlet state.

R	C_1-C_2	C_2-C_3	C_4-C_5	C_5-C_6	C_1-C_6	C_3-C_4	N_1-C_1	N_2-C_3	C_4-N_3	C_6-N_4
H	1.3900	1.3900	1.4000	1.4000	1.4600	1.4600	1.3500	1.3500	1.3400	1.3400
Me	1.4032	1.4032	1.4006	1.4006	1.4604	1.4604	1.3667	1.3667	1.3418	1.3418
Et	1.4034	1.4034	1.4004	1.4004	1.4629	1.4629	1.3679	1.3679	1.3423	1.3423
Vinyl	1.3990	1.3990	1.4017	1.4017	1.4606	1.4606	1.3693	1.3693	1.3429	1.3429
Tolyl	1.3900	1.4000	1.4000	1.4000	1.4600	1.4600	1.3700	1.3600	1.3400	1.3400
Ethynyl	1.3990	1.3928	1.4020	1.4020	1.4571	1.4571	1.3842	1.3842	1.3451	1.3451

The lateral C-C bonds C_1-C_6 and C_3-C_4 on the *N*-substituted systems are the longest compared to the rest C-C bonds as a consequence of the zwitterionic character and the separate subunits. The plots in Figure 18 can give a clearer picture relating ΔE_{ST} with C_1-C_6 bonds. Indeed from the three plots there can be seen a linear correlation where ΔE_{ST} is reduced as C_1-C_6 decreases.

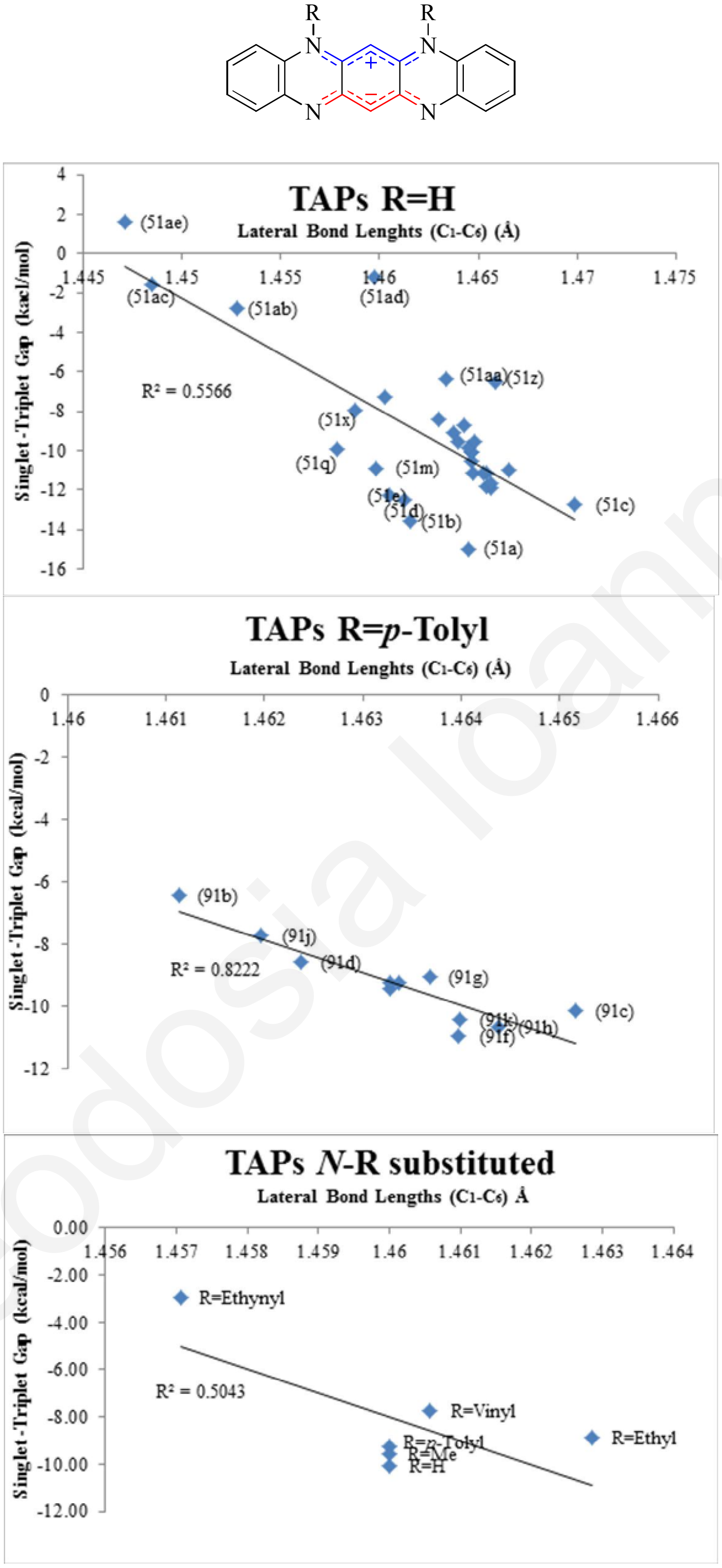


Figure 18. Graphs plotting lateral bond length (C_1-C_6) *vs* ΔE_{ST} for linear substituted tetraazapentacenes with R=H, *p*-Tolyl and *N*-R substituted, respectively.

Since some of the theoretical substituted systems were also synthesized with *N*-tolyl substituent (see Chapter 3), it was important to compare the computational geometric data of *N*-H and *N*-tolyl (compounds name **91** for *N*-tolyl systems as in following Chapter 3) substituted systems (Tables 9 & 10). A comparison indicates, however, that the *N*-substituent does not affect significantly any bond lengths or angles since most of them are very similar. This was also observed on *N*-Me, Et, vinyl, tolyl and ethynyl comparison (Table 8).

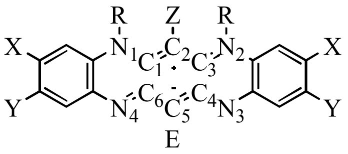


Table 9. Selected bond lengths (Å) of parent and substituted systems with *N*-H and *N*-tolyl substituents on singlet state.

TAP	R	C_1-C_2	C_2-C_3	C_4-C_5	C_5-C_6	C_1-C_6	C_3-C_4	N_1-C_1	N_2-C_3	C_4-N_3	C_6-N_4
51i	H	1.3944	1.3944	1.4020	1.4020	1.4654	1.4654	1.3532	1.3532	1.3451	1.3451
91h[a]	Tolyl	1.3982	1.3982	1.4002	1.4002	1.4644	1.4644	1.3685	1.3685	1.3432	1.3432
51j	H	1.3943	1.3943	1.4015	1.4015	1.4647	1.4647	1.3535	1.3535	1.3459	1.3459
91f[a]	Tolyl	1.3979	1.3979	1.3997	1.3997	1.4640	1.4640	1.3684	1.3684	1.3439	1.3439
51k	H	1.3947	1.3947	1.3997	1.4027	1.4653	1.4653	1.3529	1.3529	1.3448	1.3448
91k[a]	Tolyl	1.3985	1.3985	1.4009	1.4009	1.4640	1.4640	1.3685	1.3685	1.3429	1.3429
51l	H	1.3948	1.3948	1.4033	1.4033	1.4666	1.4666	1.3524	1.3524	1.3439	1.3439
91c[a]	Tolyl	1.3986	1.3986	1.4015	1.4015	1.4652	1.4652	1.3681	1.3681	1.3420	1.3420
51o	H	1.3948	1.3949	1.4034	1.4034	1.4647	1.4647	1.3536	1.3536	1.3452	1.3453
91e[a]	Tolyl	1.3987	1.3987	1.4016	1.4016	1.4633	1.4633	1.3694	1.3694	1.3433	1.3433
51p	H	1.3948	1.3947	1.4033	1.4033	1.4646	1.4647	1.3535	1.3535	1.3449	1.3449
91a[a]	Tolyl	1.3987	1.3986	1.4015	1.4015	1.4633	1.4633	1.3694	1.3694	1.3430	1.3430
51r	H	1.3943	1.3943	1.4026	1.4026	1.4645	1.4645	1.3542	1.3542	1.3451	1.3451
91i[a]	Tolyl	1.3981	1.3981	1.4007	1.4007	1.4634	1.4634	1.3699	1.3699	1.3431	1.3431
51t	H	1.3940	1.3940	1.4022	1.4022	1.4648	1.4648	1.3547	1.3547	1.3446	1.3446
91g[a]	Tolyl	1.3979	1.3979	1.4004	1.4004	1.4637	1.4637	1.3703	1.3703	1.3427	1.3427
51u	H	1.3949	1.3948	1.4036	1.4036	1.4638	1.4638	1.3543	1.3543	1.3456	1.3457
91d[a]	Tolyl	1.3988	1.3988	1.4017	1.4017	1.4624	1.4624	1.3704	1.3704	1.3437	1.3437
51w	H	1.3946	1.3946	1.4034	1.4034	1.4629	1.4629	1.3554	1.3554	1.3453	1.3453
91j[a]	Tolyl	1.3984	1.3984	1.4016	1.4016	1.4620	1.4620	1.3712	1.3712	1.3434	1.3434
51y	H	1.3947	1.3947	1.4041	1.4041	1.4603	1.4603	1.3574	1.3574	1.3475	1.3475
91b[a]	Tolyl	1.3986	1.3986	1.4022	1.4022	1.4611	1.4611	1.3720	1.3720	1.3440	1.3440

[a] Substitution same as in structure **51** but named after the synthesized systems **91** in Chapter 3.

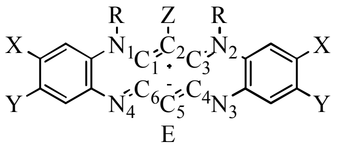


Table 10. Selected angles (°) of parent and substituted systems with *N*-H and *N*-tolyl substituents on singlet state.

TAP	R	$C_1C_2C_3$	$C_4C_5C_6$	$C_2C_3C_4$	$C_2C_1C_6$	$C_3C_4C_5$	$C_1C_6C_5$	$N_1C_1C_6$	$N_2C_3C_4$	$C_1C_6N_4$	$C_3C_4N_3$
51i	H	119.38	123.17	121.46	121.46	117.27	117.27	116.94	116.94	121.37	121.37
91h[a]	Tolyl	120.38	123.56	120.62	120.62	117.41	117.41	117.77	117.77	122.01	122.01
51j	H	119.32	123.02	121.45	121.45	117.38	117.38	116.93	116.93	121.39	121.39
91f[a]	Tolyl	120.33	123.42	120.61	120.61	117.51	117.51	117.75	117.75	122.04	122.04
51k	H	119.43	123.26	121.46	121.46	117.20	117.20	116.91	116.91	121.39	121.39
91k[a]	Tolyl	120.41	123.67	120.63	120.63	117.33	117.33	117.72	117.72	122.04	122.04
51l	H	119.49	123.42	121.46	121.46	117.08	117.08	116.89	116.89	121.47	121.47
91c[a]	Tolyl	120.44	123.82	120.66	120.66	117.21	117.21	117.67	117.67	122.10	122.10
51o	H	119.49	123.37	121.46	121.46	117.11	117.12	116.95	116.95	121.36	121.36
91e[a]	Tolyl	120.44	123.77	120.65	120.65	117.25	117.25	117.73	117.73	122.00	122.00
51p	H	119.46	123.33	121.47	121.30	117.13	117.13	116.99	116.98	121.30	121.30
91a[a]	Tolyl	120.43	123.74	120.64	120.64	117.27	117.27	117.77	117.77	121.94	121.94
51r	H	119.36	123.20	121.50	121.50	117.22	117.22	117.01	117.01	121.28	121.28
91i[a]	Tolyl	120.36	123.59	120.66	120.66	117.36	117.36	117.82	117.82	121.92	121.92
51t	H	119.30	123.15	121.53	121.53	117.25	117.25	117.02	117.02	121.27	121.27
91g[a]	Tolyl	120.31	123.54	120.68	120.68	117.40	117.40	117.85	117.85	121.91	121.91
51u	H	119.49	123.35	121.46	121.46	117.12	117.12	117.03	117.03	121.28	121.28
91d[a]	Tolyl	120.46	123.75	120.63	120.63	117.26	117.26	117.82	117.82	121.92	121.92
51w	H	119.40	123.28	121.51	121.51	117.15	117.15	117.11	117.11	121.21	121.21
91j[a]	Tolyl	120.39	123.71	120.69	120.69	117.27	117.27	117.89	117.89	121.88	121.88
51y	H	119.51	123.35	121.47	121.47	117.10	117.10	117.22	117.22	121.30	121.30
91b[a]	Tolyl	120.46	123.80	120.66	120.66	117.21	117.21	117.97	117.97	121.86	121.86

[a] Substitution same as in structure **51** but named after the synthesized systems **91** in Chapter 3.

There is a slight increase of the N_1-C_1 and N_2-C_3 bond lengths of the positive cyanine of the *N*-tolyl substituted systems (1.3681 Å - 1.3720 Å) compared to the *N*-H substituted systems (1.3524 Å - 1.3574 Å) (Table 9). Furthermore, compared to the parent there is a slight increase of the central bond angles of both positive and negative cyanines ($C_1C_2C_3$ and $C_4C_5C_6$) in the *N*-tolyl systems while there is a small decrease of the $C_2C_3C_4$ and $C_2C_1C_6$ bond angles of the positive cyanine (Table 10). In addition all the CCN angles of *N*-tolyl systems are also increased in a small degree (*e.g.* on $N_1C_1C_6$: 117.67° - 117.99° on *N*-tolyl systems *vs* 116.89° - 117.22°).

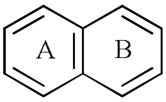
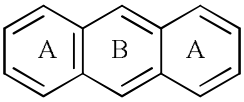
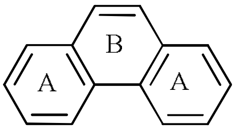
2.4.3 NICS Calculations

Polycyclic conjugated hydrocarbons have been extensively studied regarding their aromaticity. There are many criteria used to estimate aromaticity *e.g.*, aromatic stabilization energy (ASE), and isomerization stabilization energy (ISE), are energy criteria.[267] Geometry criteria are also used having as prototype the benzene ring where all the C-C bonds are equal having bond lengths between single and double bond. Nucleus-Independent Chemical Shifts (NICS)[268] calculations proposed by Schleyer *et al.*, in 1996, are magnetism criteria for the determination of the ring current as diatropic (aromatic character) or paratropic (antiaromatic character). Other and older magnetism criterions are the diamagnetic susceptibility exaltation Λ and nuclear magnetic resonance NMR.[269]

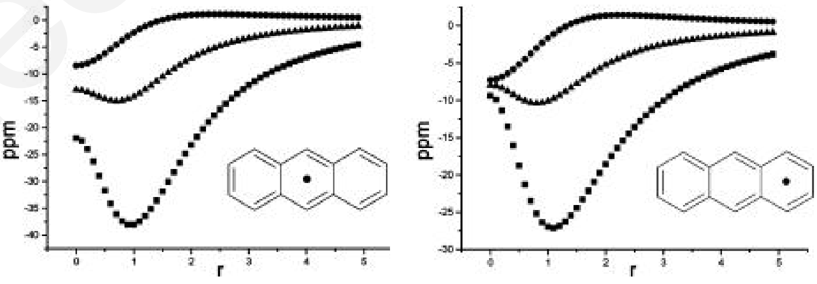
NICS is a computational method that estimates ring current locally, in each ring separately. The π electron current is estimated in the center of each planar ring where a Bq ghost atom is introduced. In the plane of the ring the σ orbital contributions to NICS prevails but 1 Å above the ring center, the π orbitals have their maximum density and thus the estimation of the π delocalization can be done more accurately. Therefore NICS(1) (1 Å above the ring center) is recommended compared to NICS(0) (at the ring center and same plane) for the estimation of aromaticity since it avoids σ orbital contributions.[270] Near zero NICS values designate non aromaticity. Negative NICS values denote diatropic ring current *i.e.*, aromaticity, while positive values denote paratropic ring current *i.e.*, +28.8 for cyclobutadiene. Furthermore, qualitative comparisons can be made to benzene's ring currents (-11.5 ppm).[268]

Linear polycyclic hydrocarbons have been studied using NICS calculations and other methods for the aromaticity estimation of each ring.[271] It is observed that the central ring of a linear polycyclic system is more aromatic than the outer rings. For example with anthracene NICS(1) = -13.06 ppm on the central ring is whereas on the outer rings NICS(1) = 9.80 ppm. In contrast, in the angular analogous systems, *e.g.*, phenanthrene, the central ring is less aromatic than the outer rings (Table 11).[271]

Table 11. NICS values (ppm) on RB3LYP/6-311+G** level of theory.[223]

	NICS (0) Ring A	NICS (1) Ring A	NICS (0) Ring B	NICS (1) Ring B
	-8.55	-10.71	-8.55	-10.71
	-7.50	-9.80	-11.47	-13.06
	-8.53	-10.71	-5.72	-8.40

NICS calculations cannot be used strictly in such complicated systems. Thus NICS-scan technique is preferred where NICS values are estimated in a larger range *e.g.*, 0 to 4.9 Å and a plot of the NICS values *vs* the distance of the Bq atoms indicates the degree of aromaticity. A deep negative minimum denotes diatropic ring current, a positive maximum stands for paratropic and when there can be seen negative NICS values that decrease (becoming more positive) when distance increases and asymptotically are going to zero, then no ring current is present.[272] For example, anthracene has a deeper minimum for the central ring (≈ - 40 ppm) than the outer ring (≈ - 28 ppm), which indicates more aromaticity on the centre than on the edges. The graph is composed by the out of plane components (above the plane of the molecule), in plane components (away from the center of the ring but in the same plane) and the isotropic chemical shift (Figure 19).[272]



(α) (β)

NICS values as a function of diastance r (Angstrom) of anthracene.
(α) Central ring (β) Terminal ring
▪ Out of plane ● In plane ◄ Isotropic chemical shift

Figure 19. NICS (ppm) *vs* distance (Å) for middle and outer rings of anthracene.[272]

The singlet ground state of the substituted molecules is determined by their ability to form two independent cyanines which necessitates the sacrificing of the aromaticity of the central arene. The loss of aromaticity should be reflected by a bond length analysis (see Section 2.3.2) but also by studying the magnetic ring currents using NICS. As such, NICS calculations performed on the zwitterionic tetraazapentacene biscyanines are expected to show antiaromaticity or at least non aromaticity for the central ring and aromaticity on the outer rings which are not affected by the zwitterionic character of the system, while for the triplet ground state, the central ring is expected to be aromatic (Figure 20).

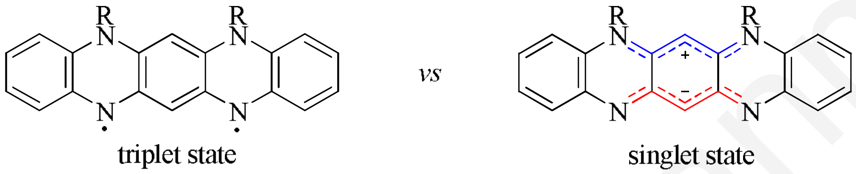


Figure 20. Linear TAP in triplet and singlet state.

The out of plane NICS values were estimated in the B3LYP/6-31G(d) level of theory for the parent system **16** to show the aromatic character on each ring. Unlike linear polycyclic systems, this tetraazapentacene system owing to the zwitterionic biscyanine character shows less aromaticity at the central benzene ring. The graph of each ring of the parent system shows that the central ring (ring 1) is less aromatic than the outer rings (ring 3) while the diazine rings (ring 2) are antiaromatic (Figure 21). TAP systems substituted by F and OMe substituents on X and Y positions were also studied regarding their aromaticity in each ring *via* NICS calculations to confirm the aromaticity behavior observed on the parent system since the same aromaticity behavior is estimated in all these singlet ground state systems. The resulting plots are identical to the parent system as expected.

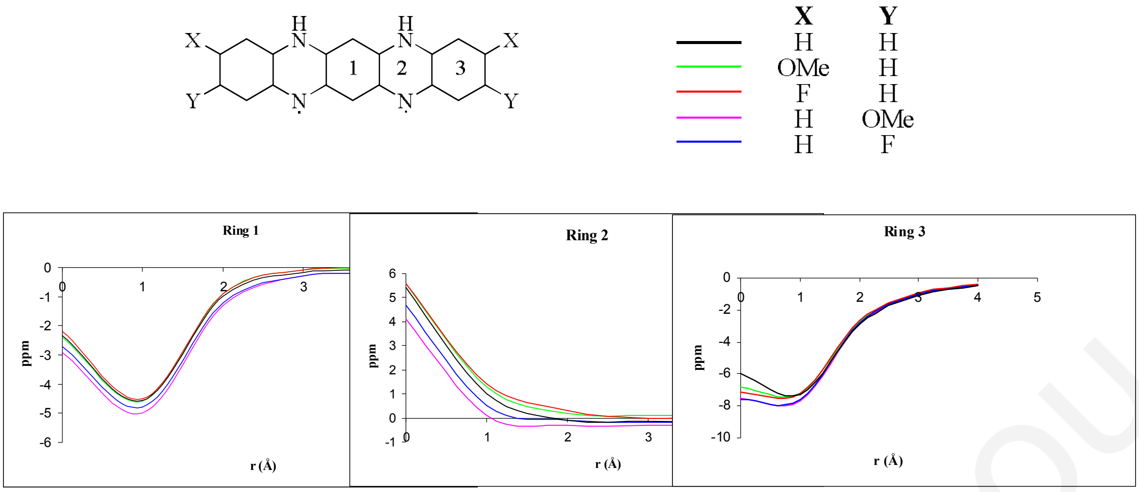


Figure 21. NICS (ppm) *vs* distance (Å) for the three rings of substituted TAPs **51k**, **51l**, **51p**, **51w** and **51y**.

NICS(0) and NICS(1) on selected substituted analogs **51a**, **51k**, **51l**, **51p**, **51w**, **51y**, **51ae** are listed in Table 12. Systems **51k**, **51l**, **51w**, **51y** show similar behavior to the parent system **51p** as was also observed in the plots in Figure 21. In the two extreme cases though, substituted structures **51a** and **51ae**, NICS calculations successfully show the difference on the aromaticity of each benzene ring, as the singlet or the triplet state is approached respectively.

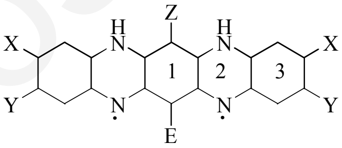


Table 12. NICS values (ppm) on parent **51p** (X = Y = Z = E = H) and selected substituted systems **51a** (X = NO_2, Y=Z = NH_2), **51k** (Y = F), **51l** (Y = OMe), **51w** (X = F), **51y** (X = OMe) and **51ae** (X = E = NH_2, Y = NO_2).

	Ring 1		Ring 2		Ring 3	
	NICS (0)	NICS (1)	NICS (0)	NICS (1)	NICS (0)	NICS (1)
51a	-4.0	-5.7	2.1	1.6	-7.3	-7.1
51k	-2.7	-4.8	4.7	0.5	-7.6	-7.6
51l	-2.9	-5.0	4.1	0.1	-7.5	-7.7
51p	-2.3	-4.6	5.4	1.0	-6.0	-7.3
51w	-2.2	-4.5	5.6	1.4	-7.1	-7.2
51y	-2.4	-4.6	5.6	1.3	-6.8	-7.2
51ae	-15.9	-16.3	13.1	7.4	-2.7	-3.3

Structure **51a**, with NO_2 substituents on X positions and NH_2 substituents on Y and Z positions, gives the most negative ΔE_{ST} (-17.48 kcal/mol) and thus the most singlet ground state character. NICS calculations give slight aromacity on the central ring (ring 1) and aromaticity on the outer rings (ring 3) similarly to systems **51k**, **51l**, **51p**, **51w** and **51y**. On the other hand structure **51ae**, with NH_2 substituents on X and E positions and NO_2 substituents on Y positions, gives the most positive ΔE_{ST} and reaches the triplet ground state (+1.61 kcal/mol). NICS estimate much more aromatic character on ring 1 [NICS(1) = -16.3 ppm] of system **51ae** compared to the rest rings of the system and the other systems herein. These results confirm that NICS studies can be used in extreme cases to study and differentiate the singlet-triplet behavior of zwitterionic tetraazapentacenes.

Similar to benzene, aromatic systems have usually NICS values around -10 to -15 ppm depending on the structure and the computational method used. For instance NICS calculations [B3LYP/6-31G(d)/GIAO/SCF] estimate NICS (1) for monocyclic aromatic systems furan, thiophene and pyrolle, -10.5, -11.1 and -12.5 ppm, respectively. When these monocyclic systems are fused to a benzene ring though their NICS (1) values change and become -9.2, -9.1 and -11.7 ppm, respectively.[273] These numbers show how much less the aromaticity is on the central ring of the linear tetraazapentacene systems studied here. S zwitterionic systems like tetraphenylhexaaza-anthracene (TPH-athracene) and tetraphenylhexaaza-acridine (TPH-acridine) have NICS(1) values -2.0 and +2.6 ppm for central and outer ring respectively of TPH-anthracene and -1.1 and +1.4 ppm for central and outer ring respectively of TPH-acridine.[175] These numbers are comparable to ring 1 and ring 2 of TAPs studied here.

2.4.4 Time Dependent Calculations

Time Dependent (TD) calculations estimate the energetic difference between the ground and excited states (band gap) and provide helpful data regarding the molecules' singlet-triplet gap. As the frontier orbitals of the molecule become closer in energy the band gap between the ground and first excited state is reduced and when close enough lead to destabilization of the singlet state and formation of a singlet biradical or triplet ground state.

The TD data can be compared with the experimental data provided by the UV/*vis* spectroscopy. TD calculations were performed using a range of methods such as

ZINDO, BLYP, B3LYP, PBE and PBE0. The energetic difference of the ground state and the first singlet excited state in eV shows a noticeable difference among the results of the various methods (Table 13).

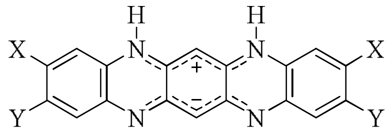


Table 13. TD data (eV) in various methods for selected substituted molecules compared with experimental results.

TAP	TD-ZINDO	TD-BLYP	TD-B3LYP	TD-PBE	TD-PBE0	λmax UV/Vis (DCM) (eV)
51i	1.43	1.63	1.75	1.65	1.80	1.67
51j	1.43	1.63	1.75	1.65	1.80	1.67
51k	1.43	1.66	1.78	1.68	1.83	1.71
51l	1.42	1.62	1.75	1.64	1.80	1.72
51o	1.42	1.60	1.72	1.62	1.77	1.65
51p	1.41	1.58	1.60	1.60	1.75	1.64
51r	1.41	1.55	1.66	1.56	1.71	1.61
51t	1.39	1.48	1.61	1.49	1.65	1.56
51u	1.38	1.55	1.66	1.56	1.71	1.59
51w	1.39	1.47	1.60	1.49	1.64	1.56
51y	1.34	1.38	1.50	1.39	1.55	1.50

On going from molecule **51i** to molecule **51y** ΔE_{ST} is reduced and if the energetic difference between the ground and first singlet state is also reduced, then there is a good agreement of the TD data and the ΔE_{ST} results. Indeed in all the methods used, this reduction is achieved with some exceptions and these are molecules **51w** in TD-ZINDO, **51k** and **51u** in TD-BLYP, **51k**, **51r** and **51u** in TD-B3LYP, and **51k** and **51u** in TD-PBE and TD-PBE0. These exceptions, according to the TD data have bigger energetic gaps than what was expected from the ΔE_{ST} resulting series. In general though, the decrease of this energetic difference is similarly followed in all the methods studied. The most accurate method can only be discerned by comparison with the experimental UV/*vis* data (*i.e.*, synthesized *N*-tolyl substituted systems **51i**, **51j**, **51k**, **51l**, **51o**, **51p**, **51r**, **51t**, **51u**, **51w**, **51y**) from which the energetic gap can be estimated from the $\lambda_{\max}$ value (see Section 3.4). This comparison showed that of the methods investigated, TD-B3LYP was the more accurate method.

Band gaps calculated using TD-B3LYP were compared to HOMO-LUMO energetic gaps (ΔE_{HL}) for the theoretical structures **51a-51ae** (Table 14). In general the decreasing trend of the calculated band gaps on going from structure **51a** (most stable singlet structure, ΔE_{ST} -17.48 kcal/mol) to structure **51ae** (least stable singlet structure, ΔE_{ST} 17.61 kcal/mol) were in line with decreasing ΔE_{HL}, as expected. Furthermore, there was in most cases a linear relationship between band gap and ΔE_{ST} (Figure 22).

Table 14. Band gap (TD-B3LYP) for the parent and substituted molecules, the HOMO-LUMO energetic difference (ΔE_{HL}) and the singlet - triplet energy gap (ΔE_{ST}).

TAP	X	Y	E	Z	Band Gap (eV)	ΔE_{HL} (eV)	ΔE_{ST} (kcal/mol)
51a	NO_2	NH_2	H	NH_2	1.75	1.74	-15.02
51b	H	H	CN	H	1.76	1.90	-13.57
51c	NO_2	NH_2	H	H	1.79	1.74	-12.74
51d	H	H	H	NO_2	1.42	1.88	-12.54
51e	H	NH_2	H	NH_2	1.72	1.72	-12.27
51f	NO_2	H	H	H	1.85	1.84	-11.89
51g	CN	OMe	H	H	1.76	1.78	-11.83
51h	H	NH_2	H	H	1.81	1.84	-11.65
51i	CF_3	H	H	H	1.75	1.83	-11.15
51j	CN	H	H	H	1.75	1.77	-11.13
51k	H	F	H	H	1.78	1.83	-11.12
51l	H	OMe	H	H	1.75	1.82	-11.01
51m	H	H	H	NH_2	1.74	1.84	-10.88
51n	H	Br	H	H	1.71	1.81	-10.53
51o	H	Me	H	H	1.72	1.81	-10.10
51p	H	H	H	H	1.70	1.80	-10.06
51q	H	H	H	CN	1.66	1.78	-9.90
51r	H	CF_3	H	H	1.66	1.79	-9.88
51s	Br	H	H	H	1.65	1.75	-9.55
51t	H	CN	H	H	1.61	1.77	-9.51
51u	Me	H	H	H	1.66	1.77	-9.07
51v	H	NO_2	H	H	1.48	1.70	-8.68
51w	F	H	H	H	1.60	1.71	-8.42
51x	NH_2	NO_2	H	H	1.44	1.62	-7.93
51y	OMe	H	H	H	1.51	1.63	-7.27
51z	NH_2	H	H	H	1.47	1.58	-6.53
51aa	OMe	CN	H	H	1.50	1.66	-6.35
51ab	H	H	NH_2	H	1.12	1.38	-2.82
51ac	NH_2	H	NH_2	H	1.09	1.26	-1.55
51ad	NH_2	NO_2	H	H	1.00	1.24	-1.18
51ae	NH_2	NO_2	NH_2	H	0.56	0.88	1.61

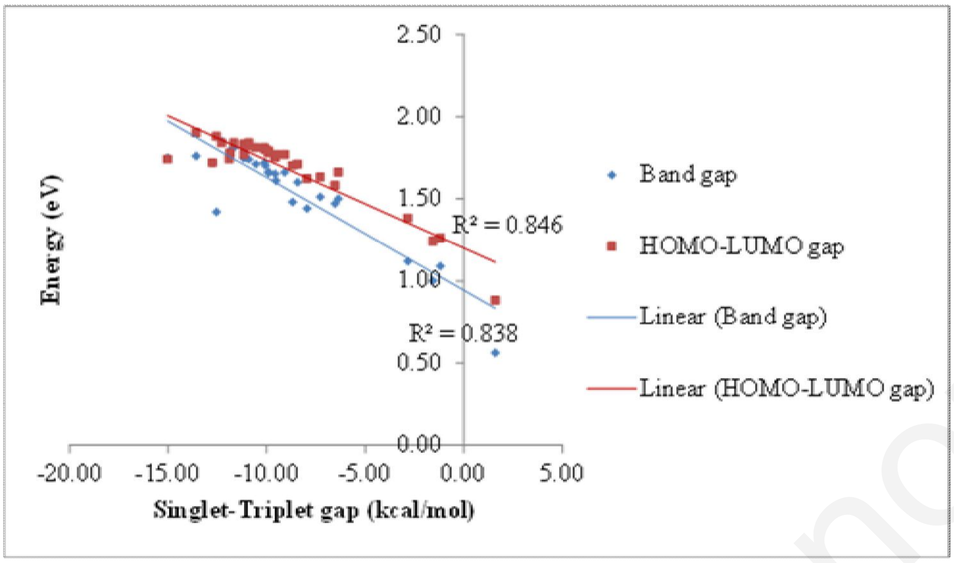


Figure 22. Band Gap and ΔE_{HL} *vs* ΔE_{ST} for systems **51a-51ae**.

The linear correlation between the Band Gap and ΔE_{ST} supports the hypothesis that the optical band gap can be used to estimate the ΔE_{ST} and furthermore the TD computations validated the computational methods used for structure optimization. This was also observed on HOMO-LUMO gap *vs* ΔE_{ST} correlation. Furthermore, experimental UV/*vis* data for several derivatives (see Chapter 3) was closely in agreement with the computed band gaps which further validated the chosen computational method.

2.5 Summary

A range of substituted linear zwitterionic tetraazapentacenes were studied computationally in an effort to determine the effect of substitution on ΔE_{ST}. The strategic addition of suitable EDG and EWG's can be used to manipulate ΔE_{ST} by as much as the range -17.48 to +1.61 kcal/mol while in the case of a tetra substituted analog structure **31**, a positive ΔE_{ST} of 1.61 kcal/mol was obtained. Worthy of note was that the introduction of an amino group directly on the negative cyanine at C_{13}, had the most dramatic affect lowering the ΔE_{ST} from -10.06 to -2.81 kcal/mol. B3LYP/6-31G(d) which was chosen for the optimization of the studied structures also proved to be accurate in estimating TD data since they correlate well with the experimental UV/*vis* data and also the geometric data as discussed in Chapter 3.

CHAPTER 3

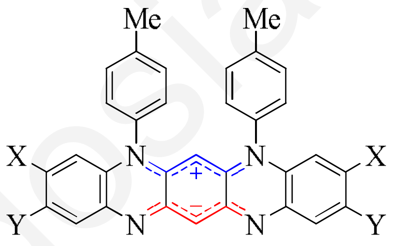
Synthesis of Substituted 5,7-Di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides

3.1 Introduction

The synthesis of a range of substituted 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides (5,7-DTQP's) **91** was carried out to obtain experimental data such as UV/*vis* absorption and single crystal X-ray spectroscopy for comparison with and validation of the DFT computational study (Chapter 2).

Ten substituted analogs of 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **91** were synthesized. The *p*-tolyl group was selected for the positive cyanine N5 and N7 nitrogen atoms because it helped simplify both the ^{1}H and ^{13}C NMR spectra by providing an upfield CH_3 signal which was a useful spectroscopic handle in the NMR spectra. Electron Donating Groups (EDGs) [MeO- (σ_{para} = -0.27, σ_{meta} = 0.12) and Me- (σ_{para} = -0.17, σ_{meta} = -0.07)] and Electron Withdrawing Groups (EWGs) [F- (σ_{para} = 0.06, σ_{meta} = 0.34), N≡C- (σ_{para} = 0.66, σ_{meta} = 0.56) and F_3C- (σ_{para} = 0.54, σ_{meta} = 0.43)] were chosen for the C_3 and C_9 positions (X position) or the C_2 and C_{10} positions (Y) (Table 15).

Table 15. 5,7-DTQP targets with substituents at C_3/C_9 (X) or C_2/C_{10} (Y).

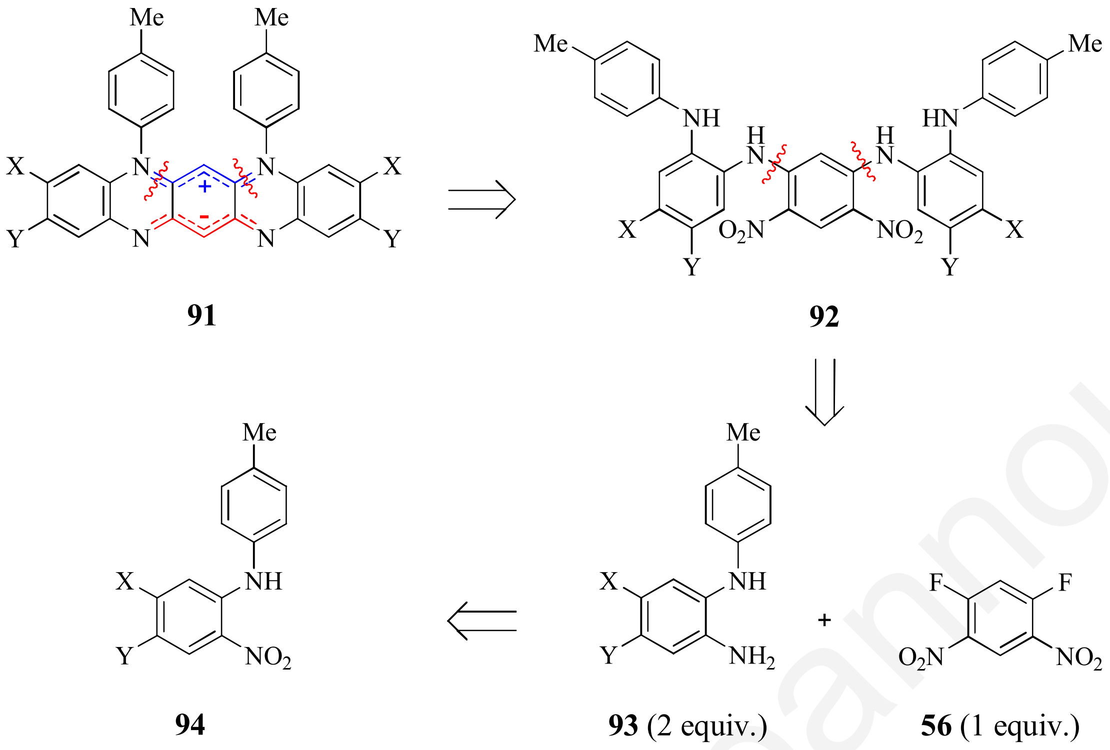


DTQP	X	Y		σ_{meta}	σ_{para}
91a	H	H			
91b	OMe	H	EDG	0.12	-0.27
91c	H	OMe		0.12	-0.27
91d	Me	H		-0.07	-0.17
91e	H	Me		-0.07	-0.17
91f	CN	H	EWG	0.56	0.66
91g	H	CN		0.56	0.66
91h	CF_3	H		0.43	0.54
91i	H	CF_3		0.43	0.54
91j	F	H		0.34	0.06
91k	H	F		0.34	0.06

The methoxy and cyano substituents predominantly influence the electronics *via* strong mesomeric effects as EDG and EWG, respectively, while the methyl, fluoro, and trifluoromethyl substituents predominantly influence the electronics *via* a weaker inductive effect. Hammett values indicate the effect of each substituent at *meta* and *para* positions. Positive signs specify electron withdrawing effect while negative signs are for electron donating effect. The cyano substituent (C≡N) has the strongest electron withdrawing effect due to positive inductive (-I) and mesomeric (-M) effect. The trifluoromethyl substituent (CF_3) also has electron withdrawing effect. The fluorine substituent (F) on the other hand may have a positive σ value but the ratio of σ_{meta} and σ_{para} values ($\sigma_{meta} = 0.34$, $\sigma_{meta} = 0.06$) shows the fluorine acts more inductively than mesomerically, *i.e.*, affects the *meta* positions more effectively that the *para* position. The methoxy substituent (OMe) has opposite signs for the substituent constant due to opposing inductive and mesomeric effect, however, since σ_{para} (-0.27) is significantly larger than σ_{meta} (0.12) then the mesomeric effect dominates, while methyl (Me) is electron-releasing in both respects (see Table 1, Chapter 2). The chosen range of substituents provided a thorough picture of the substitution effect regarding the electronic properties of 5,7-DTQP.

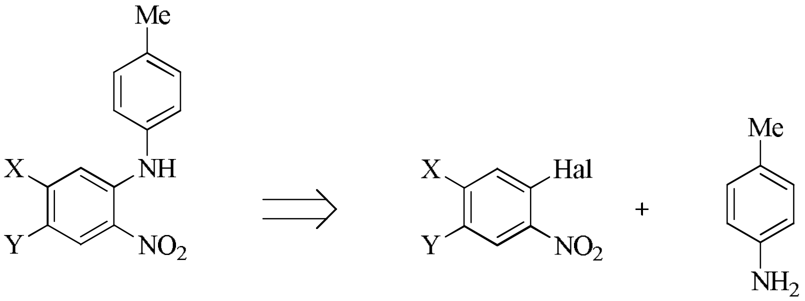
3.2 Methodology and Synthesis

The retrosynthetic analysis of substituted 5,7-DTQPs **91a-k** was based on the synthetic method proposed by Koutentis[155] and required access to substituted 2-nitro-*N*-(*p*-tolyl)benzeneamines **94** (Scheme 13).



Scheme 13

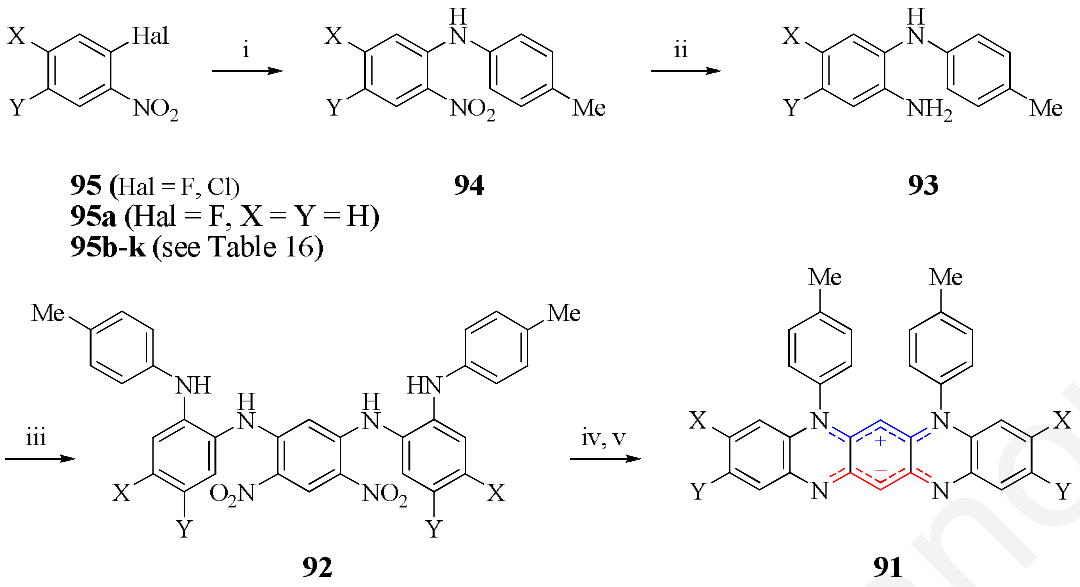
2-Nitro-*N*-(*p*-tolyl)benzeneamine **94** can be prepared *via* three routes: 1) *via* copper mediated Ullmann C-N coupling,[274-277] 2) *via* Pd or Cu catalysed Buchwald-Hartwig C-N coupling[278,279] and 3) *via* base catalysed nucleophilic aromatic substitution (S_NAr)[280,281] of anilines on 2-halonitrobenzenes. The starting materials required in all the above methods are aryl halides and anilines. The first two methods, which require metal catalysts, work well for Br and I substituted nitrobenzenes since the ease of halogen displacement from the aromatic ring is generally I > Br > Cl. The opposite trend was observed on halogen displacement using the uncatalysed S_NAr reaction and thus the latter procedure favors F and Cl substituents.[281] Since 2-chloro and 2-fluoronitrobenzenes were more readily available than the 2-bromo and 2-iodonitrobenzenes the S_NAr route was chosen for the synthesis of the substituted 2-nitro-*N*-(*p*-tolyl)benzeneamines **94**. In addition, the *ortho* nitro substituent, strongly activated the halo substituent towards displacement and favored aromatic nucleophilic substitution (S_NAr). Thus, the substituted 2-halogenated nitrobenzenes **95** and 4-toluidine **96** were the required staring materials (Scheme 14).



94 **95** (Hal = F, Cl) **96**

Scheme 14

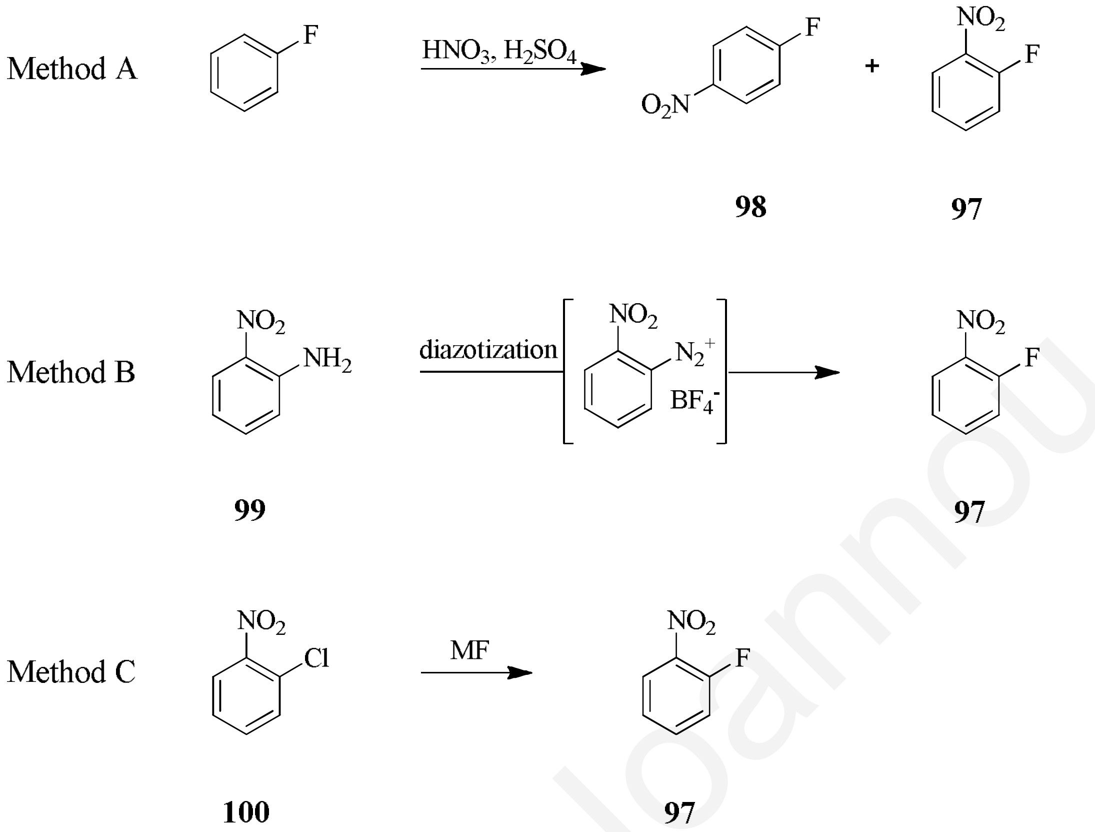
2-Nitro-*N*-(*p*-tolyl)benzeneamines **94** gave *N*-(*p*-tolyl)-1,2-benzenediamines **93** after reduction of the nitro group. Benzenediamines **93** reacted with 1,5-difluoro-2,4-dinitrobenzene **56** under basic conditions to give the disubstituted 1,5-bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes **92**. Hydrogenation of the nitro groups using Pd/C followed by filtration (Celite®) to remove the heterogenous catalyst and partial oxidation under the atmospheric air in refluxing EtOH led to the formation of a deep green solution from which the target 5,7-di-(*p*-tolyl)-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides **91** were isolated as lustrous blue green microcrystals (Scheme 15).



Scheme 15. *Reagents and conditions:* i) *p*-$MeC_6H_4NH_2$ (2 equiv.), KF (1 equiv.), 180 °C, 48 h; ii) H_2, Pd/C (5 mol%), EtOH, 20 °C, 1-3 h; iii) 1,3-F_2-2,4-$(O_2N)_2C_6H_2$ (0.5 equiv.), *i*-Pr_2EtN (1 equiv.), EtOH, 80 °C, 1-3 d; iv) H_2, Pd/C (5 mol%), EtOH, 20 °C, 4-6 h; v) air, EtOH, 80 °C, 0.5-1 h.

3.2.1 Synthesis and Characterisation of Substituted 2-Halonitrobenzenes

2-Fluoronitrobenzene **97** has been synthesized by three basic synthetic methods (Scheme 16):[282] The first (Method A) was *via* direct nitration of fluorobenzene using a mixture of sulfuric and nitric acids. The resulting product was an isomeric mixture of *para* and *ortho*-fluoronitrobenzenes in a 9:1 ratio favoring the *para* product **98**. The second (Method B) was the diazotization of 2-nitroaniline **99** and its conversion to 2-nitrodiazonium fluoroborate. Thermal decomposition of the latter, gave 2-fluoro-nitrobenzene **97** in low yields. The thermal decomposition of fluoroborates was achievable only when the nitro group was at the *ortho* position and thus only the *ortho* product can be synthesized *via* this method. Finally, the third and most preferred (Method C) involved halogen exchange using an alkali metal fluoride on 2-chloronitrobenzene **100**. Long reaction times and high temperature are required affording the product in moderate to good yields.



Scheme 16

Heating a solvent free mixture of 2-chloronitrobenzene **100** and KF (1 equiv.) without stirring at 290 °C for 1 d under pressure in a sealed tube, gave 2-fluoronitrobenzene **97** in 61% yield based on recovered 2-chloronitrobenzene (50%).[283] Using DMF at 170 °C or DMSO at 185 °C for 7 d and 4.5 h, respectively the reaction gave similar yields around 40%.[284] The yield was improved to 56% though when the reaction in DMSO was kept for 10 h and in tetramethylene sulfone (240 °C, 22 h).[282]

An improved method of halogen displacement by fluorination on 2-chloronitrobenzene involved the use of ultra-fine particulate KF in tetramethylene sulfone with a macrocyclic ether or a quaternary ammonium halide catalyst. The product yield reached 87% with 13% unreacted 2-chloronitrobenzene. The latter procedure was also applicable when the chloro and nitro substituents were in the *para* positions.[285]

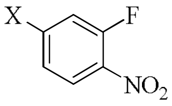
Other ways of synthesizing fluoronitrobenzene have also been reported. An effort to synthesize fluoronitrobenzene by Appelman *et al.*, by reacting nitrobenzene with cesium fluoroxysulfate ($CsSO_4F$) in the presence of an acid catalyst, showed that the *meta* product was mostly favored and that the yields were very low but could be enhanced with the use of an acid catalyst such as BF_3, FSO_3H or “magic acid” $SbF_5.FSO_3H$.[286]

2-Fluoronitrobenzene was also synthesized by fluorodenitration of 1,2-dinitrobenzene using tetraphenylphosphonium hydrogendifluoride.[287]

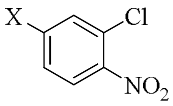
Fortunately, the following 2-chloro and 2-fluoronitrobenzenes were commercially available and did not need to be synthesized (Table 16). Nevertheless, 3-fluoro-4-nitroanisole **95b** and 3-chloro-4-nitrobenzonitrile **95f** had to be prepared.

Table 16. Availability of 2-halonitrobenzenes.

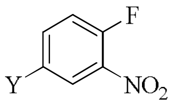
Commercial



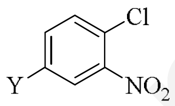
X = Me **95d**
X = F **95j**



X = CF_3 **95h**

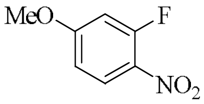


Y = CF_3 **95i**
Y = F **95k**

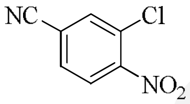


Y = OMe **95c**
Y = Me **95e**
Y = CN **95g**

Noncommercial



95b

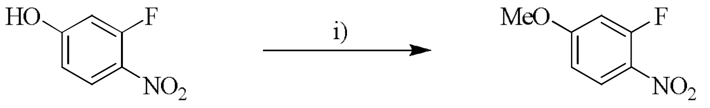


95f

3.2.1.1 *Synthesis of 3-fluoro-4-nitroanisole **95b***

3-Fluoro-4-nitroanisole **95b**, required for the preparation of 3,9-dimethoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **91b**, was synthesized *via* O-methylation of the analogous phenol. In general, alkylation of phenols can usually be carried out by reaction of an alkali metal phenolate with alkyl halides or sulfates. O-Methylation can occur with simple refluxing of phenols with excess MeI, using either anhydrous K_2CO_3 in DMF,[288] KOH in DMSO[289] or NaH in THF/DMF mixtures.[290] The use of more powerful alternative methylating agents such as Me_2SO_4,[291] and the less hazardous dimethyl carbonate (DMC) in the presence of a base and a catalyst such as the couple of K_2CO_3 and Bu_4NBr[292,293] or DBU as catalyst,[294] or in the presence of an ionic liquid like 1-*n*-butyl-3-methylimidazolium chloride ([BMIm]Cl)[295] have been used. Furthermore, diazomethane has been used to methylate acidic hydroxyl groups in the presence of an acid catalysts such as fluoroboric acid.[296]

3-Fluoro-4-nitroanisole **95b** was eventually synthesized *via* O-methylation of the commercially available 3-fluoro-4-nitrophenol **101** using Me_2SO_4 in the presence of K_2CO_3 and acetone under reflux (Equation 1).[297]



(1)

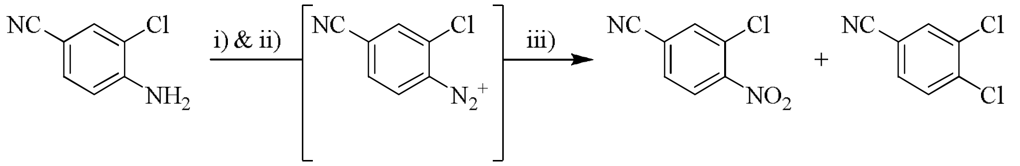
101 **95b**

Reagents and conditions: i) Me_2SO_4 (1.5 equiv.), K_2CO_3 (4 equiv.) Me_2CO, *ca.* 50 °C (reflux), 3 h, 81% (lit.,[297] 85%).

The work up involved addition of H_2O to the reaction mixture, followed by neutralization with acetic acid (AcOH). After extraction (DCM) and collection of the organic layer, a dark oil was isolated. On cooling (fridge, *ca.* 3 °C) this oil solidified to afford a light brown solid. A short chromatograph removed the dark polar material (baseline TLC) to afford a yellow oil which on trituration with *n*-pentane gave 3-fluoro-4-nitroanisole **95b** as a colorless solid [mp 48 °C (*n*-hexane), lit.,[297] 56 °C] in good yield (81%). The reaction could be performed comfortably on 1 g scale to provide enough material for the subsequent chemistry.

*3.2.1.2 Synthesis of 3-chloro-4-nitrobenzonitrile **95f***

3-Chloro-4-nitrobenzonitrile **95f**, required for the preparation of 3,9-dicyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **91f**, was prepared from the commercially available 4-amino-3-chlorobenzonitrile **102**[298] *via* Sandmeyer nitration. The procedure involved the classic diazotization method with $NaNO_2$ and $Cu(I)NO_2$ (Equation 2). To a suspension of 4-amino-3-chlorobenzonitrile **102** in concentrated HCl at *ca.* 0 °C, an aqueous solution of $NaNO_2$ (1.5 equiv.) was added. The mixture was stirred (10 min) and then added to a suspension of $NaNO_2$ and freshly prepared Cu_2O[299,300] in H_2O at *ca.* 0 °C. After stirring for 30 min at *ca.* 0 °C and then 30 min at *ca.* 20 °C, the reaction mixture was extracted (DCM), washed with brine, and dried (Na_2SO_4). Chromatography gave 3-chloro-4-nitrobenzonitrile **95f** as colorless crystals, [mp 77-78 °C (*n*-pentane), lit.,[298] yellow oil] in 70% yield. Interestingly, although not reported in the literature procedure, we also isolated from this reaction 3,4-dichlorobenzonitrile **104** [mp 64-65 °C (*n*-pentane)] as a trace side-product.



102 **103** **95f** (70%) **104** (trace)

Reagents and conditions: i) HCl (conc.), H_2O, 0 °C; ii) aqueous $NaNO_2$ (1.5 equiv.), 0 °C, 10 min; iii) suspension of aqueous $NaNO_2$ (7 equiv.), Cu_2O (0.4 equiv.), *ca.* 0 to 20 °C, 1 h, **95f** 70% (lit.,[298] 87%), **104** (trace).

With the 2-chloro- and 2-fluoronitrobenzenes either purchased or synthesized the preparation of the required diarylamines could be pursued.

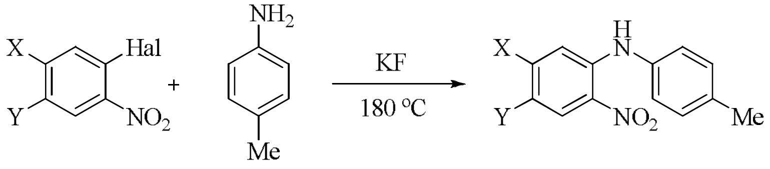
3.2.2 Synthesis and Characterisation of 2-Nitro-*N*-(*p*-tolyl)benzeneamines **94**

*Synthesis of 2-nitro-*N*-(*p*-tolyl)benzeneamines* ***94***

The next synthetic step involved the formation of the 2-nitro-*N*-(*p*-tolyl)benzene-amines **94** *via* nucleophilic aromatic substitution (S_NAr). The reaction of 2-chloro-nitrobenzene with 4-toluidine has been previously reported and heating a mixture at 170 °C for 12 h[301] or under MW irradiation (90 W) for 8 min[302] gave the desired product in 74 and 90% yields, respectively. Because of the required multigram scale for the synthesis of the 2-nitro-*N*-(*p*-tolyl)benzeneamines **94**, conventional heating methods (woods metal bath) were chosen instead of MW irradiation.

As such, the halogenated nitrobenzenes were mixed with 4-toluidine and KF, and heated at *ca.* 180 °C for about 48 h without stirring (Table 17). The reaction was judged complete when all the halogenated nitrobenzene had been consumed (TLC). At this point the mixture was allowed to cool to *ca.* 20 °C, dissolved in DCM and extracted with aqueous HCl (5-10%) to remove unreacted amine. In most cases dry flash chromatography was also needed to remove minor side-products.

Table 17. Reaction of 2-halonitrobenzenes **95** (1 equiv.) with *p*-toluidine **96** (2 equiv.) and KF (1 equiv.) at 180 °C.



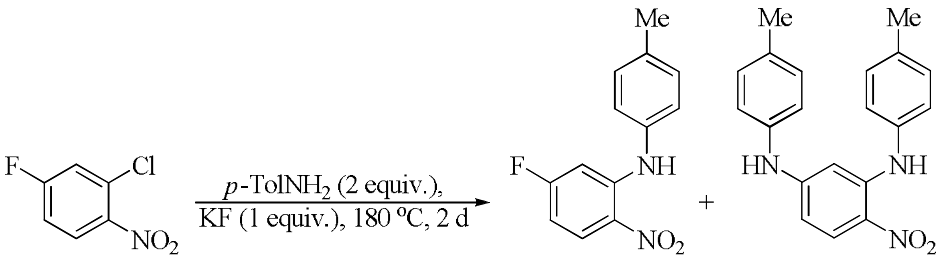
95 **96** **94**

95	Hal	X	Y	Time (d)	Yields **94** (%)
95a	F	H	H	2	**94a** (87)
95b	F	MeO	H	2	**94b** (75)
95c	Cl	H	MeO	4^a	**94c** (17)
95d	F	Me	H	2	**94d** (84)
95e	Cl	H	Me	> 2	**94e** (37)
95f	Cl	CN	H	< 1	**94f** (64)
95g	Cl	H	CN	2	**94g** (92)
95h	Cl	F_3C	H	2	**94h** (85)
95i	F	H	F_3C	2	**94i** (99)
95j	F	F	H	2	**94j** (82)
95k	F	H	F	2	**94k** (79)

[a] *p*-Toluidine (3 equiv.) and KF (1.5 equiv.)

The 2-nitro-*N*-(*p*-tolyl)benzeneamines **94** were generally isolated in good yields especially when additional electron withdrawing substituents were present, however, where electron releasing substituents were *para* with respect to the halogen (*e.g.*, Y = Me and Y = OMe) the reactions were sluggish, gave mixtures that were difficult to extract with aqueous HCl, and furthermore, were difficult to chromatograph due to excess formation of polar material (baseline on TLC). These products were isolated in very low yields, presumably because these substituents deactivated the arene towards nucleophilic attack. At best, for a 1 g scale reaction the use of 4-toluidine (3 equiv.) and KF (1.5 equiv.) heated over 4 d gave 37% yields of the Y = Me product and 17% of Y = OMe product.

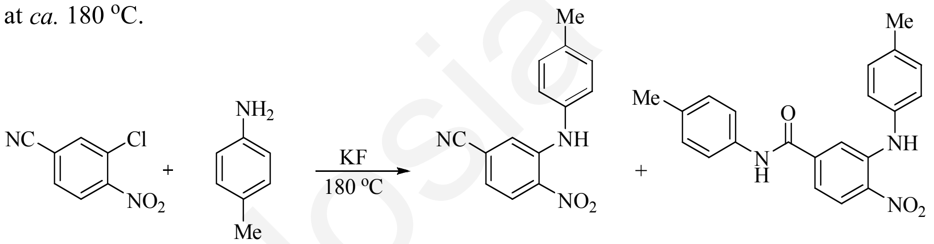
Interestingly 4-nitro-*N,N'*-[di-(*p*-tolyl)]benzene-1,3-diamine **105** was isolated as a very minor side-product (1%) from the reaction of 2-chloro-4-fluoro-1-nitrobenzene **95j** with *p*-toluidine in order to get 5-fluoro-2-nitro-*N*-(*p*-tolyl)-benzeneamine **94j** (Eq. 3). This supported that the 5-fluoro of **94j** was reactive enough to be displaced under the reaction conditions.


(3)

95j **94j** (82%) **105** (1%)

Another important side-product, 4-nitro-*N*-(*p*-tolyl)-3-(*p*-tolyl-amino)-benzamide **106**, was also isolated from the reaction of chloronitrobenzonitrile **95f** with 4-toluidine. Under the specific conditions and depending on the reaction scale, the carbon of the cyano group could be attacked by excess 4-toluidine and on work up the carboxamide **106** was isolated. Increasing the reaction scale led to longer reaction times, higher yields of side-product **106**, and a decreased yield of the target molecule **94f** (Table 18).

Table 18. Reaction of 3-chloro-4-nitrobenzonitrile **95f** with *p*-toluidine **96** and KF (1 equiv.) at *ca.* 180 °C.



95f **96** **94f** (major) **106** (minor)

95f (mmol)	**96** (equiv.)	Time (h)	Yields (%) **94f**	 **106**
0.16	2	4	63	-
0.22	2	<24	64	-
1.48	2	>24	57	trace
3.83	2	>24	42	2
1.10	1.25	4 d	49	-
1.10	1.5	3 d	35	-

The reaction was best performed on a small scale (30 mg, 0.16 mmol or 40mg, 0.22 mmol) of 3-chloro-4-nitrobenzonitrile **95f** using 4-toluidine (2 equiv.) and anhydrous KF (1 equiv.), at *ca.* 180 °C. These conditions led to a complete consumption of the halonitrobenzene in less than 24 h to afford the target molecule 3-(*p*-toluidino)-4-nitrobenzonitrile **94f** in 63% - 64%. This side reaction was observed only during the reaction of 3-chloro-4-nitrobenzonitrile **95f** (X = C≡N) with 4-toluidine. The isomeric 4-chloro-3-nitro-benzonitrile **95g** (Y = C≡N), which has the cyano group *meta* to the activating nitro group, when treated with 4-toluidine gave only the target molecule 4-(*p*-toluidino)-3-nitrobenzonitrile **94g** in 92% yield. Clearly the carbon of the C≡N group on 3-chloro-4-nitrobenzonitrile **95f** (X = C≡N) was more strongly activated towards nucleophilic attack by the *para* electron withdrawing nitro group.

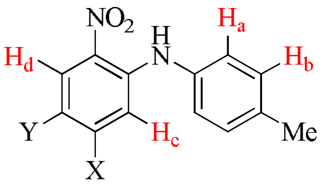
*Characterisation of 2-nitro-*N-*(*p-*tolyl)benzeneamines **94***

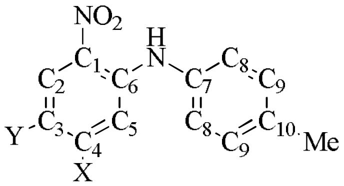
2-Nitro-*N*-(*p*-tolyl)benzeneamines **94** were isolated as orange crystals, usually needles, and recrystallized from *n*-hexane. Their molecular weights were determined by mass spectrometry (MS) which also provided information about characteristic fragmentations. Bulk purity was determined by melting point, by quantitative element analysis (EA), which also supported the molecular formulae, and by ^{1}H- and ^{13}C-NMR spectroscopy. Infrared (FTIR) spectroscopy helped identify of characteristic functional groups while UV/*vis* spectroscopy described electronic transitions.

MS analysis not only provided the parent ion but also gave details about important fragmentations such as the loss of the NO_2 group (M^+-NO_2). The UV/*vis* spectroscopy of these systems showed an absorption between 400 and 200 nm. Infrared spectroscopy shows among others, the vibrations of the aromatic Ar NH and Ar CH as well as the nitro group (Table 19).

Table 19. Experimental data of 2-nitro-*N*-(*p*-tolyl)benzeneamines **94**.

#	**Mp (^{o}C)**	**EA (%)**		**λ_{max} (DCM)/**	***m*/*z* (EI)**	**ν_{max}**
	(hexane)	**Found**	**Required**	**nm (log ε)**	**M$^+$ (100%)**	**(cm^{-1})**
94a	66-67 Lit.,[374](68)	C, 68.52 H, 5.33 N, 12.14	C, 68.41 H, 5.30 N, 12.27	205 (3.88) 262 (3.96) 434 (3.60)	228	3335w (Ar NH) 1504s (NO$_2$, as) 1352s (NO$_2$, sy)
94b	85-86	C, 65.23 H, 5.50 N, 10.94	C, 65.11 H, 5.46 N, 10.85	265 (4.02) 477 (3.60)	258	3343w (Ar NH) 3116w (Ar CH) 1505s (NO$_2$, as) 1339m (NO$_2$, sy)
94c	86-87 Lit.,[375] (85-86)	C, 65.15 H, 5.39 N, 10.87	C, 65.11 H, 5.46 N, 10.85	204 (4.02) 266 (4.18) 477 (3.72)	258	3343w (Ar NH) 3115w (Ar CH) 1506s (NO$_2$, as) 1339m (NO$_2$, sy)
94d	92-93 Lit.,[376] (80)	C, 69.38 H, 5.73 N, 11.67	C, 69.41 H, 5.82 N, 11.56	273 (3.97) 433 (3.60)	242	3351m (Ar NH) 3032w (Ar CH) 1507s (NO$_2$, as) 1338s (NO$_2$, sy)
94e	83-84 Lit.,[377] (85)	C, 69.42 H, 5.86 N, 11.58	C, 69.41 H, 5.82 N, 11.56	203 (4.06) 263 (4.01) 450 (3.58)	242	3358m (Ar NH) 2924w (Ar CH) 1511s (NO$_2$, as) 1339s (NO$_2$, sy)
94f	139-140	C, 66.40 H, 4.29 N, 16.48	C, 66.40 H, 4.38 N, 16.59	205 (4.08) 262 (4.11) 442 (3.61)	253	3317m (Ar NH) 2236w (CN) 1512s (NO$_2$, as) 1339s (NO$_2$, sy)
94g	122-123 Lit.,[378] (128)	C, 66.39 H, 4.26 N, 16.49	C, 66.40 H, 4.38 N, 16.59	228 (4.01) 260 (4.10) 286 (4.10) 419 (3.96)	253	3318m (Ar NH) 2222m (CN) 1512s (NO$_2$, as) 1358s (NO$_2$, sy)
94h	64-65	C, 56.81 H, 3.71 N, 9.33	C, 56.76 H, 3.74 N, 9.46	254 (3.95) 431 (3.52)	296	3364w (Ar NH) 2926w (Ar CH) 1496s (NO$_2$, as) 1331m (NO$_2$, sy)
94i	111-112 Lit.,[379] (113.5-114)	C, 56.70 H, 3.68 N, 9.37	C, 56.76 H, 3.74 N, 9.46	254 (4.03) 418 (3.57)	296	3351w (Ar NH) 3104w (Ar CH) 1509m (NO$_2$, as) 1323s (NO$_2$, sy)
94j	123-124	C, 63.32 H, 4.43 N, 11.25	C, 63.41 H, 4.50 N, 11.38	269 (3.81) 416 (3.49)	246	3329m (Ar NH) 3105w (Ar CH) 1499s (NO$_2$, as) 1343s (NO$_2$, sy)
94k	119-121	C, 63.43 H, 4.38 N, 11.22	C, 63.41 H, 4.50 N, 11.38	257 (3.93) 449 (3.58)	246	3347m (Ar NH) 3107w (Ar CH) 1511s (NO$_2$, as) 1346m (NO$_2$, sy)





In ^{1}H-NMR the NH proton gave the most downfield singlets (δ_H 9.33-9.78 ppm) while the tolyl methyl groups were in most cases, the most upfield singlets (δ_H 2.36-2.41 ppm). The exceptions were the methyl substituted systems **94d** (X = Me) and **94e** (Y = Me) which gave more upfield signals at δ_H 2.25 and 2.28 ppm, respectively for the non tolyl methyl groups. The methoxy groups of the substituted systems **94b** (X = OMe) and **94c** (Y = OMe) gave a more downfield singlets at 3.72 and 3.81 ppm, respectively. The Ar Hs were in the region 8.53-6.30 ppm. Regardless of the substitution, the most upfield signal of Ar Hs belongs to hydrogens next to the nitro groups (H_d). The substituent though affected the signal and multiplicity of the rest Ar Hs. Usually hydrogens H_a and H_b were observed as multiplets (7.35-7.02 ppm) but they were resolved cleanly in the trifluoromethyl and fluoro substituted systems. Hydrogen H_c was also observed as a multiplet peak except when the X position was substituted.

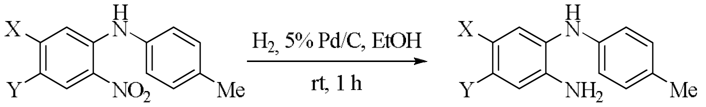
In the ^{13}C-NMR spectra, the most downfield C signals were C_7 (δ_C 137.0-165.5 ppm), C_6 (δ_C 134.4-146.2 ppm) and C_1 (δ_C 134.7-143.6 ppm), depending on the substitution of the system. Surprisingly, C_4 also gave the most downfield signal (165.5, 147.8 and 168.9 ppm) when the system is substituted on the X position with OMe, Me and F substituent, respectively. The tolyl methyl groups gave the most upfield signals (20.0-21.4 ppm). The methyl group on systems **94d** (X = Me) and **94e** (Y = Me) gave a more downfield signal than the tolyl methyl at 22.4 and 20.9 ppm, respectively while the methoxy group on systems **94b** (X = OMe) and **94c** (Y = OMe) gave a more downfield signal at 55.6 and 55.8 ppm, respectively.

3.2.3 Synthesis and Characterisation of *N*-*p*-Tolyl-1,2-benzenediamines **93**

Synthesis of N-p-*tolyl-1,2-benzenediamines* ***93***

Hydrogenation of 2-nitro-*N*-(*p*-tolyl)benzeneamines **94** was carried out in a Parr hydrogenator apparatus (H_2, 2 bar) using ethanol as solvent and Pd/C (5 mol%) as catalyst to afford the *N*-*p*-tolyl-1,2-benzenediamines **93** in good yields (Table 20).

Table 20. Hydrogenation of 2-nitro-*N*-(*p*-tolyl)benzeneamines **94** (1 equiv.) in EtOH using H_2 (2 bar) and 5% Pd/C (1 mass equiv.) at rt for 1 h.



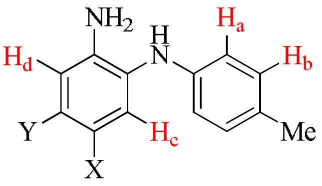
94 **93**

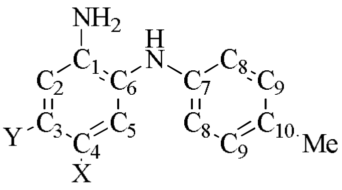
94	X	Y	Yields **93** (%)
94a	H	H	**93a** (76)
94b	OMe	H	**93b** (81)
94c	H	OMe	**93c** (96)
94d	Me	H	**93d** (84)
94e	H	Me	**93e** (77)
94f	CN	H	**93f** (59)
94g	H	CN	**93g** (74)
94h	CF_3	H	**93h** (98)
94i	H	CF_3	**93i** (77)
94j	F	H	**93j** (66)
94k	H	F	**93k** (81)

After the hydrogen pressure was stabilised, the orange color of the nitroanilines disappeared and no more starting material was observed (by TLC), the reaction was stopped and the solution was filtered through Celite® directly onto crushed ice. In most cases the resulting *N*-(*p*-tolyl)-1,2-benzenediamines **93** crystallized in the cold water and were isolated by filtration. Diamines **93h** (X = CF_3) and **93i** (X = F) were isolated after extraction by DCM as colorless oils. The colorless 1,2-diamines readily oxidized to give colored impurities and as such they were stored at low temperatures in the fridge.

Characterisation of N-p-*tolyl-1,2-benzenediamines* **93**

Microanalysis, melting point, UV/*vis*, FTIR spectroscopy and LRMS which among other fragmentations showed the loss of NH_2 were used to confirm the structure of diamines **93** (Table 21).





^{1}H-NMR spectroscopy showed that the tolyl methyl groups were the most upfield singlets (δ_H 2.23-2.35 ppm). Diamine **93e** (Y = Me) gave signals at 2.32 and 2.30 ppm for the tolyl methyl and methyl on Y position, respectively while the diamine **93d** (X = Me) gave methyl singlets at 2.23 and 2.29 ppm, respectively. The methoxy groups of the substituted systems **93b** (X = OMe) and **93c** (Y = OMe) gave a more downfield singlets at 3.70 and 3.81 ppm, respectively. The N*H* and NH_2 protons in some cases [**93a** (parent), **93e** (Y = Me), **93i** (Y = CF_3) and **93k** (Y = F)] overlapped to give a broad singlet peak (δ_H 3.82-4.15 ppm). All other substituted diamines gave separate broad singlets for N*H* (δ_H 4.97-5.58 ppm) and NH_2 (δ_H 3.18-4.15 ppm). The Ar *H*s were in the region 6.28-7.35 ppm.

^{13}C-NMR spectroscopy, indicated that the most downfield C signals were C_7 (δ_C 138.8-159.6 ppm) and C_1 (δ_C 131.9-145.5 ppm) depending on the substitution of the system, as well as C_4 at 153.5 and 158.5 ppm on **93b** (X = OMe) and **93j** (X = F) and C_3 at 158.3 and 162.8 ppm on **93c** (Y = OMe) and **93k** (Y = F). The tolyl methyl groups gave the most upfield signals (20.4-20.7 ppm). The methyl group on systems **93d** (X = Me) and **93e** (Y = Me) gave a more downfield signal at 20.5 and 21.0 ppm, respectively while the methoxy group on systems **93b** (X = OMe) and **93c** (Y = OMe) gave downfield signals at 55.5 and 55.2 ppm, respectively.

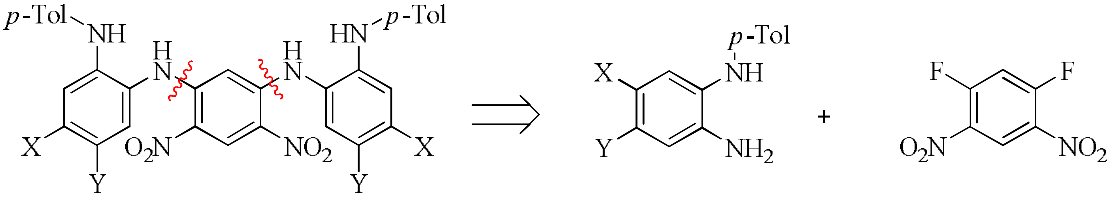
Table 21. Experimental data of *N*-*p*-tolyl-1,2-benzenediamines **93**.

#	**Mp (°C)**	**EA (%)**		**λ_{max} (DCM)/**	***m/z* (EI)**	**ν_{max}**
	(water)	**Found**	**Required**	**nm (log ε)**	**M$^+$ (100%)**	**(cm^{-1})**
93a	73-74 Lit.,[380] (74)	C, 78.69 H, 7.23 N, 14.06	C, 78.75 H, 7.12 N, 14.13	235 (3.89) 275 (3.73)	198	3339m (Ar NH) 2918w (Ar CH)
93b	82-83	C, 73.76 H, 7.12 N, 12.23	C, 7366 H, 7.06 N, 12.27	237 (3.98) 296 (3.63)	228	3329w (Ar NH) 2918w (Ar CH)
93c	74-76	C, 73.76 H, 7.11 N, 12.22	C, 73.66 H, 7.06 N, 12.27	227 (3.79) 275 (3.70)	228	3359w (Ar NH) 2918w (Ar CH)
93d	103-104 Lit.,[381] (103)	C, 79.30 H, 7.48 N, 13.02	C, 79.21 H, 7.60 N, 13.20	237 (3.94) 274 (3.73) 301 (3.66)	212	3330m (Ar NH) 2916w (Ar CH)
93e	102-103 Lit.,[382] (109)	C, 79.30 H, 7.67 N, 13.11	C, 79.21 H, 7.60 N, 13.20	238 (3.94) 270 (3.74)	212	3328m (Ar NH) 3027w (Ar CH)
93f	96-97	C, 75.28 H, 5.75 N, 18.81	C, 75.31 H, 5.87 N, 18.82	261 (4.01)	223	3340m (Ar NH) 2916w (Ar CH) 2218s (CN)
93g	160-161 Lit.,[383] (162-163)	C, 75.42 H, 5.92 N, 18.90	C, 75.31 H, 5.87 N, 18.82	228 (3.99) 295 (3.85) 327 (3.86)	223	3379m (Ar NH) 2862w (Ar CH) 2209s (CN)
93h	oil	C, 63.08 H, 4.94 N, 10.59	C, 63.15 H, 4.92 N, 10.52	235 (3.87) 292 (3.68)	266	3370w (Ar NH) 2923w (Ar CH)
93i	72-74 Lit.,[379] (semi-solid)	C, 63.11 H, 4.91 N, 10.53	C, 63.15 H, 4.92 N, 10.52	228 (3.92) 282 (3.88)	266	3376m (Ar NH) 2919w (Ar CH)
93j	oil	C, 72.36 H, 6.26 N, 13.02	C, 72.20 H, 6.06 N, 12.95	269 (3.81) 416 (3.49)	216	3365w (Ar NH) 3030w (Ar CH)
93k	85-86	C, 72.30 H, 6.00 N, 12.93	C, 72.20 H, 6.06 N, 12.95	257 (3.93) 449 (3.58)	216	3336m (Ar NH) 3061w (Ar CH)

3.2.4 Synthesis and Characterisation of 1,5-Bis[1-*N*-(*p*-tolyl)-1,2-benzene-diamino]-2,4-dinitrobenzenes **92**

*Synthesis of 1,5-bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes* ***92***

1,5-Difluoro-2,4-dinitrobenzene **56** was chosen as the reagent for the synthesis of compounds **92** since it readily undergoes nucleophilic aromatic substitution (S$_N$Ar) (Scheme 17). The synthesis of dinitrobenzenediamines having *N*-substituents Ph, *p*-(*t*-Bu)-C_6H_4, *p*-(*n*-Bu)-C_6H_4 and *n*-Bu instead of the tolyl group, has already been described in the literature.[155]

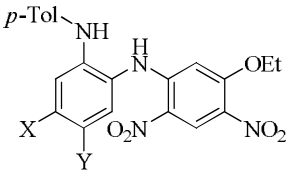


92 **93** (2 equiv.) **56** (1 equiv.)

Scheme 17

For the synthesis of 1,5-bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes **92**, *N*-*p*-tolyl-1,2-benzenediamines **93** were treated with 1,5-difluoro-2,4-dinitrobenzene **56** (0.5 equiv.) and Hünig's base (2 equiv.) in EtOH heated at reflux (80 ^{o}C) for 1-4 d. The reaction was followed by TLC and judged completed when reagent **56** was consumed. On cooling to room temperature, the desired disubstituted products **92** precipitated since they were poorly soluble in ethanol. The usual work up of the reaction included the filtration of the solid, followed by recrystallization from hot EtOH where any monosubstituted product remained dissolved and the disubstituted product preferentially crystallized as red needles.

In some cases, **92f** (X = C≡N), **92g** (Y = C≡N) and **92h** (X = CF_3), the main product of the reaction was the substituted *N*-(5-ethoxy-2,4-dinitrophenyl)-*N'*-*p*-tolyl-benzene-1,2-diamine **107**. These products formed *via* nucleophilic attack of the solvent on C_5 of the monosubstituted product which could be easily attacked due to the EWG substitutes that enhances its electrophilicity.

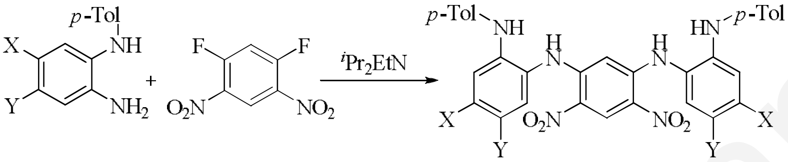


107a (X = CN, Y = H)
107b (X = H, Y = CN)
107c (X = CF3, Y = H)

As such, for these examples, the reaction solvent was switched to tetrahydrofuran (THF). The lower reflux temperature (65 ^{o}C), however, led to lower yields and longer reaction times. Furthermore, the products **92** dissolved in THF and thus for the work up, the solvent was evaporated and the residue column chromatographed to afford the target compounds. Recrystallisation (EtOH) furnished the desired disubstituted products **92** as red crystals.

The yields of 1,5-bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes **92** were moderate (Table 22). Their recrystallisation was difficult due to their low solubility in EtOH, but necessary to avoid any monosubstituted product that remained.

Table 22. Reaction of *N*-(*p*-tolyl)-1,2-benzenediamines **93** (1 equiv.) with 1,5-difluoro-2,4-dinitrobenzene **56** (0.5 equiv.) and Hünig's base (1 equiv.).

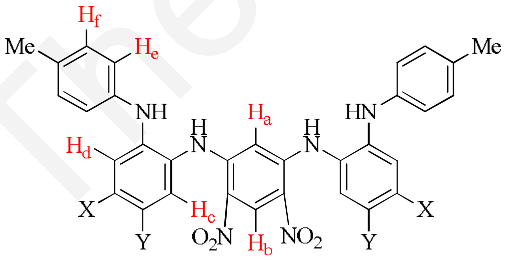


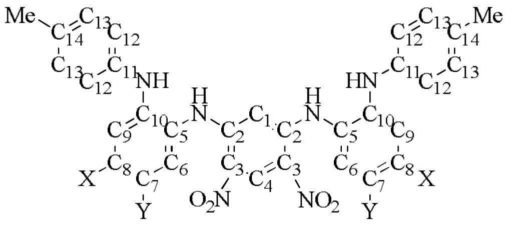
93 **56** **92**

93	X	Y	Solvent	Temp. (^oC)	Time (d)	Yields **92** (%)
93a	H	H	EtOH	80	1	**92a** (76)
93b	MeO	H	EtOH	80	1	**92b** (51)
93c	H	MeO	EtOH	80	1	**92c** (44)
93d	Me	H	EtOH	80	2	**92d** (84)
93e	H	Me	EtOH	80	3	**92e** (74)
93f	CN	H	THF	65	4	**92f** (42)
93g	H	CN	THF	65	4	**92g** (49)
93h	F_3C	H	THF	65	3	**92h** (40)
93i	H	F_3C	EtOH	80	3	**92i** (73)
93j	F	H	EtOH	80	1	**92j** (79)
93k	H	F	EtOH	80	1	**92k** (69)

Characterisation of 1,5-bis[1-N-(p-tolyl)-1,2-benzenediamino]-2,4-dinitro-benzenes **92**

Compounds **92** were characterized by melting point, microanalysis, UV/*vis*, LRMS, FTIR (Table 23) and NMR spectroscopy.





^{1}H-NMR spectroscopy showed the tolyl methyl groups as the most upfield singlets (δ_H 2.13-2.26 ppm). Compound **92d** (X = Me) gave two signals at 2.15 ppm for the tolyl methyl and methy on X position, respectively while the methyl signals of compound **2e** (Y = Me) were overlapped in one singlet at 2.21 ppm. The methoxy groups of the systems **92b** (X = OMe) and **92c** (Y = OMe) gave more downfield singlets at 3.66 and 3.62 ppm, respectively. The two different N*H* groups gave downfield singlets at 9.19-9.54 ppm and 7.19-8.10 ppm. The Ar *H*s were in the region 5.32-9.00 ppm. Most upfield signals belong to H_a and most downfield signals belong to H_b. Compound **92g** (Y = C≡N) gave the most upfield (5.33 ppm) and most downfield (9.00 ppm) singlets that belong to H_a and H_b, respectively.

^{13}C-NMR spectroscopy, indicated the most downfield *C* signal as C_2 (δ_C 146.1 - 151.8 ppm) for all compounds except from the methoxy- and fluoro-substituted compounds **92b**, **92c**, **92j** and **92k**. The most downfield signal on these compounds were the tertiary substituted carbons C_7 for compounds **92c** (δ_C 155.1 ppm) and **92k** (δ_C 157.4 ppm) that are substituted on the Y position and C_8 for compounds **92b** (δ_C 158.9 ppm) and **92j** (δ_C 163.3 ppm) that are substituted on the X position. The tolyl methyl groups gave the most upfield signals (20.3 - 21.3 ppm). The non-tolyl methyl groups on the systems **92d** (X = Me) and **92e** (Y = Me) gave more downfield signals at 21.4 and 21.1 ppm, respectively while the methoxy group on the systems **92b** (X = OMe) and **92c** (Y = OMe) were even more downfield at 55.0 and 56.1 ppm, respectively.

Table 23. Experimental data of 1,5-bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes **92**.

#	**Mp (°C)** (EtOH)	**EA (%)** **Found**	**Required**	**λ_{max} (DCM)/ nm (log ε)**	***m/z* (EI) M^+ (100%)**	**ν_{max} (cm^{-1})**
92a	219-220	C, 68.68 H, 5.09 N, 15.07	C, 68.56 H, 5.03 N, 14.99	228 (4.16) 283 (4.32) 331 (4.19) 379 inf (3.94)	560	3322m (Ar NH)
92b	241-242	C, 65.78 H, 4.99 N, 13.66	C, 65.80 H, 5.20 N, 13.54	229 (4.18) 281 (4.16) 327 (4.11) 388 inf (3.81)	620	3334m (Ar NH) 3001w (Ar CH)
92c	187-188	C, 65.72 H, 5.09 N, 13.51	C, 65.80 H, 5.20 N, 13.54	228 (4.22) 284 (4.30) 336 (4.19) 383 inf (3.94)	620	3333m (Ar NH) 2916w (Ar CH)
92d	254-255	C, 69.37 H, 5.56 N, 14.33	C, 69.37 H, 5.48 N, 14.28	228 (4.22) 284 (4.35) 331 (4.22) 383 inf (3.96)	588	3336m (Ar NH) 2918w (Ar CH)
92e	197-199	C, 69.45 H, 5.54 N, 14.15	C, 69.37 H, 5.48 N, 14.28	228 (4.10) 278 (4.36) 331 (4.11) 381 inf (3.92)	588	3334m (Ar NH) 2916w (Ar CH)
92f	268-270	C, 66.71 H, 4.32 N, 18.26	C, 66.88 H, 4.29 N, 18.35	228 (4.33) 287 (4.33) 327 (4.21) 381 inf (4.06)	610	3335m (Ar NH) 2230m (CN)
92g	303-305	C, 66.97 H, 4.33 N, 18.16	C, 66.88 H, 4.29 N, 18.35	229 (4.19) 303 (4.50) 388 inf (3.83)	610	3379w (Ar NH) 2220m (CN)
92h	246-247	C, 58.57 H, 3.78 N, 11.92	C, 58.62 H, 3.76 N, 12.06	230 (4.31) 283 (4.49) 326 (4.41) 380 inf (4.14)	696	3313m (Ar NH)
92i	185-187	C, 58.58 H, 3.75 N, 11.86	C, 58.62 H, 3.76 N, 12.06	228 (4.20) 287 (4.37) 322 (4.29) 388 inf (3.89)	696	3396m (Ar NH) 3316m (Ar CH)
92j	240-241	C, 64.52 H, 4.31 N, 14.09	C, 64.42 H, 4.39 N, 14.09	228 (4.22) 277 (4.32) 323 (4.26) 393 inf (3.88)	596	3317m (Ar NH)
92k	200-202	C, 64.36 H, 4.22 N, 13.94	C, 64.42 H, 4.39 N, 14.09	223 (4.46) 277 (4.47) 321 (4.33) 396 inf (4.47)	596	3312m (Ar NH)

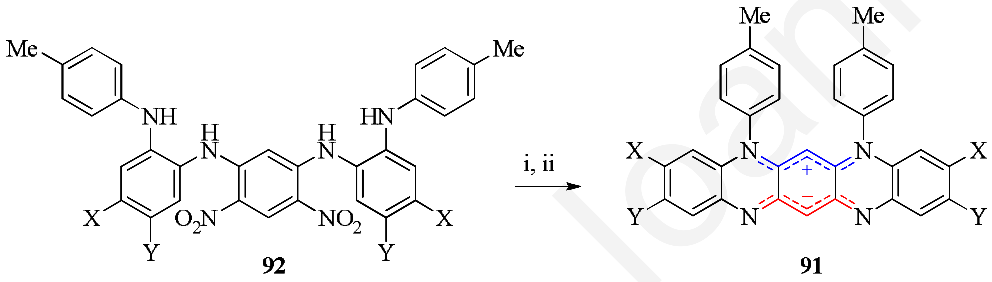
3.2.5 Synthesis and Characterisation of 5,7-Di-*p*-tolyl-13,7-dihydro-quinoxalino[2,3-*b*]phenazin-5-ium-13-ides **91**

*Synthesis of 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides* ***91***

1,5-Bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes **92** were hydrogenated in EtOH using a Parr shaker hydrogenator in the presence of *ca.* 3 bar of H_2 and Pd/C (5 mol%). The reaction was judged complete when: a) the uptake of hydrogen ceased (H_2

pressure stabilized), b) the red color of the starting material had dissipated and c) there was no more starting material checked by TLC. As soon as the reaction was stopped, the solution was filtered (Celite®) to remove Pd/C and the filtrate (manually agitated) was heated (heat gun) under an air atmosphere until its color turned from colorless to brown and finally to deep green. At this point the filtrates were left to cool to room temperature whereupon in nearly all cases green crystalline solids, DTQP's **91**, were collected by filtration and recrystalllized from either EtOH or chlorobenzene (Table 24). Treatment of the DTQP's with acid (HCl) gave a deep blue solution of the mono protonated DTQP.[155]

Table 24. Synthesis of 5,7-di-*p*-tolyl-13,7-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides **91** *via* 1,5-bis[1-*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes **92**.



Reagents and conditions: i) H_2, Pd/C (5 mol%), EtOH, 20 °C, 4-6 h; ii) air, EtOH, 80 °C, 0.5-1 h.

92	X	Y	Yields 91 (%)
92a	H	H	**91a** (87)
92b[a]	MeO	H	**91b** (31)[a]
92c	H	MeO	**91c** (20)
92d	Me	H	**91d** (87)
92e	H	Me	**91e** (41)
92f	CN	H	**91f** (50)
92g	H	CN	**91g** (38)
92h	F_3C	H	**91h** (57)
92i	H	F_3C	**91i** (50)
92j	F	H	**91j** (36)
92k	H	F	**91k** (57)

[a] Addition of drops of HCl (35%) before heating and subsequent neutralization (NaOH) to collect **91b**.

With the exception of compound **91b** (X = OMe), all the substituted DTQPs were synthesized in this manner. The filtrate containing compound **91b**, however, on heating did not give the desired green color but remained brown. Also, addition of acid to this brown filtrate did not turn its color to blue but lilac-brownish. After intense heating and stirring, only traces of the desired green product could be formed. The filtrate, however, contained the *trans* isomer **108** as supported by UV/*vis* spectroscopy (Figure 23).[208-211] A short study indicated that, after hydrogenation acidification of the filtrate assisted the formation of the target compound **91b** (X = OMe), while neutral or slightly basic conditions gave predominantly the *trans* analog **107**.

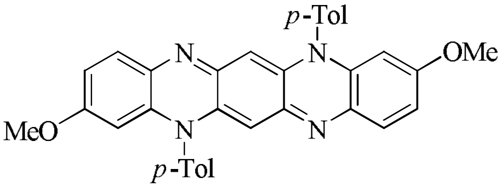
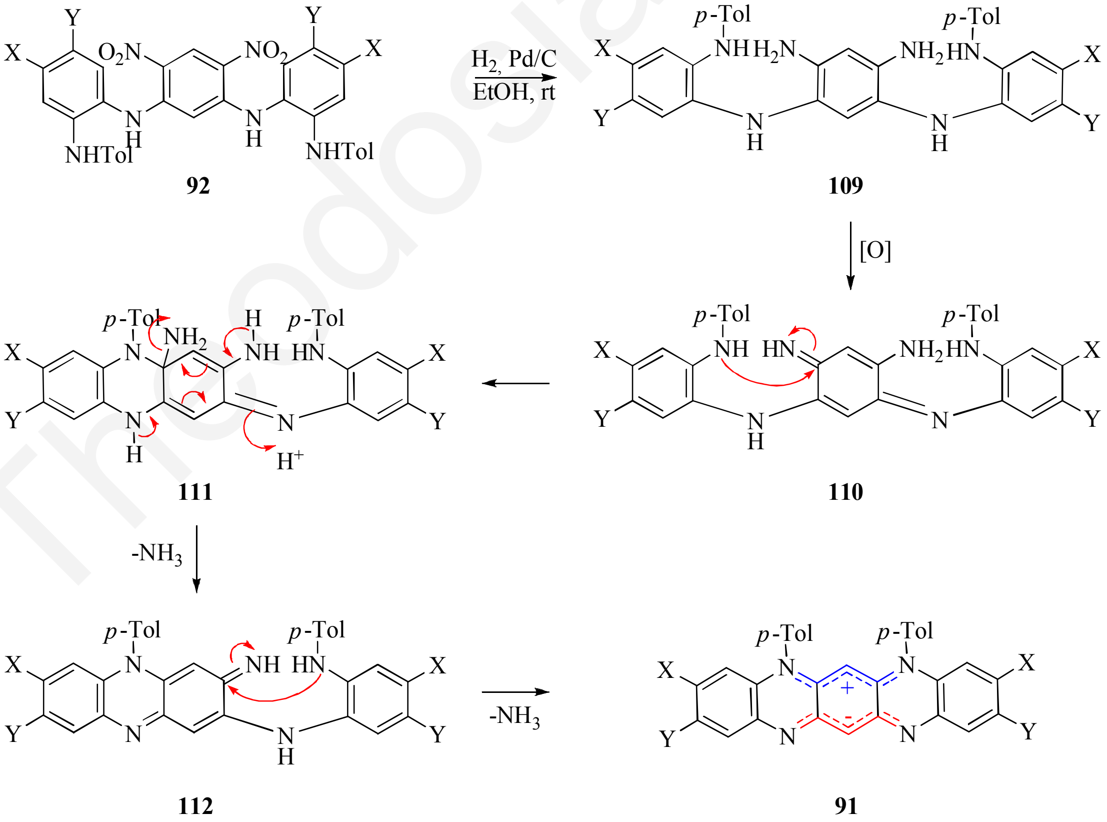


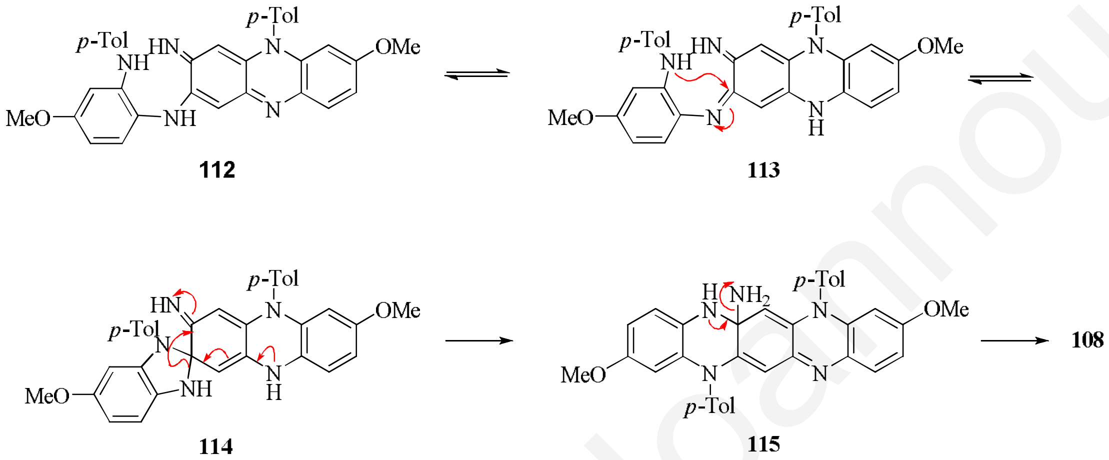
Figure 23. Structure of *trans* isomer **108**.

The mechanism for the ring closure to give DTQP was studied for better understanding of the influence of the conditions on the formation of the main product. Reduction of the dinitrobenzene **92** affords the hexamino **109**, although not isolated in this study one example of hexamino **109** has been previously isolated and fully characterized.[155] On heating in air hexamino **109** presumably oxidizes to the *ortho* or *para* quinonedimine and then undergoes an intramolecular ring closure to give phenazine **110**. Loss of ammonia affords a new phenazinimine which undergoes a final intramolecular ring closure with loss of ammonia to give the target DTQP (Scheme 18).



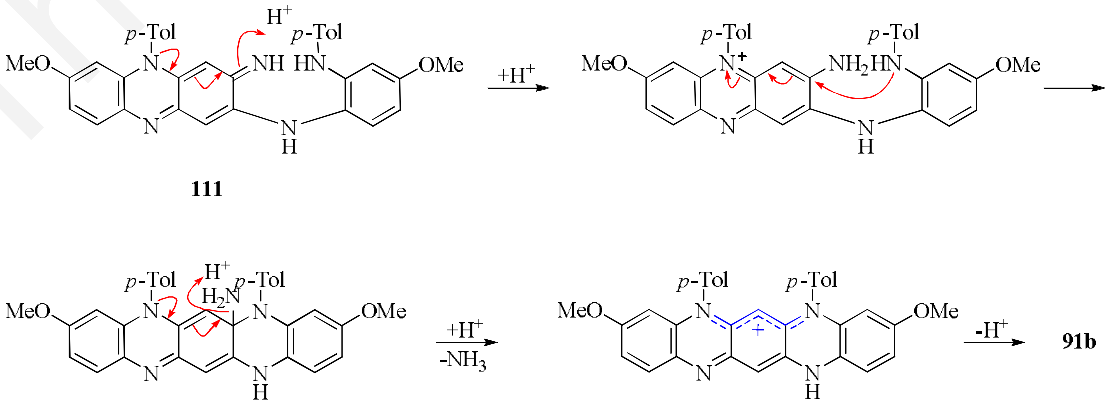
Scheme 18

It is proposed that after the first intramolecular cyclization, the phenazine intermediate can prototautomerise to reveal the *N*-arylimino form **113** which could encourage formation of the spirocyclic intermediate **114**. A subsequent aza-Smiles type rearrangement[303] could lead to isomerisation affording the phenazine **114** which can then cyclise to give the *trans*-DTQP **108** (Scheme 19).



Scheme 19

In the case of compound **91b** (X = OMe), the reaction under neutral conditions prefers to give a mixture of both *cis* and *trans* products, which suggests the OMe substituent encourages spirocyclic formation. To understand this requires additional studies. Nevertheless, the addition of acid facilitated ring closure to give the *cis* DTQP presumably because of preferential protonation of the exocyclic imine of the phenazine intermediate **112** which is electron rich owing to the electron release from the tolylamino group (Scheme 20).



Scheme 20

Thus, an alternative work up procedure was followed in the case of system **91b**. After the filtration, drops of HCl (35%) acid was added in the filtrate and heated under atmospheric air until a deep blue color developed. The crystalline material that precipitates is the protonated product and can be isolated by filtration, dissolved in the least amount of MeOH and treated with base (sat. NaOH) to get the free base.

*Characterisation of 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides **91***

The target compounds **91** were characterized by melting point, microanalysis, LRMS, FTIR, some of them by NMR spectroscopy but most importantly with UV/*vis* and X-ray. The latter two are the most important since they can be compared with the Time Dependence (TD) and geometric computational data, respectively (see Section 2.3) and thus help validate the computational methods chosen.

DTQPs have green color, are sparingly soluble and most of them have melting points above 300 °C. Their exact melting or decomposition points were detected using Differential Scanning Calorimetry (DSC). Their crystalization was difficult but achieved using EtOH, pyridine or chlorobenzene. Attempts to obtain single crystals from the tolyl analogs failed, however, suitable crystals for X-ray crystallography were obtained for the *N*-Ph **116**, *N*-^{n}Bu **117** and *N*-*n*-dodecyl **118** analogs (the first two are known compounds)[155] and thus we were able to analyze the structures of these systems.

X-Ray Studies

X-ray crystallography was achieved for the synthesized *N*-Ph (**116**), *N*-*n*-Bu (**117**) and *N*-*n*-dodecyl (**118**) analogs (Figure 24).

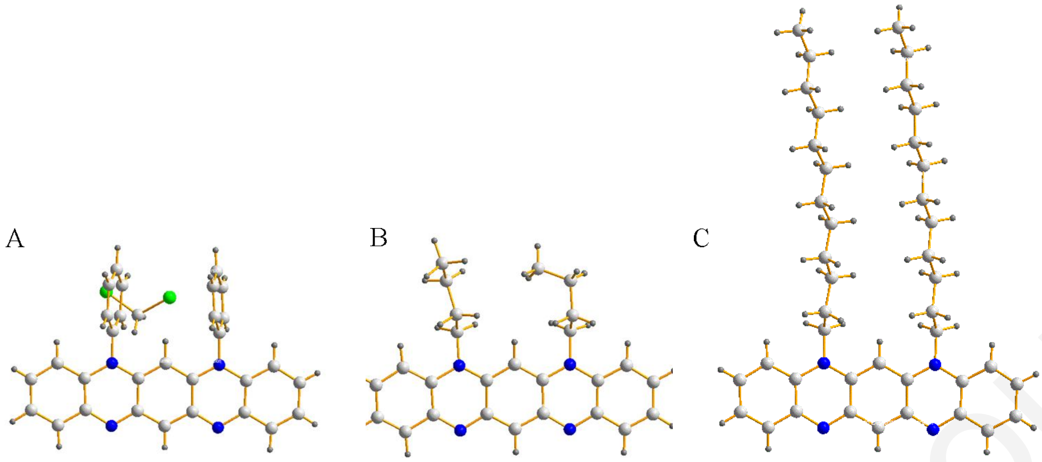


Figure 24. Crystal structures of A) 5,7-diphenyl-7,13-dihydroquinoxalino[2,3-*b*]-phenazin-5-ium-13-ide **116**, B) 5,7-di-*n*-butyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **117** and C) 5,7-di-*n*-dodecyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **118**.

It can be tentatively assumed that the 5,7-di-phenyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116** (5,7-DPQP), which gave the suitable crystal for the X-ray studies will have similar packing properties and geometric data with the *N*-tolyl analog. The system **116** has a near planar conformation with a small degree of torsion of the outer fused benzene rings which is estimated in about 1.2° (Figure 25). The analogous dihedral angles of *N*-*n*-butyl and *N*-*n*-dodecyl are 5.0° and 8.6°, respectively. This can be measured by the angle between the planes of the two outer rings. In addition, the two *N*-Ph rings, which are orthogonal to the plane of the five fused rings, are not aligned in parallel, but show a deviation of 7.9°.

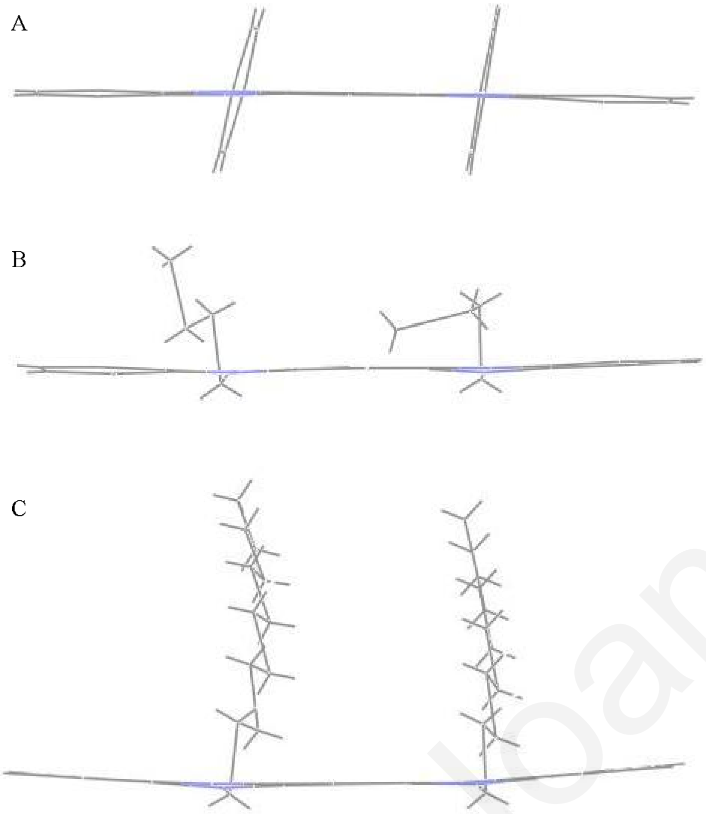
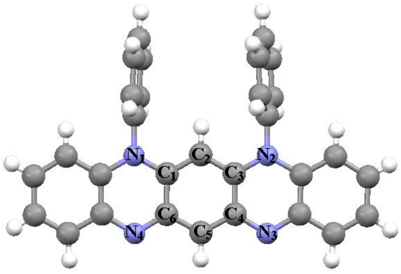


Figure 25. Planarity of A) 5,7-diphenyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116**, B) 5,7-di-*n*-butyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **117** and C) 5,7-di-*n*-dodecyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **118**.

Selected bond lengths and angles are shown in Table 25. The larger bond lengths between C_1-C_6 and C_3-C_4 compared to the parallel C-C bonds of the outer benzene rings (1.41 Å) are characteristic of 5,7-di-phenyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116** due to its separate positive and negative cyanines.

Table 25. Selected bond lengths and angles of 5,7-diphenyl-13,7-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116**.



Bond	**C_1-C_2**	**C_2-C_3**	**C_4-C_5**	**C_5-C_6**	**C_1-C_6**	**C_3-C_4**	**N_1-C_1**	**N_2-C_3**	**C_4-N_3**	**C_6-N_4**
(Å)	1.389(4)	1.394(5)	1.399(4)	1.395(5)	1.458(4)	1.456(5)	1.362(5)	1.357(4)	1.343(5)	1.344(4)
Angle	**$C_1C_2C_3$**	**$C_4C_5C_6$**	**$C_2C_3C_4$**	**$C_2C_1C_6$**	**$C_3C_4C_5$**	**$C_1C_6C_5$**	**$N_1C_1C_6$**	**$N_2C_3C_4$**	**$C_1C_6N_4$**	**$C_3C_4N_3$**
(°)	120.5(3)	123.5(0)	120.6(0)	120.6(0)	117.2(7)	117.4(1)	118.0(8)	118.1(9)	122.0(0)	121.7(1)

The molecules pack in a face to face alignment with the *N*-Ph substituents facing in the opposite directions (Figure 26). The distance between heterocyclic moieties is 3.420 Å and suggests a weak π-π intermolecular interaction. In Figure 27 the view of 5,7-diphenyl-5*H*,12*H*-quin-oxalino[2,3-*b*]phenazine **116** along *a*-, *b*- and *c*-axis is shown.

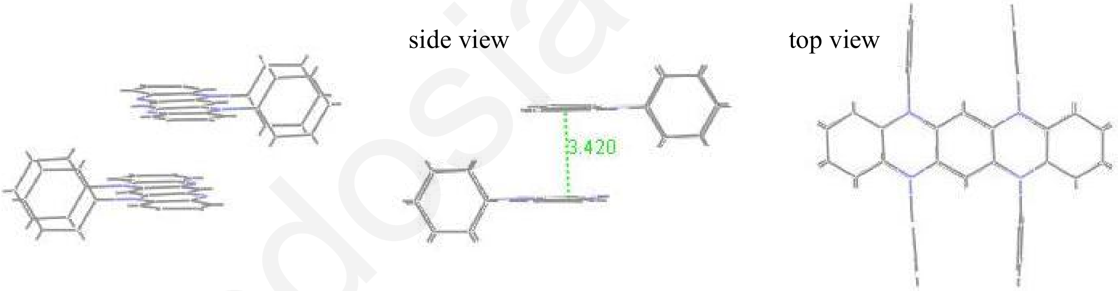
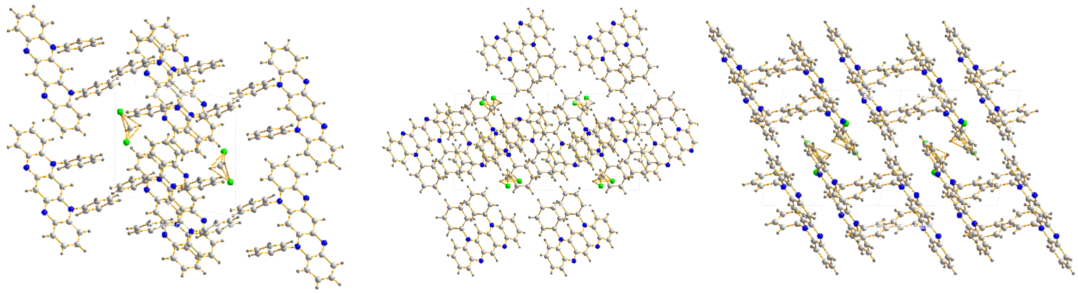


Figure 26. π-π Stacking of 5,7-diphenyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116**.



a-axis *b*-axis *c*-axis

Figure 27. 5,7-Diphenyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116** viewed along *a*-, *b*- and *c*-axis.

UV/vis Studies

The most important spectroscopy of the synthesized DTQPs is the UV/*vis* spectroscopy since it reflects the energetic difference between the ground and first excited state and thus the optical Band Gap [E_g(opt)]. The smallest energetic difference or in other words the longest wavelength λ_{max}, suggests better electronic movement within the system and thus potentially better conductivity. Systems with unpaired electrons - radicals - absorb in large absorption maxima, near IR. The comparison of the substituted DTQPs in UV/*vis* spectroscopy will show if indeed the substitution on the system affects the energetic difference between the singlet and triplet state. It is expected to have a noticeable red shift of λ_{max} on going from the X = EWG and Y = EDG substitution to the X-EDG and Y-EWG substitution, having the parent system somewhere between. These experimental results can be readily compared with the Band Gap estimations by TD calculations and therefore can validate the theoretical results that support this research.

The synthesized substituted DTQPs (the parent system and 10 substituted analogs), are shown and compared on the UV/*vis* spectrum below (Figure 28).

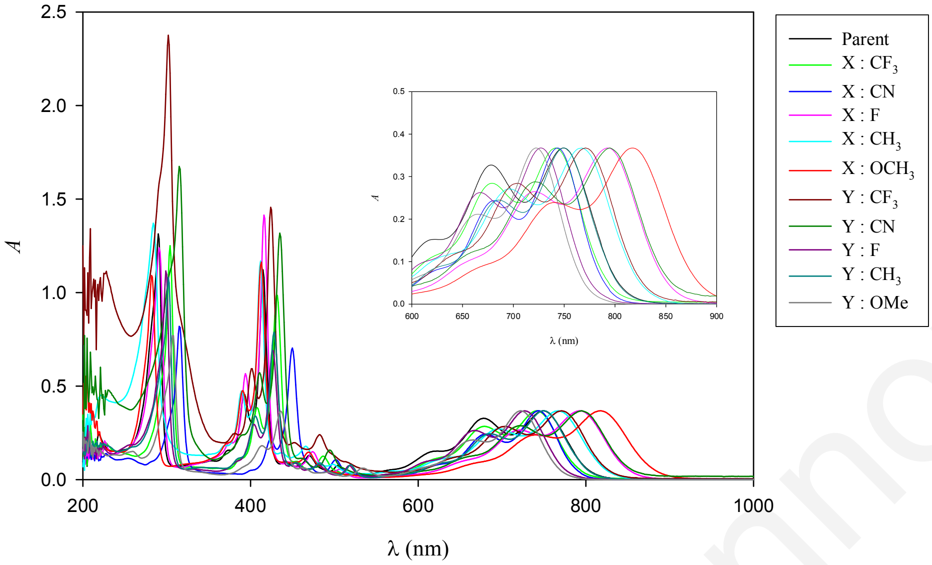


Figure 28. The UV/*vis* spectra for the parent and substituted DTQPs normalized with respect to the longest wavelength absorption.

The above λ_{max} comparison shows that the series of increase of the absorption maxima or in other words reduction of the Band Gap is: Y:OMe > Y:F > X:CF_3 > X:C≡N > Y:Me > parent > Y:CF_3 > X:Me > X:F > Y:C≡N > X:OMe. According to these results the system **91b** (X = OMe) is closest to potential paramagnetic character and this might also explain the difficulties observed in its synthesis. The λ_{max} shift from Y:OMe (λ_{max} = 722 nm, log ε 4.36) to the X:OMe (λ_{max} = 825 nm, log ε 4.22) system is 103 nm which is a noteworthy influence on the position of substitution on the electronic properties of the system.

By plotting separately X-substituted, Y-substituted, EDG-substituted and EWG-substituted systems the influence of substitution on the parent system is more noticeable (Figure 29).

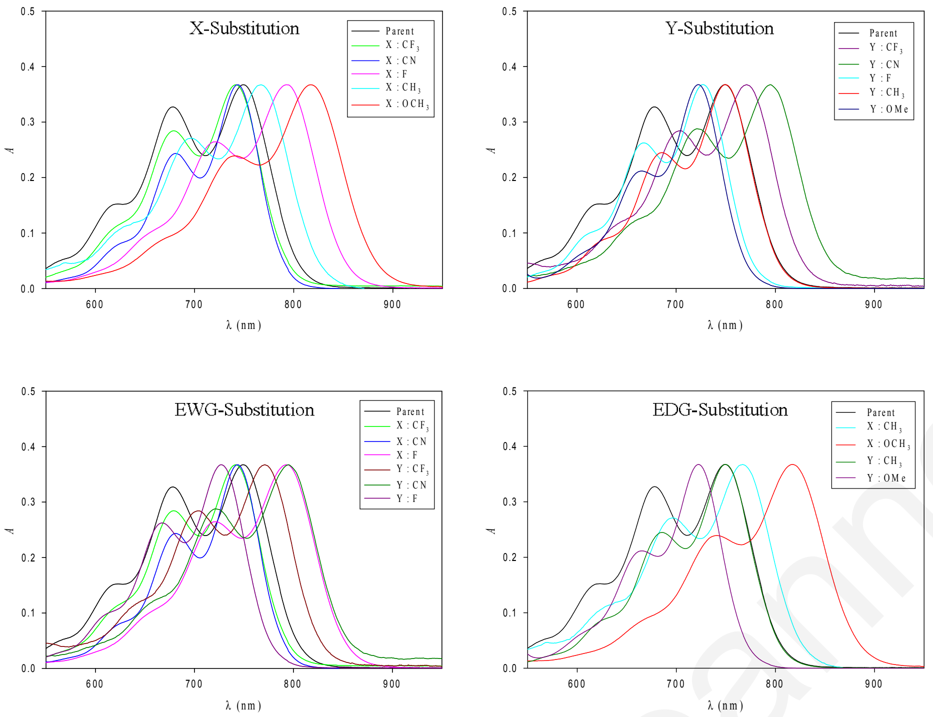


Figure 29. Separate plots for X-substituted, Y-substituted, EDG and EWG substituted DTQPs normalized with respect to the longest wavelength absorption.

The UV/*vis* spectroscopy also supports the zwitterionic character of the system by showing negative solvatochromism which is typical for zwitterions. A series of different polarity solvents are used in which the parent compounds as well as the substituted systems Y:OMe, Y:F, X:F and X:OMe, showed a marked decrease of their absorbance maxima as the solvent polarity [$E_T(30)$] increased (Figure 30).

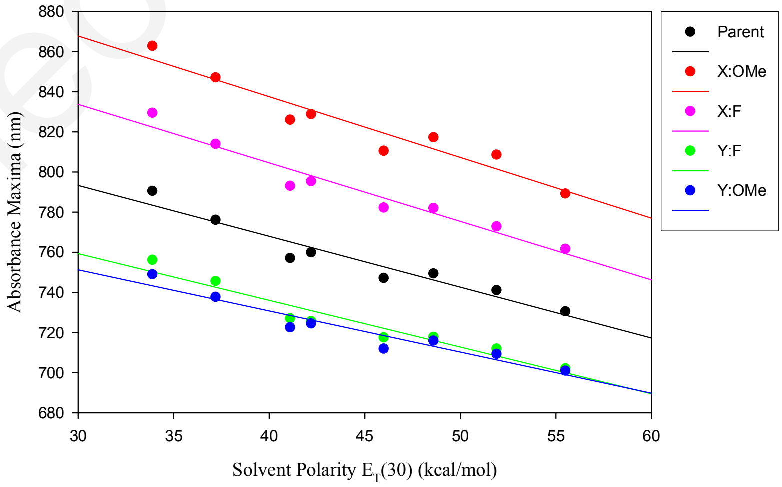


Figure 30. Correlation between solvent polarity $E_T(30)$ and absorbance maxima λ_{max} of parent, X:OMe, X:F, Y:F and Y:OMe systems.

3.3 Comparison of Spectroscopic and Computational Data

The comparison of the experimental and theoretical results on the substituted DTQP systems is essential. In this way the computational results of systems that were not synthesized can be validated.

3.3.1 Geometric Data

Such a comparison can be done by comparing the geometric data of the X-ray crystallography and the optimized structures. The tables below list selected bond lengths and bond angles for a comparison between the X-ray crystal of the system with *N*-Ph substituent and the computational optimized structures with *N*-Tol and *N*-H substituents.

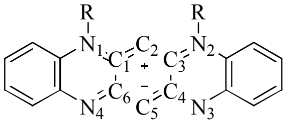


Table 26. Selected bond lenghts (Å) of X-ray crystal (*N*-Ph, *N*-Bu and *N*-dodecyl) and *N*-H and *N*-Tol substituted optimized [DFT/B3LYP/6-31G(d)] structures.

	C_1-C_2	**C_2-C_3**	**C_4-C_5**	**C_5-C_6**	**C_1-C_6**	**C_3-C_4**	**N_1-C_1**	**N_2-C_3**	**C_4-N_3**	**C_6-N_4**
X-Ray (R = Ph)	1.389	1.395	1.399	1.396	1.458	1.457	1.363	1.357	1.344	1.344
X-Ray (R = *n*-Bu)	1.392	1.391	1.399	1.384	1.463	1.462	1.356	1.367	1.339	1.354
X-Ray (R = *n*-$C_{12}H_{25}$)	1.385	1.389	1.391	1.385	1.440	1.445	1.362	1.355	1.337	1.342
Comput. (R = *p*-Tol)	1.399	1.399	1.402	1.402	1.463	1.463	1.369	1.369	1.343	1.343
Comput. (R = H)	1.395	1.395	1.403	1.403	1.465	1.465	1.354	1.354	1.345	1.345

The bond length comparison (Table 27) shows a very good agreement in all important bonds of the central part of the molecule. The bonds that connect the two cyanines (C_1-C_6 and C_3-C_4) are identical (1.46 Å) and larger than the C-C bonds of the cyanines (1.38 - 1.40 Å) which are very similar on experimental and theoretical computed structures. The bond lengths of the C-N bonds of the positive cyanine (1.35 - 1.37 Å) are also very close and slightly larger from the C-N bonds of the negative cyanine (1.34 - 1.35 Å).

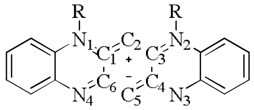


Table 27. Selected angles of X-Ray crystal (*N*-Ph, *N*-Bu and *N*-dodecyl) and *N*-H and *N*-Tol substituted optimized [DFT/B3LYP/6-31G(d)] structures.

	$C_1C_2C_3$	$C_4C_5C_6$	$C_2C_3C_4$	$C_2C_1C_6$	$C_3C_4C_5$	$C_1C_6C_5$	$N_1C_1C_6$	$N_2C_3C_4$	$C_1C_6N_4$	$C_3C_4N_3$
X-Ray (R = ph)	120.5(3)	123.5(0)	120.6(0)	120.6(0)	117.2(7)	117.4(1)	118.0(8)	118.1(9)	122.0(0)	121.7(1)
X-Ray (R = *n*-Bu)	121.1(1)	123.5(2)	120.1(9)	119.7(0)	117.3(1)	118.0(6)	118.3(4)	117.5(8)	121.4(6)	122.3(6)
X-Ray (R= n-$C_{12}H_{25}$)	120.8(8)	123.6(4)	120.0(8)	120.3(3)	117.4(1)	117.6(1)	117.9(5)	118.3(2)	122.1(4)	122.1(9)
Comput. (R = *p*-Tol)	120.4(3)	123.7(4)	120.6(4)	120.6(4)	117.2(7)	117.2(7)	117.7(7)	117.7(7)	121.9(4)	121.9(4)
Comput. (R = H)	119.4(6)	123.3(3)	121.4(7)	121.3(0)	117.1(3)	117.1(3)	116.9(9)	116.9(8)	121.3(0)	121.3(0)

The bond angles of the experimental and theoretical computed structures match very well. The biggest deviation is about 1.7° on the central CCC angle of the positive cyanine [$C_1C_2C_3$ Comput. (R = H) = 119.46° *vs* X-Ray (R = *n*-Bu) = 121.11°]. The X-ray structures (**116-118**) and the *N*-Tol optimized structure are much closer and almost identical, while the *N*-H optimized structures has some deviations *e.g.*, on the CCN angles [$C_3C_4N_3$ Comput. (R = H) = 121.30° *vs* Comput. (R = Tol) = 121.94°, X-Ray (R = Ph) = 121.71°, X-Ray (R = *n*-Bu) = 122.36° and X-Ray (R = n-$C_{12}H_{25}$) = 122.19°].

3.3.2 Time Dependence *vs* UV/*vis*

The comparison of the TD data with the experimental UV/*vis* is very important for the evaluation of the theoretical results. Since the B3LYP method on the *N*-H systems proved to be similar to the experimental, it was applied to the *N*-Tol substituted systems for a better comparison with experimental results.

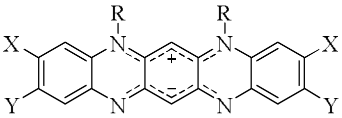


Table 28. Comparison of UV/vis data with band gap (TD-B3LYP)

	R	UVexp. (eV)	TD-B3LYP (eV)
51l	H		1.75
91c	Tol	1.72	1.66
51k	H		1.78
91k	Tol	1.71	1.70
51i	H		1.75
91h	Tol	1.67	1.69
51j	H		1.75
91f	Tol	1.67	1.70
51o	H		1.72
91e	Tol	1.65	1.63
51p	H		1.60
91a	Tol	1.64	1.62
51r	H		1.67
91i	Tol	1.61	1.60
51u	H		1.67
91d	Tol	1.59	1.58
51t	H		1.61
91g	Tol	1.56	1.55
51w	H		1.60
91j	Tol	1.56	1.52
51y	H		1.50
91b	Tol	1.50	1.46

The data in the Table 28 are listed on a series where the $\lambda_{\max}$ is increased. On going from molecule **91h** to molecule **91b** we expect the $\lambda_{\max}$ to be increased and the energy in eV to be reduced since this is the series of the reduction of ΔE_{ST}. This series is indeed followed both on the UV/*vis* and TD data with exceptions on molecules **91k**, **91c** and **91g**. The theoretical and experimental results are very close to each other in every case. This agreement supports the validation of the computational data and the computational method used.

3.4 Summary

A series of linear tetraazapentacenes substituted with a range of substituents were synthesized and studied. The synthesized systems gave spectroscopic data that were compared and in agreement with the computational results. This comparison validates the computational method we used and supports the reduced singlet - triplet ground state gap upon the appropriate substitution based on our computational data.

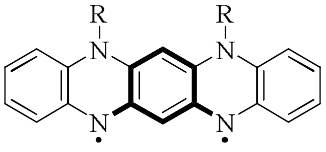
CHAPTER 4

Study on Angular Quinoxalino[2,3-*a*]phenazinediyl: Synthesis of a New Organic Radical

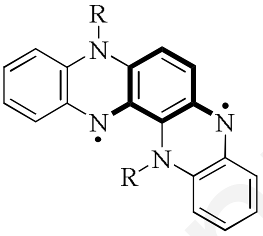
Sections **Page**

4.1 Introduction

An interesting angular analog of the quinoxalino[2,3-*b*]phenazine-12,14-diyl **119** is the quinoxalino[2,3-*a*]phenazine-8,14-diyl **89**. Both isomers have *meta* unsubstituted nitrogens that can carry single spins and avoid e^- pairing similar to *m*-phenylene, however, computational and experimental studies show that the quinoxalino[2,3-*b*]phenazine-12,14-diyl **119** exists as a singlet in the ground state as the zwitterionic biscyanine structure **51** (ΔE_{ST} = -10.05 kcal/mol) (see Chapters 2 and 3).



119



89

Nevertheless, computational studies on system **89** at the UDFT/B3LYP/6-31G(d) level of theory, support a ground state triplet structure with a ΔE_{ST} = +14.3 kcal/mol.[170] Furthermore, the energy difference between the two SOMOs (ΔE_{SS} = 0.32 eV) of the angular structure **89** was significantly less than 1.5 eV, in agreement with Hoffmann's requirement[242] for two nonbonding electrons to occupy different degenerate orbitals with a parallel-spin configuration to minimize their electrostatic repulsion (Figure 31).

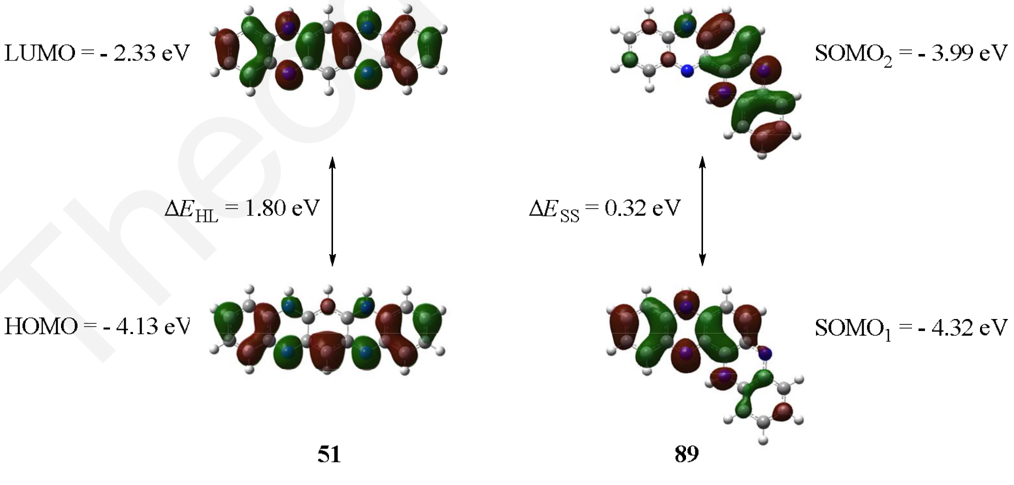
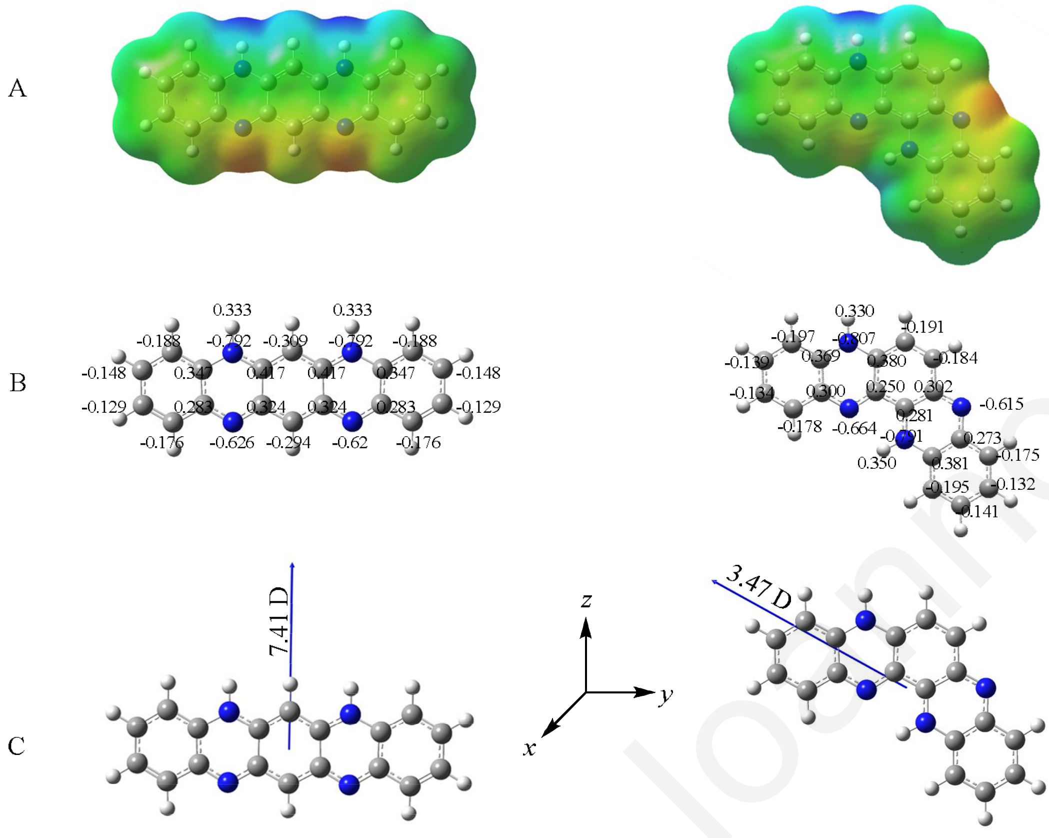


Figure 31. SOMOs of the angular quinoxalino[2,3-*a*]phenazine **89** (R = H) compared with the HOMO-LUMO orbitals of the linear quinoxalino[2,3-*b*]phenazine **51** (R = H), generated with Gaussview 3.0, isovalue 0.02.

The electrostatic surface potential (ESP), the Mulliken charges and the dipole moment of the angular quinoxalino[2,3-*a*]phenazine **89** were compared with the linear analog **51** (Figure 32). The ESP supports the zwitterionic character on the linear system **51** with negative charge on the unsubstituted nitrogens (red color) and positive charge (blue) on the substituted nitrogens. The Mulliken charges demonstrate again the positive character on the substituted cyanine and the negative character on the opposing cyanine. At first glance this was not clear because all four nitrogens carry a negative charge but it can be seen that hydrogens, which for the most part have positive charge between 0.121 - 0.144 (not shown in the scheme for simplicity), have a positive charge of 0.333 when they are *N*-substituted (the charges of these Hs are demonstrated in the picture). Thus, we can consider the substituted nitrogens as NH groups instead and then we can see a noticeable difference between unsubstituted Ns and substituted NHs. This charge separation can also be observed if we determine the sum charge (including hydrogens on each unit) of each cyanine. In contrast, the quinoxalino[2,3-*a*]phenazine **89** cannot give two independent oppositely charged units. Mulliken charges again suggest positive substituted NHs and negative unsubstituted Ns but cannot sum charges in specific regions to show charge separated moieties. Furthermore, there is an asymmetrical charge distribution at the spin centers of quinoxalino[2,3-*a*]phenazine **89**, while that of the linear analog **51** is symmetrical.

Furthermore, the dipole moment (7.41 D) of the linear quinoxalino[2,3-*b*]phenazine **51** is over twice as large as that of the angular analog quinoxalino[2,3-*a*]phenazine **89** (3.47 D). Moreover, in the linear analog **51** the dipole moment lines up with an imaginary *z*-axis, demonstrating a perfectly symmetrical charge separation involving the two opposite cyanines in the system, while this is not the case for the angular quinoxalino[2,3-*a*]phenazine **89**. The magnitude and vector of the calculated dipole moments strongly support the charge separation in the linear structure and the lack of charge separation of the angular. The above data support that systems **51** and **89** have different electronic properties attributed to their different structural motifs and reveal a potential diradical character for system **89**.



51 **89**

Figure 32. A) The electrostatic surface potential (ESP) mapped on the electron density surface generated with GaussView 3.0, isovalue 0.0004, where blue denotes positive character, while red denotes negative charge; B) Mulliken charges, and C) the dipole moment expressed as vector generated with GaussView 5.0 of the linear and angular quinoxalinophenazines **51** and **89**, respectively.

The spin density of the angular quinoxalino[2,3-*a*]phenazine **89** can be seen in Figure 33. Spin up lobes (blue) are delocalised across the carbon skeleton of the entire molecule in an odd-alternant fashion that includes all four nitrogen atoms.

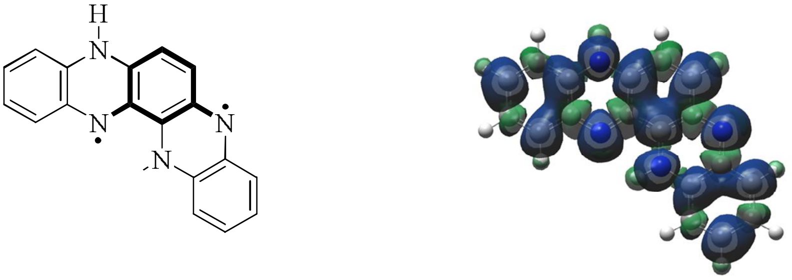


Figure 33. Spin density of angular quinoxalino[2,3-*a*]phenazine **89** generated with GaussView 3.0, isovalue 0.0004, where blue denotes spin up and green denotes spin down density.

In the hypothetical zwitterionic angular quinoxalino[2,3-*a*]phenazine **89** (Figure 34) a number of resonance structures can be proposed, which show that the two possible cyanines are cross-conjugated and overlap over the central benzene ring. Since many resonance structures can be proposed, this suggested to us that a charge separated singlet state could be feasible, challenging the computational data that supported a triplet ground state. To test this hypothesis, we required experimental evidence *i.e.* the synthesis of an analog of the angular quinoxalino[2,3-*a*]phenazine **89**.

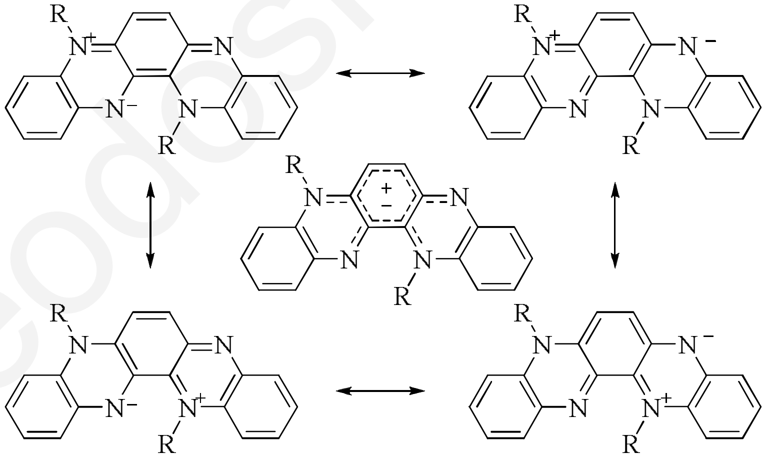
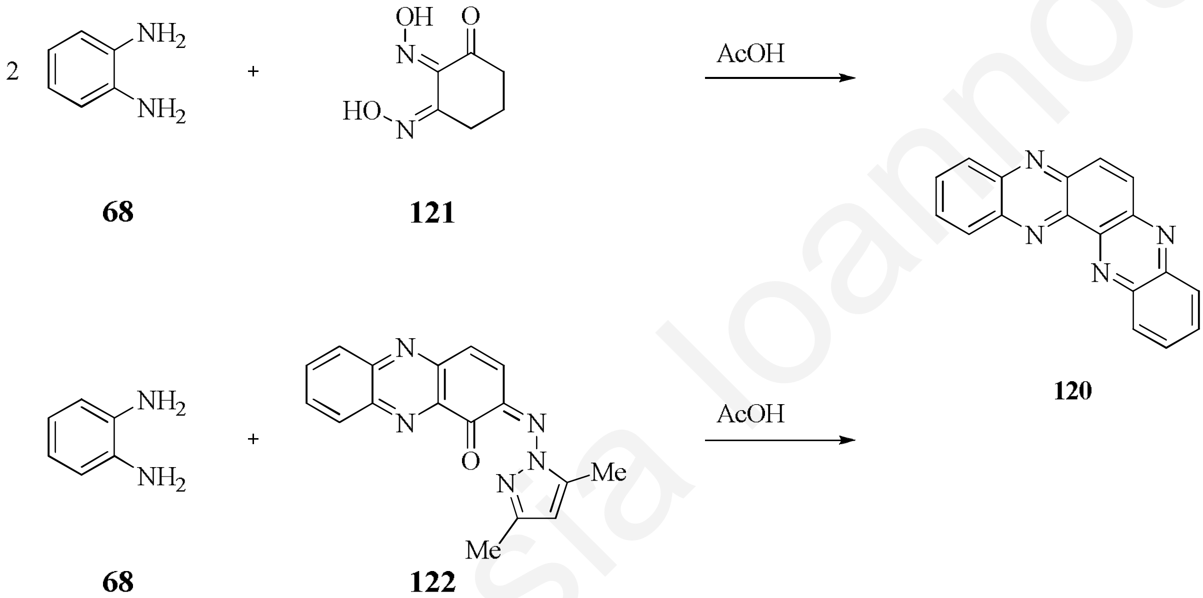


Figure 34. Selected resonance structures of the angular quinoxalino[2,3-*a*]phenazine **89**.

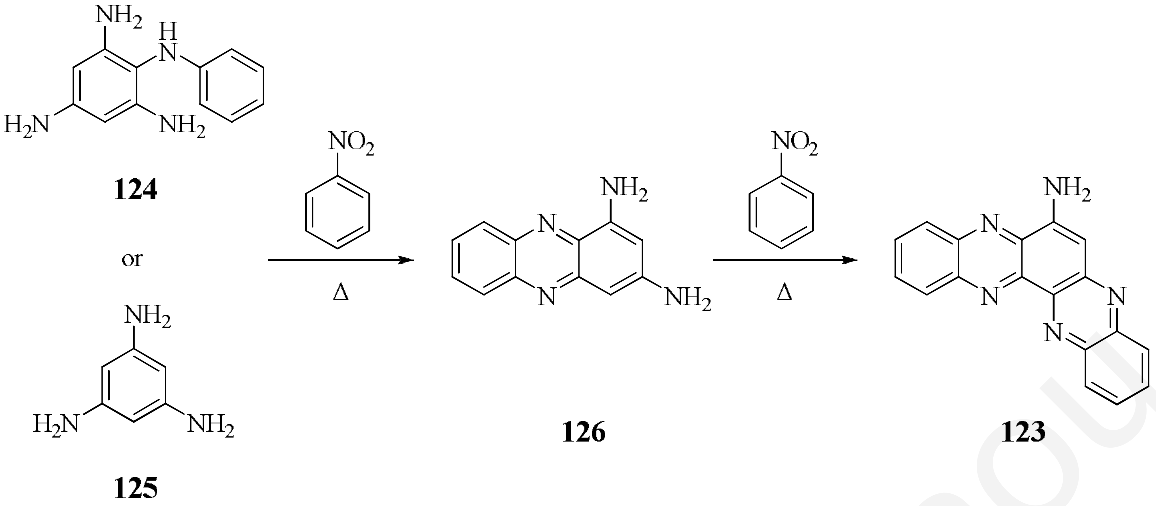
4.2 Attempted Synthesis of Angular Quinoxalino[2,3-*a*]phenazine

Angular analogs with closed shell ground states are known: Quinoxalino[2,3-*a*]phenazine **120** (5,8,13,14-tetraazapentaphene) was synthesized by Cookson[304] *via* treatment of 1,2-benzenediamine **68** with bishydroxyiminocyclohexanone **121** in acetic acid heated at reflux. The isolated brown product gave dark blue or green solutions in organic solvents that slowly changed to yellow on atmospheric oxidation or after recrystallization from nitrobenzene. The final product **120** formed yellow needles with a high melting point (304 °C).[304] Alternatevely, quinoxalino[2,3-*a*]phenazine **120** has been synthesized after refluxing quinonimine **122** and 1,2-benzenediamine **68** in acetic acid.[305] UV/vis studies of quinoxalino[2,3-*a*]phenazine **120** show a longest wavelength absorbance of 339 nm (EtOH) that shifted to 348 nm upon protonation in EtOH/HCl.[304]



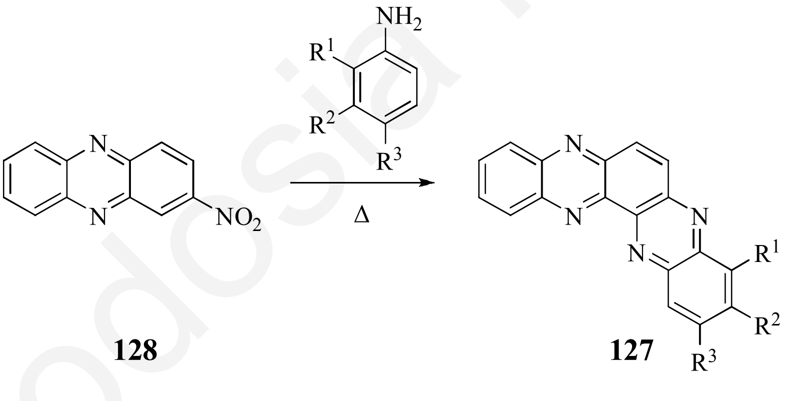
Scheme 22

6-Aminoquinoxalino[2,3-*a*]phenazine **123** was also prepared *via* a Wohl-Aue cyclization[306] starting from either diphenylamine **124** or triaminobenzene **125** in nitrobenzene heated at reflux. The reaction proceeds *via* the 1,3-phenazinediamine **126** (Scheme 23).



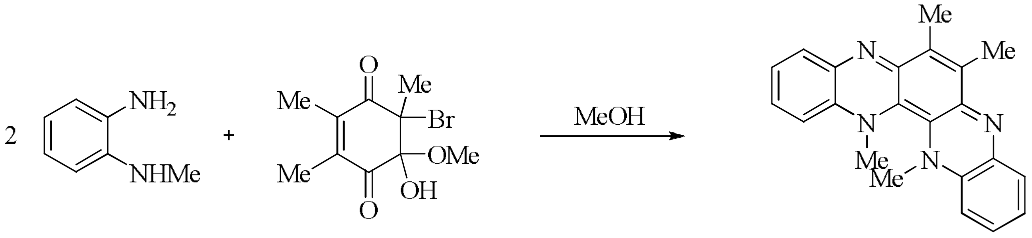
Scheme 23

Analogs with substituents on the peripheral rings such as system **127** have also been prepared from nitrophenazine **128** and substituted anilines. This synthesis worked moderately well for analogs with EDGs but failed with EWGs.[307,308]



Scheme 24

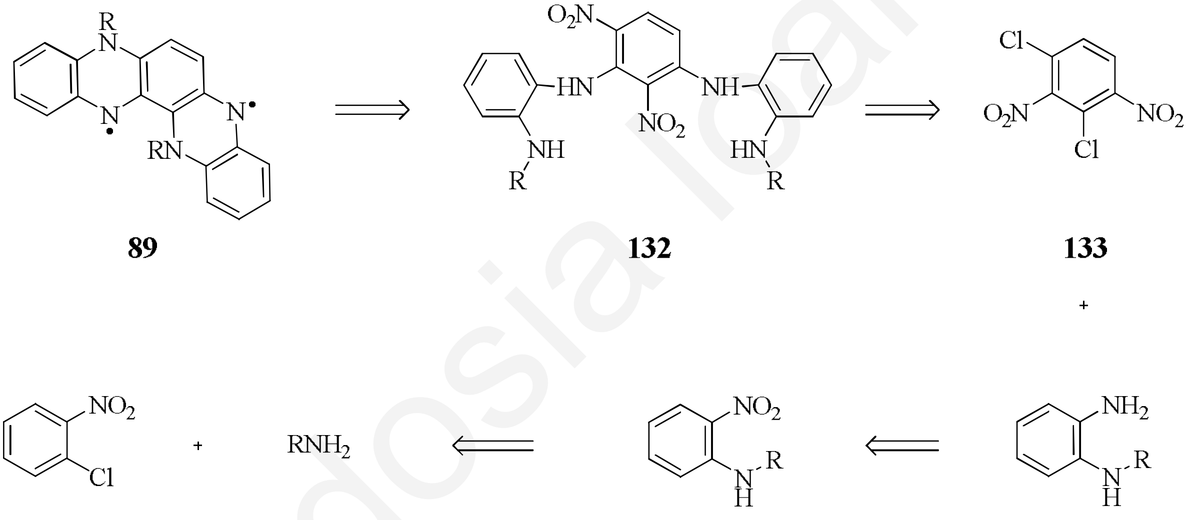
In addition, 6,7,13,14-tetramethyl-13,14-dihydroquinoxalino[2,3-*a*]phenazine **131**, was prepared from 2-methylaminoaniline **129** and cyclohexendione **130** in MeOH.[309] Compound **131** gave a longest wavelength absorption of 552 nm (EtOH), which was dramatically red shifted to 639 nm in EtOH/HCl.



129 **130** **131**

Scheme 25

For the preparation of the angular quinoxalino[2,3-*a*]phenazine **89**, a retrosynthetic analysis revealed a possible synthetic route similar to that for the linear quinoxalino[2,3-*b*]phenazine **51** (Scheme 26).

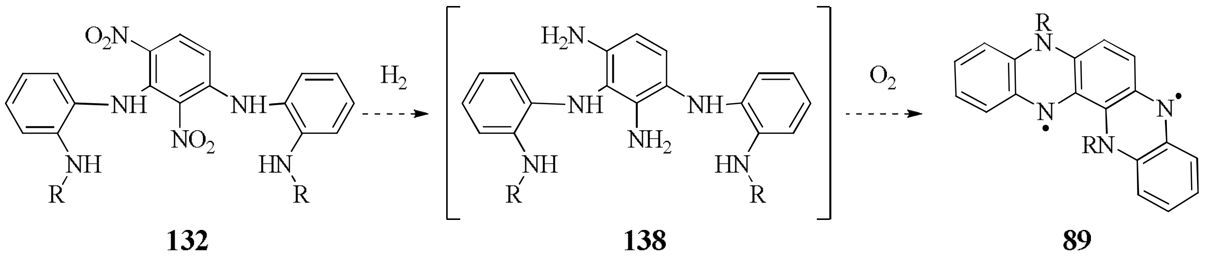


89 **132** **133**

137 **136** **135** **134**

Scheme 26

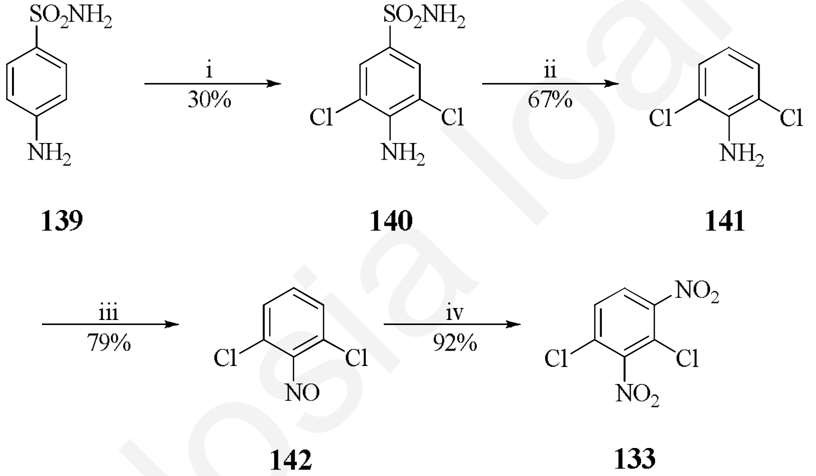
The closure of system **89** in this angular motif requires the precursor **132** to have nitro groups in *meta* positions, hydrogenation of which can afford the tetraamino substituted benzene **138** which on air oxidation and heating could cyclize to give the desired target **89** (Scheme 27). System **132** can be prepared by treating 1,3-dichloro-2,4-dinitrobenzene **133** with *N*-alkyl or aryl substituted 1,2-benzenediamine **134**. The latter compound was formed after reduction of compound **135** that was prepared *via* a KF promoted nucleophilic aromatic substitution (see Section 3.3.2).



Scheme 27

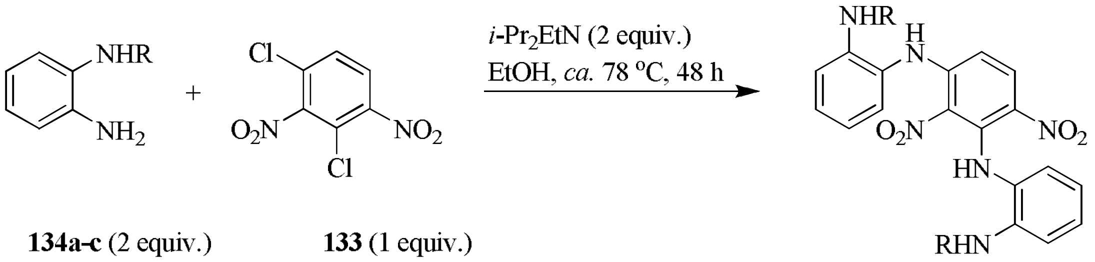
Forward synthesis

1,3-Dichloro-2,4-dinitrobenzene **133** was synthesized from 4-aminobenzenesulfinic acid **139** in four steps according to the literature procedure (Scheme 28).[310-312]



Scheme 28. *Reagents and conditions:* i) HCl (6 M), H_2O_2 (30%) (2 equiv.), H_2O, 60 °C,15 min, 67%; ii) conc. H_2SO_4 (70%) (10 equiv.), 180-190 °C, 2h, 68%; iii) H_2O_2 (30%), (7 equiv.), AcOH (glacial), rt, 48 h, 79%; iv) HNO_3 (fuming) (10 equiv.), 90-100 °C, 20-30 min, 92%.

1,3-Dichloro-2,4-dinitrobenzene **133** was treated with benzenediamines **134a-c** (**a**, R = Ph; **b**, R = *p*-Tol; **c**, R = *n*-Bu) and Hünig's base in EtOH and heated to *ca.* 78 °C to give the tetraamino-dinitrobenzenes **132a-c**, respectively (Scheme 29).



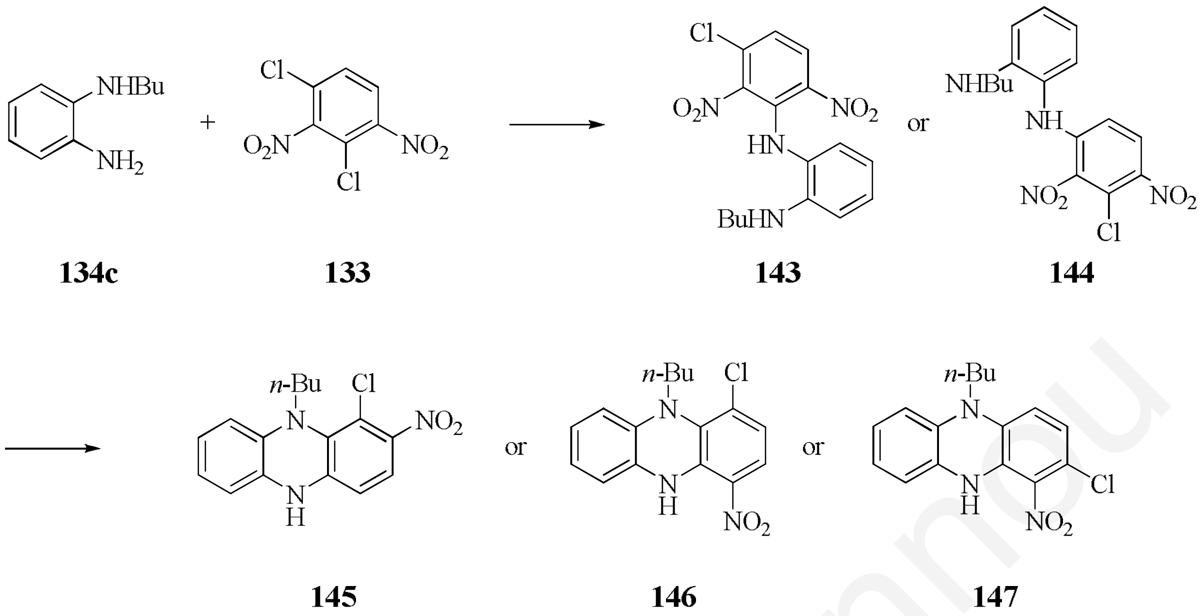
134a-c (2 equiv.) **133** (1 equiv.)

132a (R = Ph, 42%)
132b (R = p-Tol, 42%)
132c (R = n-Bu, 15%)[a]

[a] 3 equiv. of **134c** and base were used for 30 h rxn time instead

Scheme 29. Reaction of diamines **134** with 1,3-dichloro-2,4-dinitrobenzene **133** to give the corresponding disubstituted products **132**.

While the reaction of *N*-phenyl-1,2-benzenediamine (**134a**, R = Ph) or *N*-*p*-tolyl-1,2-benzenediamine (**134b**, R = *p*-tolyl) with 1,3-dichloro-2,4-dinitrobenzene **133** gave the corresponding disubstituted products **132a** (R = Ph) and **132b** (R = *p*-Tol) in moderate yield (42%), the reaction of *N*-(*n*-butyl)-1,2-benzenediamine **134c** and 1,3-dichloro-2,4-dinitrobenzene **133** was complex, giving the desired disubstituted product **132c** (R = *n*-Bu) in low yield (15%) together with a main product (47%) and a minor product in traces. In the latter reaction, three equivalents of the diamine were needed to facilitate the reaction. The main product was isolated *via* column chromatography as purple needles [λ_{max}(DCM)/nm 532 (log ε 3.69)], mp 95-96 °C (from *n*-hexane). Microanalysis (found: C, 60.42; H, 4.93; N, 13.19%) and mass spectrometry [*m/z* (EI) (M^+, 29%) 317 Da] supported the molecular formula $C_{16}H_{16}ClN_3O_2$. The ^{1}H-NMR identified six Ar Hs (7.62-6.62 ppm), one NH (9.59 ppm) and the butyl group. The ^{13}C-NMR identified the butyl group, six tertiary Ar Cs and six Ar CHs. The data suggested that on monosubstitution an intermolecular cyclization had taken place whereby the butylamino group had displaced the nitro group. Based on the data three possible phenazine structures **145**-**147** can be proposed (Scheme 30). The monosubstituted product, which could have structure **143** or **144**, unfortunately could not be isolated, presumably since it was rapidly converted to the phenazine or the disubstituted product **132c**.



Scheme 30. Proposed monosubstituted system and phenazine structures upon reaction of **134c** with **133**.

Single crystal X-ray crystallography even with very bad refinement (R = 32%) supported phenazine **146** to be the correct structure for the main product (Figure 35).

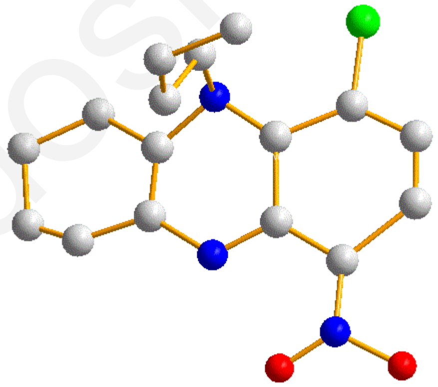
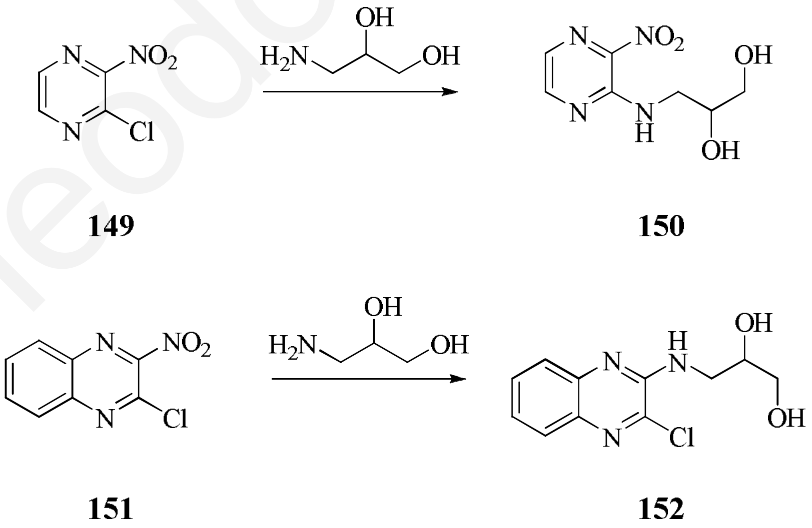


Figure 35. X-ray (R = 32%) picture of system **146**.

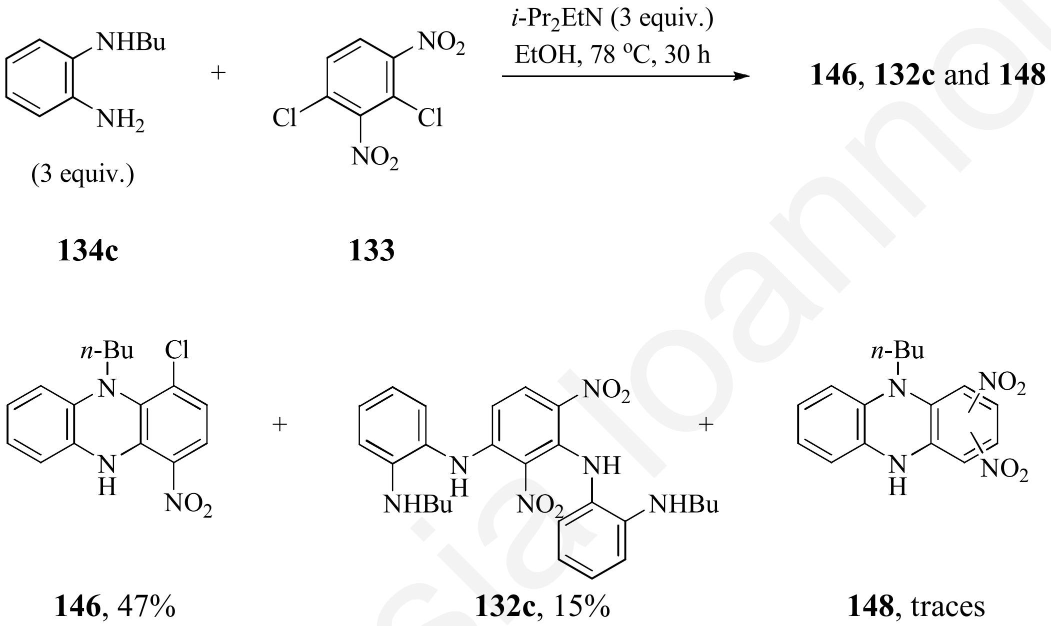
This suggested that the amine first attacked the most hindered Cl-substituted C to give the monochloro substituted **143**. This site is probably the most electrophilic since it is activated by two *ortho* nitro groups. The second attack from the butylamine-group to cyclize the system occurred at the most hindered NO_2-substituted C forming phenazine **146**.

Tentatively, the alkylamino group of *N*-(*n*-butyl)-1,2-benzenediamine **134c** was significantly more nucleophilic than the arylamino groups of the *N*-(aryl)-1,2-benzenediamine **134a** and **b** and thus displaced the nitro group. Diarylamines are typically less nucleophilic than alkylarylamines since the lone pair of electrons on the nitrogen of the diarylamines is strongly conjugated with the π electrons of the aromatic rings and is therefore less available to the nitrogen for nucleophilic or basic type reactions. On the other hand, an alkyl group attached to the amine may increase the nucleophilicity and basicity since the alkyl group inductively releases electron density to the nitrogen. Nitro groups are usually considered as activating groups in aromatic nucleophilic substitution especially in the *ortho* and *para* positions but there are many examples where nitro groups act as good leaving groups in aromatic nucleophilic reactions especially when displaced by oxygen or sulfur nucleophiles.[313-317] For example a nitro-group can be readily displaced by phenoxides in phthalimide derivatives where the leaving group ability compared to halogens F and Cl is $NO_2 > F > Cl$.[318] Usually nitro displacement is achieved when other EWGs are also attached to nitrobenzene. Moreover nitro group displacements by nitrogen nucleophiles as in our case, have also been reported.[319-322] For instance, chloronitroquinoxalines **151** react with 3-amino-1,2-propanediol to undergo preferential displacement of the nitro rather than the chloro group, while chloronitropyrazines **149** prefer to display the chloride instead (Scheme 31).[323]



Scheme 31

The minor product from the reaction of amine **134c** with 1,3-dichloro-2,4-dinitrobenzene **133** was another unknown product isolated as blue prisms. Due to the small quantity of material isolated, only mass spectroscopy data could be collected [*m/z* (EI) (M^+, 82%) 328 Da], which suggested a phenazine structure **148** where the chloro-group of the monosubstituted system **143** was substituted by nitrite, possibly released during the synthesis of phenazine **146** (Scheme 32).



Scheme 32. Reaction of diamine **134c** with 1,3-dichloro-2,4-dinitrobenzene **133**.

To investigate if product **148** can come from phenazine **146,** we treated **146** with $NaNO_2$ in DMF heated at *ca.* 100 °C. After 2.5 d the starting material was consumed and TLC analysis of the reaction mixture indicated a major purple product and some other minor colored side products, but none of the blue product **148**. Additional work to clarify this reaction and the structure of the unknowns was not pursued owing to time constraints.

The isolation of phenazine **146** indicated the difficulty in synthesizing the desired compound **89** bearing *N*-alkyl substituents. Despite this, the reaction was partially optimized to increase the yield of the desired disubstituted product **132c**. By using a 3:1 ratio of **134c**:**133**, we expected the reaction to favor the intermolecular cyclization, however, the intramolecular ring closure dominated. To prevent this intramolecular cyclization, lower reaction temperatures were also considered. Furthermore, we avoided

Hünig's base because it could activate the amine attack and favor the ring closure towards the phenazine. As such, when a 2:1 ratio of the reagents **134c**:**133** was heated in DCM at *ca.* 44 ^{o}C for 4 d, the reaction mixture gave unreacted starting material **133** (30%), phenazine **146** (20%) and disubstituted product **132c** (R = *n*-Bu) as the main product of the reaction in 48% yield.

The disubstituted products **132a** (R = Ph) and **132c** (R = *n*-Bu) (100 mg) were hydrogenated using Pd/C and H_2 in a Parr hydrogenator apparatus using EtOH (20 mL) and THF (10 mL) as the solvents. The presence of THF was needed to facilitate solubilization of the starting dinitrobenzene. The reaction was monitored by hydrogen uptake and once this had ceased the reaction was considered complete (confirmed by TLC). The reaction mixture was then filtered through Celite® to remove Pd/C and the ethanolic filtrate was then heated under an air atmosphere to give only a black mixture that was difficult to process. Thus, in subsequent reactions, to the ethanolic filtrates before heating, acid (*ca.* 1 mL) was added (*e.g.*, HCl, HBr, HI, HBF_4, $HClO_4$ and HPF_6) in the hope of trapping the cyclized quinoxalinophenazine as the mono cations, which should be more stable than the anticipated target diradical. The filtrate was heated extensively in the open air using a heat gun until the initially colorless solution became deep lilac. In each case, after the heated ethanolic solution was allowed to cool to *ca.* 20 ^{o}C, a crystalline bronze solid precipitated and was isolated by filtration. Higher yields and better quality crystals were obtained using HBF_4. Products with *N*-Ph and *N*-Bu substituents acidified with HBF_4 were obtained in 47 and 42% yields, respectively. Other acids gave smaller yields *e.g.*, with *N*-Bu system, HBr formed crystals in 37%, $HClO_4$ in 31% and HPF_6 in 27%.

The cyclized quinoxalinophenazine (R = Ph), isolated as a BF_4^- salt from the reaction of **132a** gave a LRMS (EI) with a molecular mass *m/z* 451 Da, and elemental analysis: C, 66.69; H, 3.92; N, 10.37%, which did not agree with the expected data for the targeted BF_4^- salt of system **89a** (R = Ph): molecular mass *m/z* 436 Da, and elemental analysis: C, 68.72; H, 4.04; N, 10.67%. Similarly, the cyclized quinoxalinophenazine (R = *n*-Bu) as a BF_4^- salt from the reaction of **132c** gave a LRMS (EI) with a molecular mass *m/z* 412 Da, instead of 396 of the *N*-Bu analog **89c**, while elemental analysis (found: C, 62.48; H, 5.87; N, 11.06%) did not match **89c** either (C, 64.48; H, 6.04; N, 11.57%) (Figure 36).

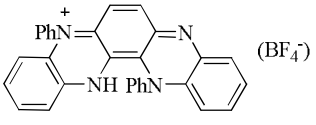
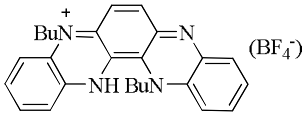
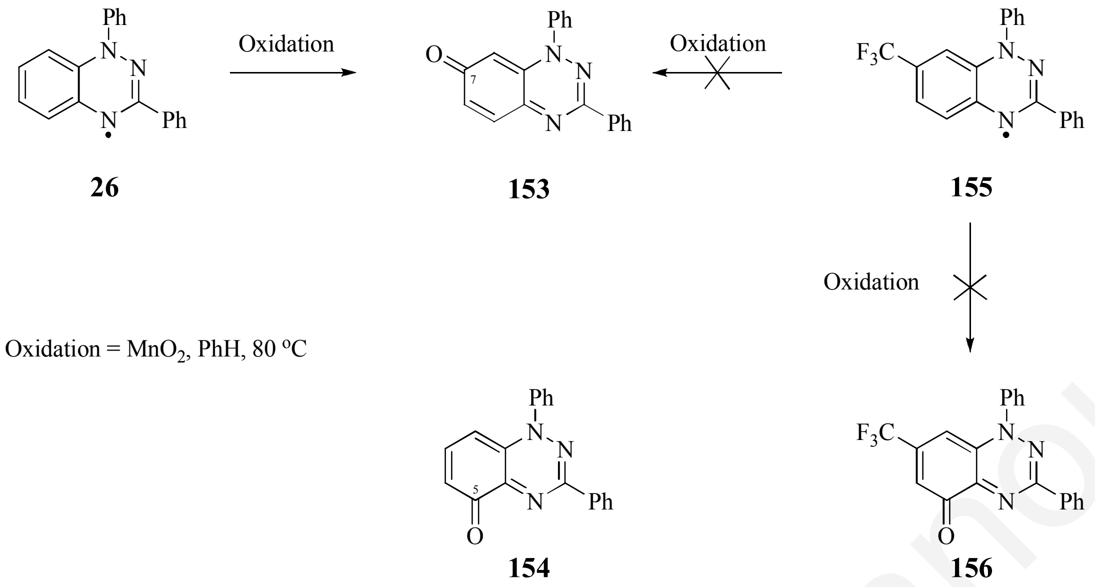
expected products		
	89a	**89c**
expected data	*m/z* 436 Da; C, 68.72; H, 4.04; N, 10.69 %	*m/z* 396 Da; C, 64.48; H, 6.04; N, 11.57 %
experimental data	*m/z* 451 Da; C, 66.69; H, 3.92; N, 10.37 %	*m/z* 412 Da; C, 62.48; H, 5.87; N, 11.06 %

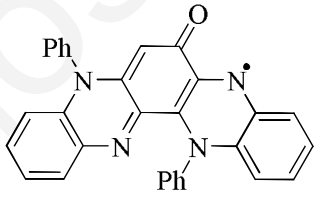
Figure 36. Expected and experimental data for system **89**.

The experimental data suggested the addition of oxygen, which can be expected for paramagnetic systems since they can be easily oxidized. For instance, Blatter radical (1,3-diphenyl-1,2,4-benzotriazinyl radical) **26** oxidizes with MnO_2 (10 equiv.) in DCM at *ca.* 20 ^{o}C for 7 d or $KMnO_4$ (10 equiv.) in refluxing PhH for 2 d to give 1,3-diphenyl-1,2,4-benzotriazin-7-one **153** in 84 and 62% yields, respectively.[324] The oxidation at the C_7 position of the benzotriazinyl **26** can be blocked potentially redirecting the oxidation to C-5 position to give the hypothetical **154** where there is also some spin density (less than C_7) as Neugebauer has reported.[92,93] Such an effort was established using the trifluoromethyl group as the substituent at C_7. The oxidation of the corresponding 7-trifluoromethylbenzotriazinyl radical **155** using either MnO_2 or $KMnO_4$ did not give either the *para*-quinonimine **153** nor the *ortho*-quinonimine **156** showing in this way the tolerance of the trifluoromethyl group towards oxidation and owing to its electron withdrawing power its stabilizing effect on the radical, preventing the possible alternative oxidation at C_5 (Scheme 33).[324]



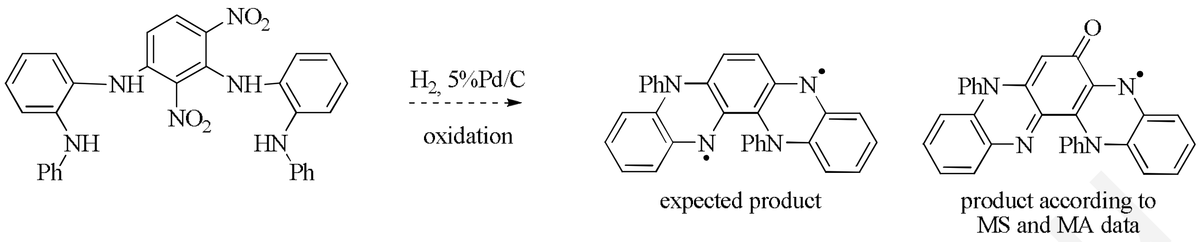
Scheme 33. Oxidation of 7-trifluoromethylbenzotriazinyl radical **155**.

Tentatively, the most likely site for oxidation on the cyclized quinoxalinophenazine should be on the central ring, since the central rings in acenes are typically more reactive.[325-327] In addition, and in light of the known oxidation of Blatter's radical to the benzotriazinone (formation of the quinone *para* to the unsubstituted nitrogen), we tentatively considered the possible structure of **157a** (R = Ph).



157a

Under acidic "work up" conditions the analogous salts were isolated and freed on treatment with base. As such, to a suspension of the salt in EtOH, NaOH (*ca.* 1 equiv. in small pieces) was added and then gentle heating was applied until the NaOH dissolved and the color of the suspension changed from lilac to brown. On cooling, the free bases were obtained as brown solids, which were isolated by filtration and then recrystallized from benzene or toluene (bulk recrystallization) or using DCE/pentane (vapor diffusion). Protic solvents were avoided since they could reprotonate the neutral radical. Elemental analysis of the isolated radical gave C, 79.76; H, 4.17; N, 12.46% which matched the suggested radical **157a** ($C_{30}H_{19}N_4O^{\bullet}$ requires C, 79.81; H, 4.24; N, 12.41%).



131a **89a** **157a**

m/z 436 Da
C, 68.72; H, 4.04; N, 10.69

m/z 451 Da
C, 66.69; H, 3.92; N, 10.37

Scheme 34. Expected product and suggested product according to MS and MA data after hydrogenation and oxidation of **131a**.

The UV/vis absorption of the neutralized compound (*N*-Ph) gave λ_{max} = 900 nm (log ε 3.35). This longest wavelength absorption supported charge transfer ability while the extensive π-π* character is supported by absorptions in the region below 700 nm. EPR spectroscopy of the same compound gave a strong signal, indicating a doublet ground state supporting the synthesis of a new organic radical (Figure 37).

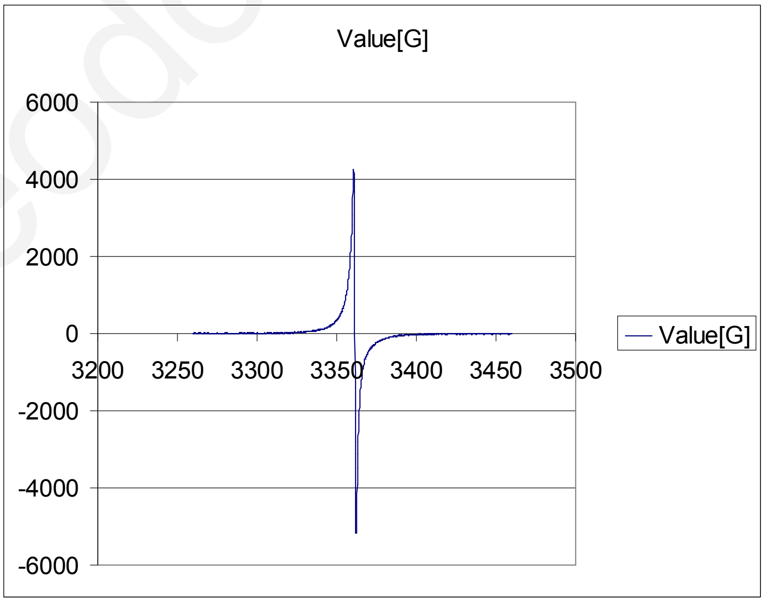
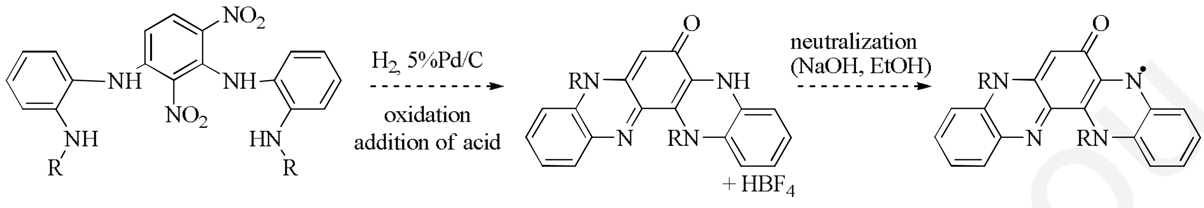


Figure 37. EPR signal for the isolated radical, (*N*-Ph).

In light of the above, we considered Scheme 35 to be rational and attempted to grow single crystals of the tetraazapentacene **157H** for structure elucidation and to confirm our hypothesis. Unexpectedly, the X-ray structure of the R = Ph analog crystallized with HBF_4 to give an altogether different structure.



132 **157H** **157·**

Scheme 35. Reaction of compound **132** to give the expected radical **157**.

According to the X-ray data, the linear system **158** was the product of the above reaction. The refinement of the X-ray was very poor and thus the only qualitative information we could get from the picture was the atom connectivity, which supported a linear motif for the radical and the position of the oxygen atom (Figure 38). This was a surprising result considering the synthetic route to the angular analog.

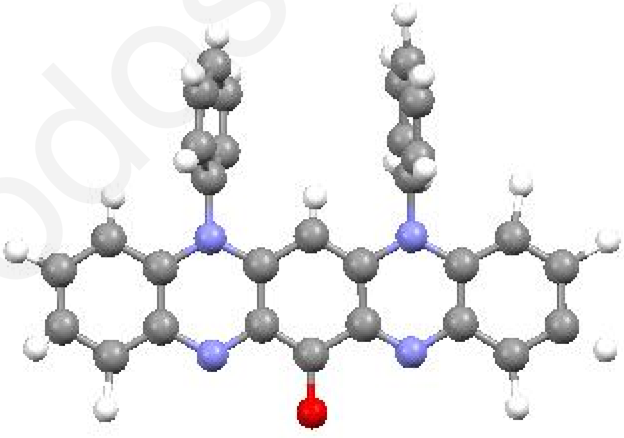
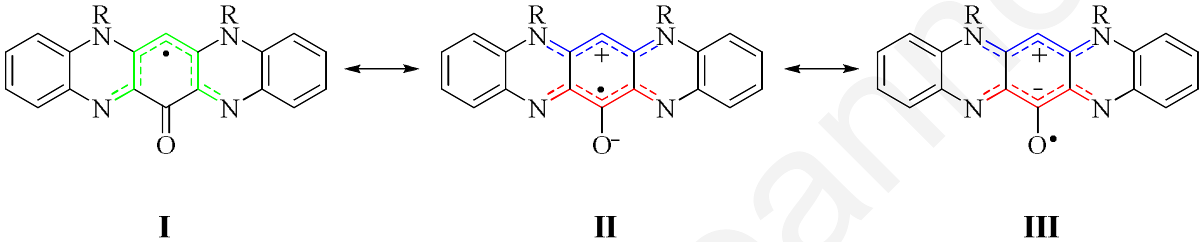


Figure 38. X-ray (R = 11%) picture of system **158a**.

Despite the fact that from this synthesis the diradical **89a** was not observed, the unusual tetraazapentacene oxy radical **158a** was unexpectedly isolated and this required further study.

4.3 Study on Tetraazapentacene Oxy Radical

Three possible resonance structures for oxy-tetraazapentacene radical **158** are **I**, **II** and **III** (Scheme 36). Two of them, beside their paramagnetic character, are also zwitterions. Structure **I**, has a carbonyl bond and the free spin is delocalized between the two unsubstituted nitrogens. Structures **II** and **III** have a positive cyanine in the site of the substituted nitrogens and have a negative charge located on the oxygen and the free spin on the opposite cyanine for structure **II** or have the negative charge on the opposite cyanine and the free spin located on the oxygen for structure **III**.

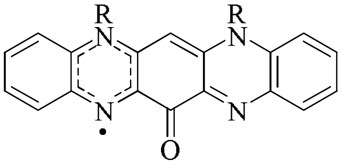


Scheme 36. Three possible resonance structures for radical **158**.

The EPR data, which shows only a single peak, strongly supports that radical is not delocalized equally among spin carriers since that should have given EPR data with hyperfine interactions with neighboring nuclei and thus splitting of the signal. This somehow excludes structures **I** and **II** where radical seems equally delocalized among nitrogens and supports the oxy-radical structure **III** where radical is mostly localized on oxygen.

Computational studies

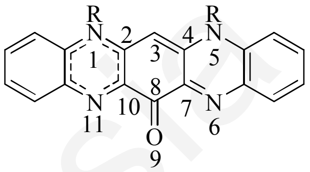
A computational study for the most preferred structure of the radical using various methods was inconclusive. Optimization of the structure using DFT/B3LYP/6-31G(d) which is a method that gives a good matching of computational and experimental data of the linear tetraazapentacene structure **119** (see Chapter 3), suggested double bond C=O as in structure **I** but gave one imaginary frequency during the frequency calculation. Other methods like HF/6-31G(d), MP2/6-31G(d), B3LYP/6311G(d) or B3PW91/6-31G(d) also suggested structure with double carbonyl bond, but only HF gave zero imaginary frequencies. The above optimized structures though are symmetrical as could be expected. However, a non-symmetrical structure with double carbonyl bond resulted in an optimization using DFT/B3LYP/6-31G(d) that gave zero imaginary frequencies. It is not that easy to draw such a structure but it could be pictured as in structure **IV**.



IV

Bond length analysis (Table 29) of the optimized structure **IV** shows the non-symmetric character of the structure. For instance C-CO bonds C_7-C_8 and C_8-C_{10} are 1.507 Å and 1.473 Å, respectively. Similarly C-C bonds C_2-C_3 and C_3-C_4 have lengths 1.430 Å and 1.373 Å, respectively indicating single and double bond character respectively (Table 29).

Table 29. Selected bond lenghts (Å) of optimized structure **IV** [B3LYP/6-31G(d)]



N_1-C_2	**C_2-C_3**	**C_3-C_4**	**C_4-N_5**	**C_4-C_7**	
1.387	1.430	1.373	1.391	1.468	
C_{10}-N_{11}	**C_8-C_{10}**	**C_7-C_8**	**N_6-C_7**	**C_2-C_{10}**	**C_8-O_9**
1.354	1.473	1.507	1.303	1.414	1.228

While EPR and computational data suggest structure **IV**, X-ray (R = 11%) suggests tentatively a single C-O bond [1.422(6) Å] as in **III** but not symmetric. However, due to the low refinement of the X-ray structure these data are not accurate. Nevertheless, the possible zwitterionic character of structures **II** and **III** was supported by a UV/vis solvatochromic study. Typically, charge separated compounds that have a less polar excited state display negative solvatochromism, *i.e.* the $\lambda_{\max}$ decreases as the polarity of the solvent increases. This was observed with zwitterionic system **119**.[154] For this study, radical **158a** (R = Ph) negative solvatochromism was also observed indicative of zwitterionic behavior (Figure 39).

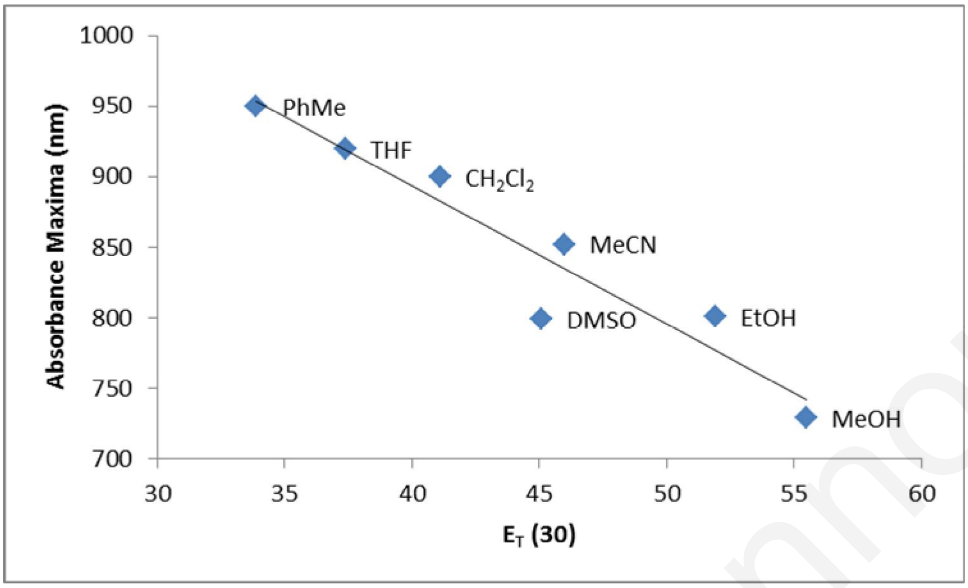


Figure 39. Correlation between solvent polarity $E_T(30)^{328-330}$ and the absorbance maxima of radical **158a**.

In EtOH/HCl, a blue shift of the low π-π^* transitions was observed when adding one drop of HCl [H^+/EtOH, λ_{max} 749 nm (log ε 0.68)] or two drops of HCl [H^+/EtOH, λ_{max} 735 nm (log ε 0.84)] on the neutral solution [EtOH, λ_{max} 801 nm (log ε 0.63)] (Figure 40). Addition of more drops HCl did not affect the spectrum. This behavior was also observed on quinoxalinophenazine **119** (R = Ph) but in a significant blue shift (100 nm).[154]

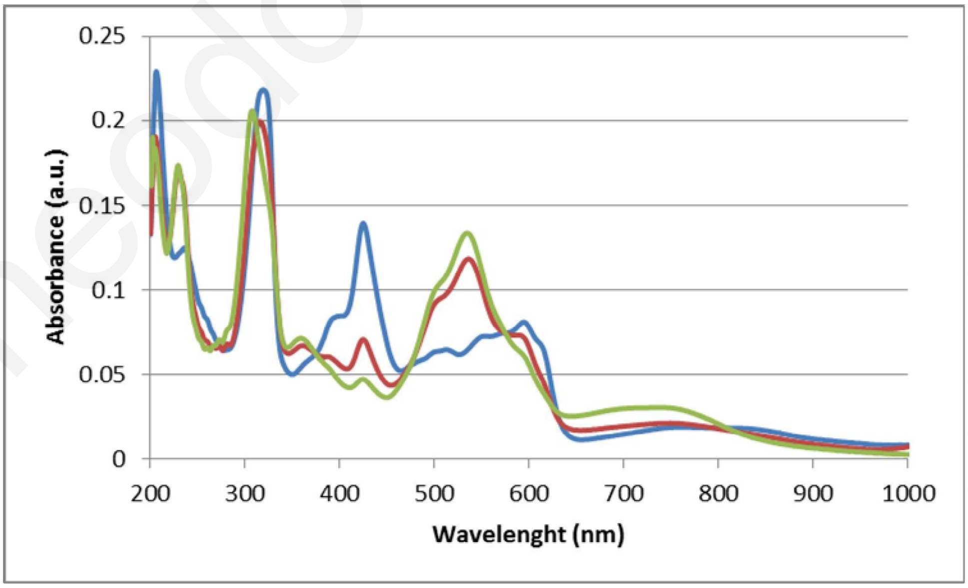
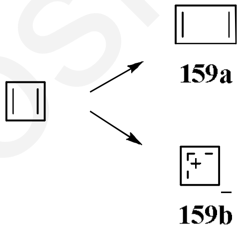


Figure 40. Absorption spectra of radical **158** in EtOH at 4.4 × 10^{-3} M; [free base (blue line) λ_{max} 801 nm (log ε 0.63); addition of one drop HCl (red line) λ_{max} 749 nm (log ε 0.68); addition of two drops HCl (green line) λ_{max} 735 nm (log ε 0.84).

The unusual proposed structures for **158** remind us the ambiguous structure of cyclobutadiene **159**.[331-336] Cyclobutadiene could be considered as a square structure but such a structure would result in a strong anti-aromatic character that needs to be avoided. That is because, the four p orbitals on each carbon will form four π orbitals, that will include a bonding, an anti-bonding and two non-bonding orbitals and following Hund's rule and Hückel molecular orbital theory cyclobutadiene should be a diradical. Though, the two non-bonding electrons will be in opposite orbitals, cyclobutadiene becomes a highly unstable diradical and therefore it is known as an anti-aromatic system. To avoid anti-aromaticity, cyclobutadiene needs to adopt a structure to prevent conjugation.

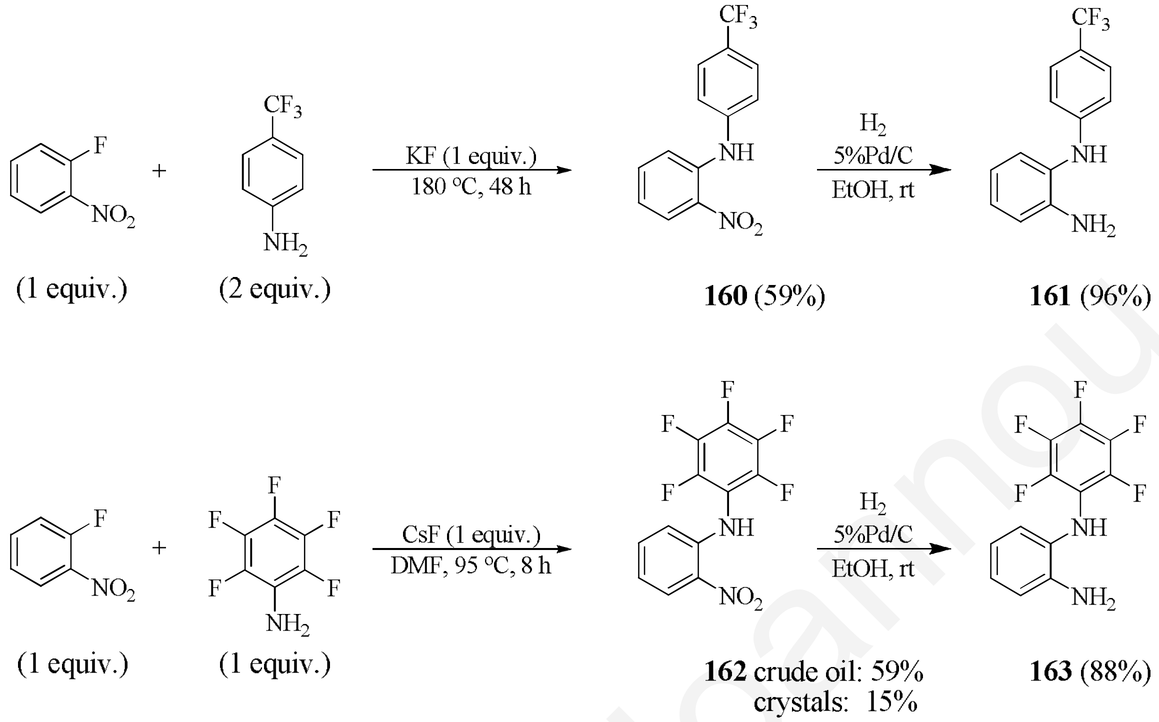
The geometric distortions **159a** and **159b** were proposed to describe the system better (Scheme 37). Both singlet and triplet ground states have been predicted computationally. Dewar's calculations though predicted singlet ground state with localized single and double bonds as in rectangular structure **159a**. In fact single C-C bonds are even longer than conventional single C-C bonds. The other proposed structure, **159b**, is an unsymmetrical zwitterionic form that also stabilizes the system. However, studies confirmed the rectangular structure **159a** as the preferred structure of cyclobutadiene.[337,338]



Scheme 37. Proposed geometric distortions of cyclobutadiene.

The crystal structure of **158** showed the linear conformation of the system but a better X-ray was required to get precise geometric data and resolve the structure assignment. The need for better single crystals led to the synthesis of analogous radicals with different *N*-substituents, such as perfluorophenyl or *p*-trifluoromethylphenyl since the C-H···C-F interactions could assist the crystal packing.[339,340] Thus, the analogous amines were used for the synthesis of the corresponding oxy radicals **158d** and **158e**.

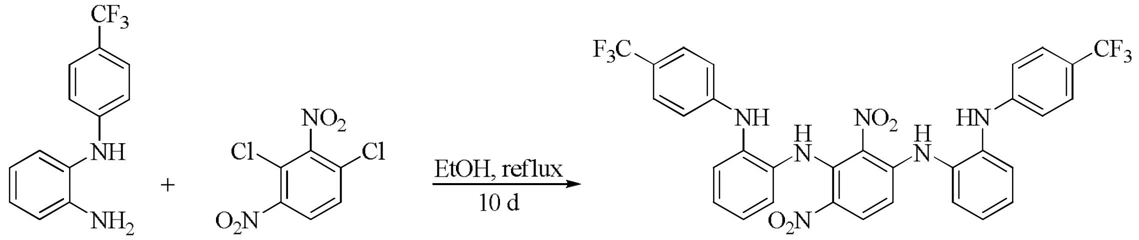
The nitro-diarylamines **160** and **162** were synthesized after reaction of 2-fluoronitrobenzene with *p*-(trifluoromerthyl)aniline and pentafluoroaniline, respectively (Scheme 38).



Scheme 38. Synthesis of amines **161** and **163**.

Amine **160** was synthesized *via* the same conditions used on *N*-Ph and *N*-Bu analogs but amine **162** could not because under these conditions the reaction rate was too slow giving the product only in traces. The reported synthesis of amine **162** required basic conditions *via* CsF, in DMF and 95 °C, and the product was isolated in 22% yield after high vacuum distillation.[341] By using chromatography we managed to get the product in a crude oily form in 59% yield and after crystallization from hexane the amine **162** was isolated clean as needles in 15% yield.

Hydrogenation (Pd/C, H_2, EtOH) of amines **160** and **162** afforded diamines **161** and **163** respectively, in high yields (Scheme 38). The reaction of diamines **161** and **163** with 1,3-dichloro-2,4-dinitrobenzene **133** followed: In the case of diamine **161** (Scheme 39) the reaction required a 4:1 ratio of reagents **161**:**133** in refluxing EtOH for 10 d and gave the product in 56% yield. Under basic conditions (Hünig's base) in refluxing EtOH, the reaction gave deep blue and purple colored products that correspond to the analogs phenazines and thus it was preferred to perform the reaction without base. On the other hand, with the diamine **163**, the reaction could not be performed without base and even then a complex reaction mixture was obtained. As such, it was abandoned. We subsequently focused our attention on the formation of the trifluoromethylphenyl analog.



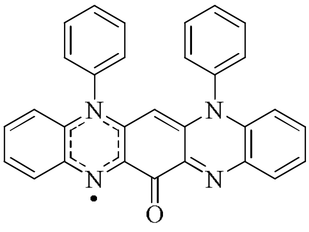
161
(4 equiv.)

133
(1 equiv.)

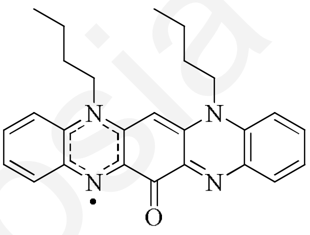
132d
(56%)

Scheme 39

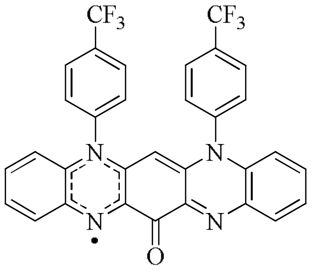
After the synthesis of the trifluoromethyl analog **132d**, reduction and then oxidation of the obtained hexamino compound, we isolated the HBr acidified product **158dH$^+$** in 40%, and after neutralization with NaOH, the radical **158d** was isolated in 80%. Disappointingly, recrystallisation of **158d** did not give crystals suitable for X-ray crystallogaphy. Eventually, three of oxy-tetraazapentacene radicals **158a**, **c** and **d** were synthesized.



158a



158c

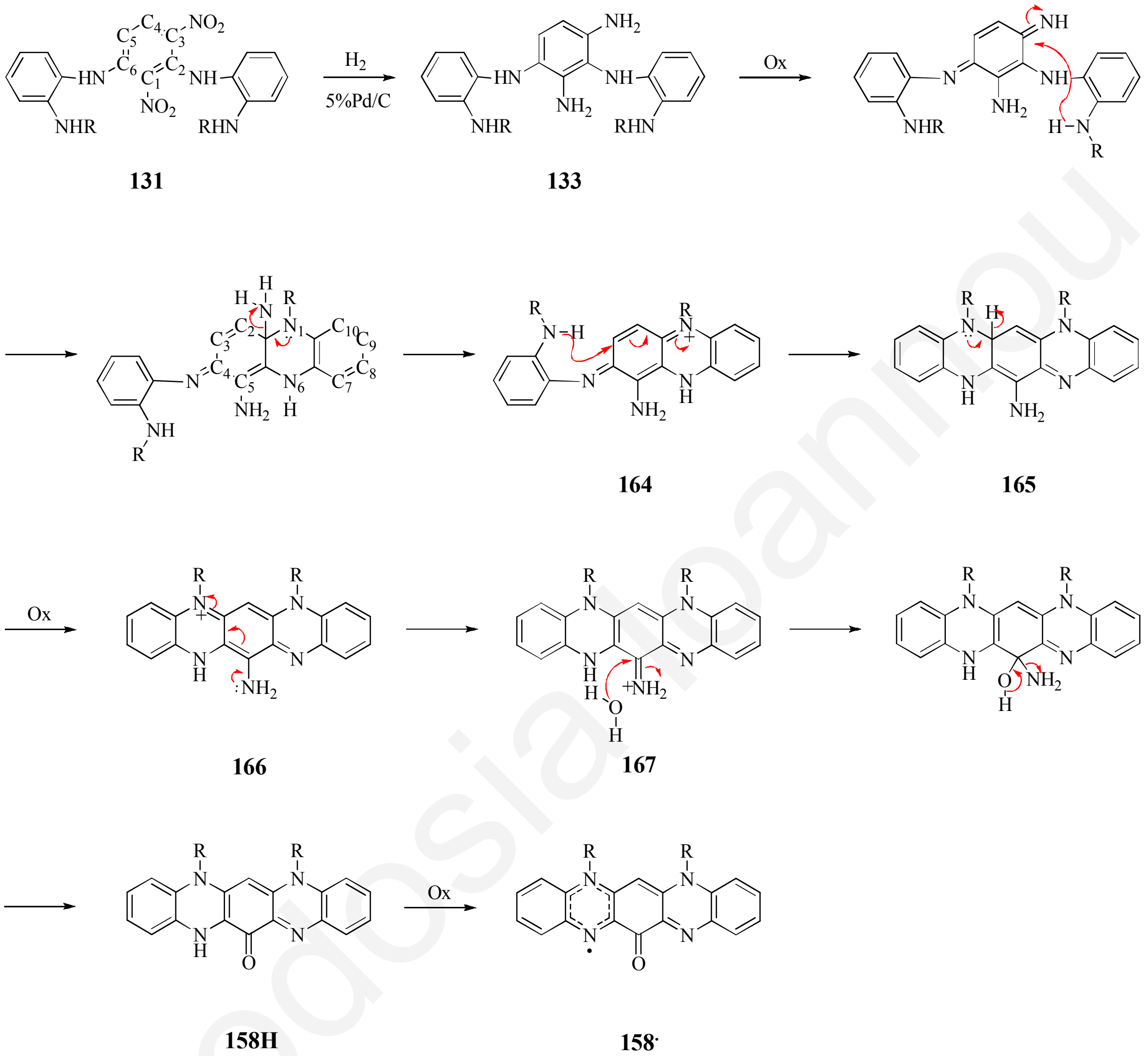


158d

4.4 Mechanistic Rationale for the Formation of Radical 158 and Alternative Pathway for Target

A rational mechanism for the formation of the linear quinoxalinophenazine radical was proposed based on the probable oxidation of the central tetraamino substituted benzene. This highly electron rich arene was likely to suffer rapid oxidation to give either an *ortho* or *para* quinonedimine, which could then undergo intramolecular cyclization to give, following loss of ammonia, the phenazine **164**. Subsequent Michael type addition by the exocyclic benzenediamine at the 5,10-dihydrophenazine C_3 position can give the linear quinoxalinophenazine **165** that can oxidize to the quinoxalinophenazine **166**. Subsequent tautomerization affords the exocyclic imine **167** that can hydrolyse to the ketone **158H**.

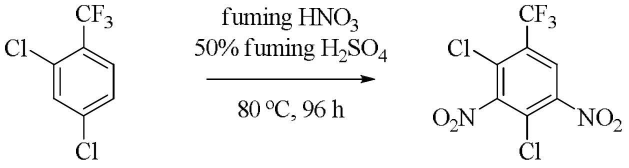
Air oxidation of the latter affords the tentative quinoxalinophenazine oxy radical **158** (Scheme 40).



Scheme 40

By analyzing the proposed mechanism for the formation of the linear quinoxalinophenazine oxy radical, it can be inferred that blocking the cyclization at C-3 in intermediate **164** could lead to the formation of the desired angular quinoxalinophenazine. A good blocking group is the trifluoromethyl group because it imparts oxidative stability to the arene owing to its electron withdrawing effects and was successfully used to stabilize azaacene radicals such as the Blatter radical.[324]

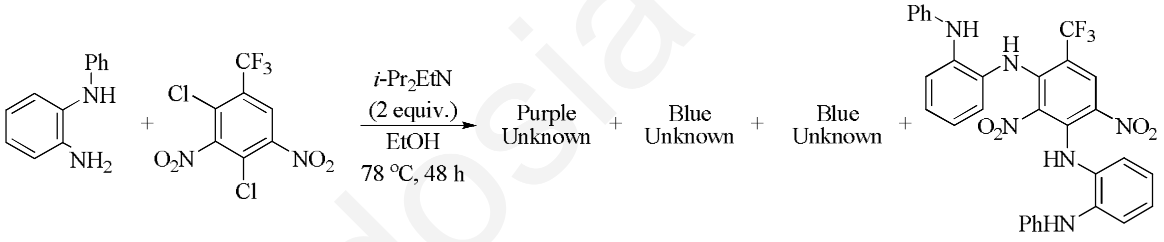
We therefore synthesized 2,4-dichloro-1,3-dinitro-5-trifluoromethylbenzene **169** from available 2,4-dichlorotrifluoromethylbenzene **168** according to a literature procedure (Scheme 41).[342]



168 **169**, 57%

Scheme 41

N-Phenyl-1,2-benzenediamine **134a** reacted with 2,4-dichloro-1,3-dinitro-5-trifluoromethyl-benzene **169** and Hünig's base (2 equiv.) in EtOH at *ca.* 78 °C to give the corresponding tetramine **170** in low yield (3%), together with three colored side products (Scheme 42).



134a **169** **A**, 54% **B**, 18% **C**, traces **170**, 3%

Scheme 42

The main product **A** (54%) was obtained as light purple-pink cotton like crystals, mp 213-214 °C (hexane). Microanalysis (found: C, 56.23; H, 2.70; N, 10.27%) and LRMS [*m/z* (EI) 405 Da (M^+, 91%)] suggested the formula $C_{19}H_{11}ClF_3N_3O_2$, indicating tentatively, that a phenazine had been formed *via* an intramolecular cyclization and displacement of a nitro group, similar to that observed during the reaction of *N*-(*n*-butyl)-1,2-benzenediamine **134c** with 1,3-dichloro-2,4-dinitrobenzene **133** (see Section 4.2). The UV/vis spectrum gave a λ_{max}(DCM)/nm 492 (log ε 3.72). The ^{1}H-NMR of the new compound identified ten Ar Hs and one NH (9.84 ppm). The ^{13}C-NMR identified eight tertiary Ar Cs, eight Ar CHs and the peak of the CF_3 group. The splittings of the CF_3 (q, $^1J_{C\text{-}F}$ 271.6 Hz), the neighboring carbon (q, $^2J_{C\text{-}F}$ 32.7 Hz) and the carbon next (q, $^3J_{C\text{-}F}$ 6.3 Hz) attributed to the three flourines were observed. Three possible structures **173-175** for unknown **A** can be proposed, tentatively originating from the possible monochloro displaced precursors **171** and **172**. Monosubstituted system **171** can lead to phenazines **173** and **174** while monosubstituted **172** can only give phenazine **175**. Unknown **B** was a purple-blue [λ_{max}(DCM)/nm 559 (log ε 3.90)] product (18%), mp 206-207 ^{o}C (hexane), [*m/z* (EI) 416 Da (M^+, 100%)] the ^{1}H and ^{13}C NMR data of which were similar to that of the phenazine above: ten Ar Hs, one NH (10.21 ppm), eight tertiary Ar Cs, eight Ar CHs and the peak of the CF_3 group, and the unknown **C** was a minor blue [λ_{max}(DCM)/nm 585 (log ε 3.14)] product in traces [*m/z* (EI) 416 Da (M^+, 100%)]. The data suggest again the formation of dinitro-analogs and thus compounds **176-177** are suggested for major purple-blue and minor blue compounds (Figure 41).

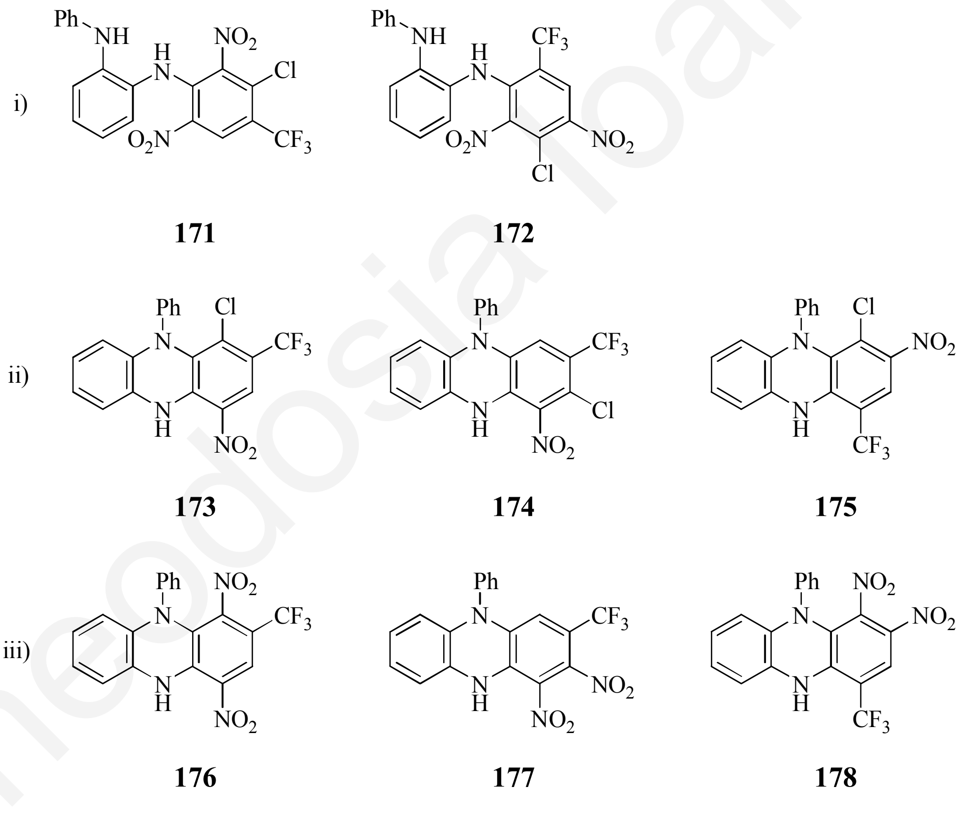
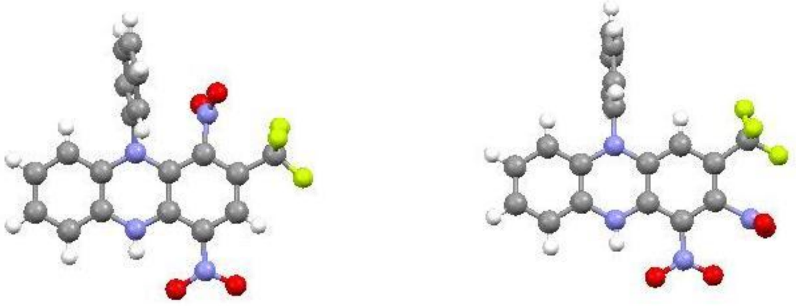


Figure 41. Possible structures of i) monosubstiututed, ii) purple unknown **A** and iii) major and minor blue unknowns **B** and **C** of the reaction of **134a** with **169**.

The structure of the two dinitro unknowns **B** and **C** were solved by single crystal X-ray crystallography and determined to be the dinitro phenazines **176** and **177**, respectively (Figure 42).



176 **177**

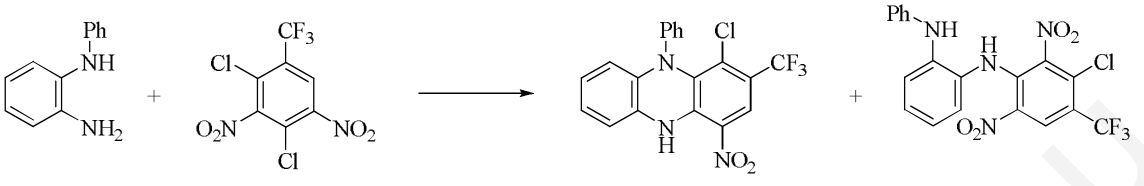
Figure 42. X-ray pictures of major and minor dinitro compounds **176** and **177**, respectively.

Having in mind that the dinitro-products from the reaction are **176** and **177**, the correct structure of the monosubstituted system must be **171**. Structure **172** would only give the dinitro-compound **178** through phenazine **175**, while compound **171** would give dinitro compound **176** through phenazine **173** and dinitro compound **177** through phenazine **174**. Considering the correct structure of phenazine **A**, we suggest structure **173** since only structures **173** and **174** can be produced from monosubstituted system **171** and since **173** agrees with the analogous phenazine **146** in the butyl analog confirmed by X-ray crystallography (see Section 4.2).

Since the desired disubstituted product **170** was formed in only 3% yield *via* these conditions (refluxing EtOH and Hünig's base) and because we had a route to the monosubstituted compound **171** we considered aiming for a two-step synthesis of disubstituted product **170** *via* the monosubstituted product **171**. This two-step synthesis could limit or avoid the formation of undesirable side products.

Using a 1:1 ratio of reagents **134a**:**169**, in the absence of base, in DCM at *ca.* 20 ^{o}C for 2 d led to an incomplete consumption of the starting dichlorodinitrobenzene but nevertheless gave the desired monosubstituted product **171** in moderate yield (26%) together with the corresponding phenazine where the Cl is displaced by a nitro group as the main product in 38%. A 2:1 ratio of **134a**:**169** and addition of Hünig's base in refluxing DCM gave in 7 h a lower yield of the phenazine to 6% and higher of the yield of the monosubstituted product to 38%. By using a 4:1 ratio of **134a**:**169** and refluxing EtOH instead, without any base, we managed to get after only 1.5 h a clean reaction without any phenazine formed and the monosubstituted product **171** as the main product in 89% (Table 30).

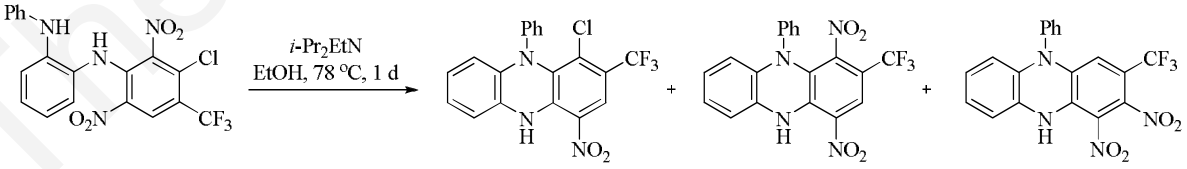
Table 30. Optimization of the reaction of **134a**:**169** to increase the yield of monosubstituted **171**.



134a **169** **173** **171**

134a (equiv.)	Conditions	Yields (%) **173**	**171**
1	DCM, 20 °C, 2 d, incomplete	38	26
2	DCM, i-Pr_2EtN (2 equiv.), 40 °C, 7 h	6	38
4	EtOH, 80 °C, 1.5 h	0	89

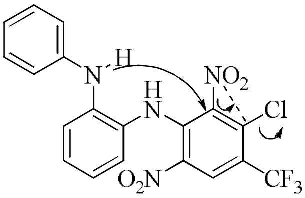
With the monosubstituted product **171** in hand we then pursued the synthesis of the disubstituted analog **170**. Initially, the behavior of the monosubstituted product **171** was examined: An ethanolic solution of the monosubstituted product **171** was treated with Hünig's base (1 equiv.) and heated to reflux. After 24 h, phenazine **173**, dinitrophenazine **176**, and some trace of dinitro-compound **177** were formed in 22, 25 and 4% yields, respectively (Scheme 43). Interestingly, heating the monosubstituted product **171** in EtOH (*ca.* 78 °C) in the absence of base led to the quantitative formation of phenazine **173** in just 10 min, while in DCM at *ca.* 40 °C only phenazine **173** was formed at a slower rate and in traces.



171 **173**, 22% **176**, 25% **177**, traces

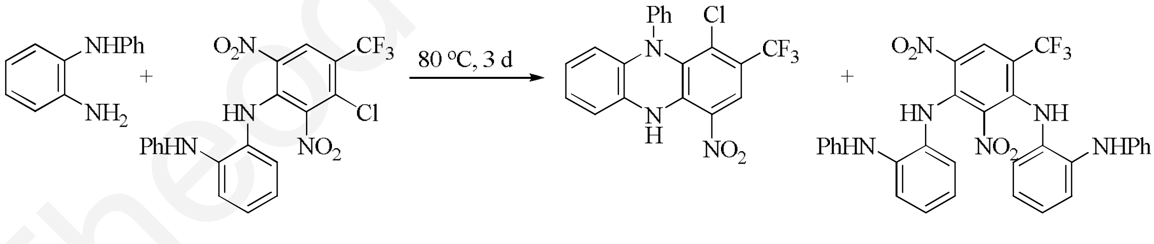
Scheme 43

To achieve the synthesis of dinitro-system **176**, basic conditions (Hünig's base) were required either in refluxing EtOH or DCM. When a weaker base was used such as pyridine, even in refluxing EtOH, the dinitro-compound **176** was not observed since phenazine **173** was the only product of the reaction. Attempts to synthesize dinitrophenazines **176** or **177** from phenazine **173** using nitration conditions [$NaNO_2$ (10 equiv.)/DMF/Δ or KNO_2 (10 equiv.), 18-C-6 (2 equiv.)/PhMe/Δ] failed. This tentatively suggested that the mechanism for their formation was not *via* an intermolecular displacement of Cl but possibly *via* an intramolecular migration of a nitro-group at the time of the proposed ring closure (Scheme 44).



Scheme 44. Formation of phenazine **173** *via* compound **171**.

Since the monosubstituted **171** readily underwent intramolecular ring closure, we considered preparing the disubstituted analog using a large excess of *N*-phenyl-1,2-benzenediamine. To do this 10 equiv. of *N*-phenyl-1,2-benzenediamine were used under solvent free conditions thus ensuring a high local concentration of the diamine reagent: Heating the reaction mixture at *ca.* 80 °C for 3 d gave the desired disubstituted product **170** in 83% and phenazine **173** in only 15%, based on recovered starting material **171** (33%) (Scheme 45).



134a
(10 equiv.)

171
(33% recovered)

173 (15%)

170 (83%)

Scheme 45

Having prepared the disubstituted system **170,** the synthesis of the diradical was attempted. Hydrogenation of **170** using Pd/C followed by the oxidative cyclization conditions (EtOH/$HClO_4$, air, heat) used for the formation of the linear quinoxalinophenazines failed to give the expected product or any products that can be handled and identified. Time constraints prevented further work.

4.5 Summary

A DFT computational study on the angular quinoxalino[2,3-*a*]phenazine **89** suggested a triplet ground state. The attempted synthesis of **89** starting from 1,3-dichloro-2,4-dinitrobenzene and *N*-(alkyl or aryl)-1,2,-benzenediamines failed but afforded an unusual linear quinoxalino[2,3-*b*]phenazine **158** supporting a zwitterionic biscyanine bearing an oxy radical. This unusual radical was partially characterised by X-ray, UV/vis and EPR and a rational mechanism for its formation was proposed.

CHAPTER 5

Manipulating the Singlet-triplet Energy Gaps of Linear and Angular Arene-fused Bis(1,2,3-dithiazoles)

Sections **Page**

5.1 Introduction

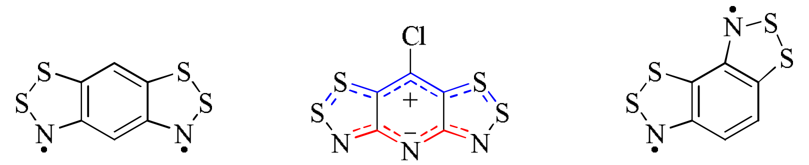
Thiazyl radicals as heteroatom radicals, hold considerable potential in the design of materials with electronic properties and, as such, have been the focus of intense study.[37,343-347] A number of thiazyl radicals displaying magnetic[348-352] and/or conductive[353,354] properties have been reported. In particular dithiazolyls (1,2,3- and 1,3,2-dithiazoles in Figure 43) are a fertile ground for promising electronic materials owing to their reduced inter-electron repulsion that lead to suppression of their solid-state dimerization.[344,346]

78 **79**

Figure 43. 1,2,3- and 1,3,2-dithiazolyls, compunds **78** and **79** respectively.

Historically, Mayer *et al.*, made early progress on 1,2,3-dithiazolyls in the 80's but this research was focused on their spectroscopic characterization[355-357] until the first stable crystalline derivatives were synthesized by Oakley some 20 years later and interesting solid-state properties were discovered.[358-361] The disproportionation energy of the 1,2,3-dithiazolyls was much lower than those reported for other thiazyl radicals indicating further enhancement of the π delocalization and promising transport properties, however, these 5-membered monocyclic radicals were more prone to dimerization. Nevertheless, 1D regular π stacks of 1,2,3-dithiazolyls have been isolated but owing to the poor orbital overlap stemming from slippage along the stacking direction, conductivity was of the order of 10^{-6} - 10^{-7} S/cm.[362,363] Incorporation of selenium in place of the 2-sulfur resulted in bulk ferromagnetic ordering of bisthiaselenazolyl radicals with T_c of *ca.* 12 - 14 K denoting their potential as promising materials for electronic devices.[364]

The bis(1,2,3-dithiazolyl) **180a** was shown computationally to have a triplet ground state 5.1 kcal/mol more stable than the singlet state, however, Oakley and co-workers have synthesized the pyrido-fused bis(1,2,3-diathiazole) **52** (Figure 44) that had a zwitterionic ground state as supported by X-ray structure and calculations.[156] In contrast, skeletal rearrangements such as switching from the linear to the angular structure led to a significant change in ΔE_{ST} strongly favoring the triplet state of angular system **181a**.



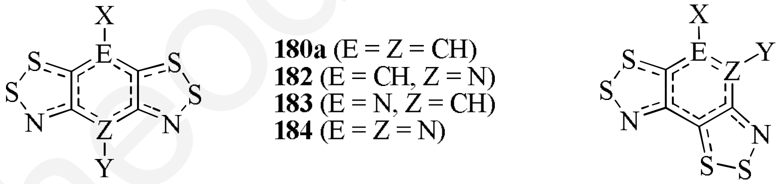
180a
ΔE_{ST} = + 5.1 kcal/mol

52

181a
ΔE_{ST} = + 16.3 kcal/mol

Figure 44. Bis(1,2,3-dithiazoles) **180a-181a** and the pyrido-fused bis(1,2,3-diathiazole) **52**.

As mentioned before (see Chapter 1.4) zwitterionic biscyanines can be considered to combine the electronic form of single carbenes and the structural motif of *m*-phenylene diradicals. Many theoretical and experimental studies on carbenes and *m*-phenylene diradicals indicated that substituents can influence their singlet-triplet energy gaps ($\Delta E_{ST} = {}^{S}E - {}^{T}E$) and hence their ground state multiplicities.[164-169] To the best of our knowledge, a broad computational study on fused 1,2,3-dithiazolyls has not been reported, but could identify structure-property-relationships (SPR) that can aid in the design of analogs with desired electronic properties. In this study we examine how structural changes, such as the direct introduction of substituents on the cyanines and the modification of the central arene to heteroazines, affects the ground state multiplicity of linear and angular bis(1,2,3-dithiazoles) **180** and **181** (Figure 45).



180a (E = Z = CH)
182 (E = CH, Z = N)
183 (E = N, Z = CH)
184 (E = Z = N)

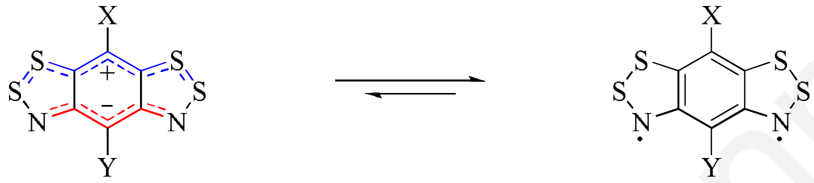
181a (E = Z = CH)
185 (E = CH, Z = N)
186 (E = N, Z = CH)
187 (E = Z = N)

Figure 45. Selected fused bis(1,2,3-dithiazoles) for the DFT study. X and Y are substituents for compounds **180-181** and are either electron donating (EDG) or electron withdrawing (EWG) groups as indicated in Tables 29-30.

5.2 Total Energies, Spin-coupling Constants and Singlet-triplet Gaps

5.2.1 Linear Fused Bis(1,2,3-dithiazoles)

The benzo bridged linear system **180a** (X = Y = CH) was compared to the pyrido **182** (X = CH, Y = N), **183** (X = N, Y = CH) and pyrazino **184** (X = Y = N) bridged analogs. Furthermore, the substitution of hydrogens (X = H, Y = H) on the parent system **180a** by electron donating (EDGs) and electron withdrawing groups (EWGs) was studied in an effort to manipulate ΔE_{ST} (Figure 45).

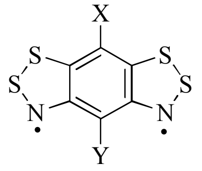


180a-q[±] **180a-q[··]**

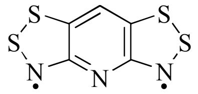
Scheme 46. Singlet and triplet structures for the linear parent fused bis(1,2,3-dithiazoles) **180**.

The energies of the open-shell singlet and triplet states, the spin-coupling constants (J), and the corresponding energy splittings (ΔE_{ST}) for linear structures **180** and **182-184** are presented in Table 29 for the full optimizations at the UB3LYP/6-31G(d) level of theory. The series of structures **180b-q** in Table 31 is in order of increasing $\Delta E^{\mathrm{U}}_{\mathrm{ST}}$ which is the result of the subtraction of the singlet state energy from the triplet state energy.

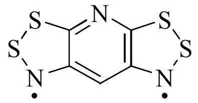
Table 31. $^{BS}\langle S^2\rangle$, $^{T}\langle S^2\rangle$, J coupling and ΔE_{ST} (kcal/mol) values for structures **180** and **182-184** calculated at the B3LYP/6-31G(d) level of theory.



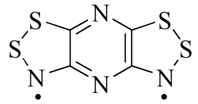
180a-q



182



183



184

#	X	Y	$^{BS}\langle S^2\rangle$	$^{T}\langle S^2\rangle$	J^1	ΔE^1_{ST}	J^2	ΔE^2_{ST}	J^3	ΔE^3_{ST}	ΔE^U_{ST}
180a	H	H	0.8138	2.0427	0.16	0.33	0.08	0.17	0.14	0.28	5.28
180b	H	CN	0.6527	2.0423	-2.06	-1.04	-1.52	-4.20	-2.12	-3.11	0.51
180c	H	Br	0.7904	2.0422	-0.17	-0.08	-0.14	-0.34	-0.17	-0.28	4.52
180d	H	Cl	0.7933	2.0427	-0.10	-0.05	-0.08	-0.21	-0.10	-0.17	4.66
180e	OMe	H	0.8236	2.0424	0.28	0.14	0.24	0.58	0.29	0.49	5.62
180f	Me	H	0.8222	2.0433	0.33	0.17	0.28	0.68	0.34	0.57	5.67
180g	CN	H	0.8244	2.0463	0.41	0.21	0.35	0.85	0.43	0.71	5.73
180h	OH	H	0.8346	2.0420	0.43	0.88	0.22	0.44	0.37	0.75	6.00
180i	F	H	0.8361	2.0416	0.46	0.23	0.39	0.94	0.47	0.80	6.06
180j	Br	H	0.8323	2.0433	0.53	0.27	0.45	1.09	0.55	0.93	6.07
180k	Cl	H	0.8329	2.0435	0.55	0.28	0.47	1.13	0.57	0.96	6.09
180l	NH_2	H	0.8415	2.0431	0.55	0.28	0.47	1.13	0.57	0.96	6.29
180m	H	Me	0.8371	2.0433	0.64	0.32	0.54	1.30	0.65	1.11	6.33
180n	H	F	0.8716	2.0424	1.02	0.52	0.90	2.09	1.05	1.84	7.76
180o	H	OMe	0.8729	2.0414	1.88	0.95	1.65	3.84	1.93	3.38	8.41
180p	H	OH	0.9328	2.0402	2.18	1.09	2.02	4.44	2.23	4.11	11.08
180q	H	NH_2	0.9745	2.0370	3.04	1.53	2.94	6.20	3.12	5.98	13.91
182	-	-	0.5379	2.0330	-4.19	-8.52	-2.11	-4.28	-2.86	-5.82	-2.69
183	-	-	0.7933	2.0388	-0.04	-0.08	-0.02	-0.04	-0.03	-0.07	4.72
184	-	-	0.4583	2.0329	-4.82	-9.79	-2.42	-4.92	-3.13	-6.35	-3.71

Our calculations for structures **180** and **182-184** indicate that the spin contaminations of the triplet states are low and the deviation from the expected value of 2.0 is at most 0.046. All the singlet wave functions are unstable denoting that even where the ground state is a zwitterionic singlet, there is a stong influence of a low-lying triplet state. A closed-shell singlet wavefunction would have been inadequate to describe a zwitterionic singlet ground state since we found considerable amount of spin contamination in the open-shell zwitterionic singlets. Spin contamination for the singlet states of structures **180** and **182-184** has a broader range of values which span from 0.4583 to 0.9745. The results from the optimizations indicate that most of the studied structures have either open-shell triplet ground states or degenerate singlet and triplet states. The equality of ΔE^1_{ST} and ΔE^3_{ST} (weak overlap of magnetic orbitals) along with a marginally positive value of *ca.* 0.28 kcal/mol for the parent structure **180a** indicates a degenerate singlet-triplet ground state. However, upon substitution at either the positive or negative cyanine the triplet open-shell state stabilizes at different degrees depending on the electronic nature of the substituent and the place of substitution at the central benzene. When electron deficient groups are placed on the positive cyanine (X = EWG) the effect on the singlet-triplet gap was minimal with ΔE^3_{ST} taking values between 0.80 (X = F, **180i**) to 0.96 kcal/mol (X = Cl, **180k**). Even when CH was replaced by N at the centre of the positive cyanine, structure **183** possessed a degenerate singlet-triplet ground state ($\Delta E^1_{ST} \approx \Delta E^3_{ST}$) as did the parent **180a**. Interestingly, substitution with electron donating groups (X = EDG) at the same position provided similar numbers with ΔE^3_{ST} between 0.49 (X = OMe, **180e**) to 0.96 kcal/mol (X = NH_2, **180l**). Modifications directly on the positive cyanine did not lead to dramatic changes demonstrating its limited significance to the ground state multiplicity.

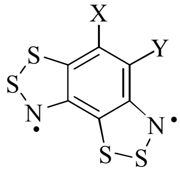
A reverse behavior is observed with substituents directly attached to the negative cyanine. The higher spin contamination in the BS singlet states of structures **180o-q** (0.872 - 0.974) indicate that EDG groups (Y = EDG) destabilized the singlet states as they pushed electron density in the already electron rich negative cyanine. These structures cannot avoid anymore their overall antiaromaticity through the formation of the bicyanines and therefore the ground states are triplets with ΔE^3_{ST} of 3.38, 4.11 and 5.98 kcal/mol for **180o-q**, respectively. Electron withdrawing groups (Y = EWG) help to stabilize the single states by reducing the electron density on the negative cyanine. The structures avoid their antiaromaticity but the effect is less since the ΔE^3_{ST} are marginally negative for **180d** (Y = Cl) and **180c** (Y = Br) with -0.17 and -0.28 kcal/mol deviation from parent system, respectively. Stronger EWGs have a more profound effect on stabilizing the zwitterionic singlet states (*e.g.*, ΔE^3_{ST} = -3.11 kcal/mol for **180b** Y = C≡N). The replacement of CH by N at the centre of the negative cyanine in structure **182** has the greatest impact on the singlet-triplet gap (ΔE^3_{ST} = -5.82 kcal/mol) indicating the importance of this position in controlling the ground state multiplicity of bis(1,2,3-dithiazoles). Worthy of note, is the pyrazino-fused bis(1,2,3-dithiazole) **184** that has the most stable zwitterionic singlet state with ΔE^3_{ST} = -6.35 kcal/mol.

5.2.2 Angular Fused Bis(1,2,3-dithiazoles)

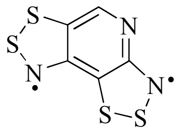
The analogous structural modifications were also applied to the corresponding angular structures. The benzo bridged angular system **181a** (X = Y = CH) was studied by adding EDGs and EWGs at X and Y positions and was compared to the pyrido **185** (X = CH, Y = N), **186** (X = N, Y = CH) and pyrazino **187** (X = Y = N) bridged analogs.

The energies of the open-shell singlet and triplet states, the spin-coupling constants (*J*), and the corresponding energy splittings (ΔE_{ST}) for structures **181** and **185-187** are presented in Table 32.

Table 32. $^{BS}\langle S^2\rangle$, $^{T}\langle S^2\rangle$, *J* coupling and ΔE_{ST} (kcal/mol) values for structures **181** and **185-187** calculated at the B3LYP/6-31G(d) level of theory.



181a-q



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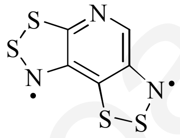

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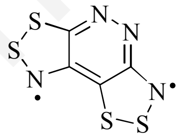


187

#	X	Y	$^{BS}\langle S^2\rangle$	$^{T}\langle S^2\rangle$	J^1	ΔE^1_{ST}	J^2	ΔE^2_{ST}	J^3	ΔE^3_{ST}	ΔE^U_{ST}
181a	H	H	1.0018	2.0397	3.43	6.99	1.72	3.52	3.39	6.91	16.33
181b	H	CN	1.0147	2.0390	1.66	3.37	0.83	1.70	1.49	3.04	8.86
181c	H	Br	1.0042	2.0389	2.23	4.54	1.12	2.29	2.07	4.22	11.14
181d	H	Cl	1.0038	2.0392	2.62	5.35	1.32	2.69	2.45	4.99	11.70
181e	OMe	H	1.0014	2.0377	3.12	6.37	1.57	3.20	3.05	6.22	15.30
181f	Me	H	1.0018	2.0402	3.30	6.74	1.66	3.39	3.25	6.63	15.59
181g	CN	H	1.0098	2.0420	3.34	6.81	1.68	3.43	3.31	6.74	15.90
181h	OH	H	1.0051	2.0379	3.55	7.01	1.79	3.65	3.52	7.19	16.15
181i	F	H	1.0078	2.0386	3.55	7.25	1.79	3.65	3.51	7.17	16.43
181j	Br	H	1.0088	2.0401	3.45	7.03	1.74	3.54	3.42	6.98	16.45
181k	Cl	H	1.0088	2.0403	3.42	6.97	1.72	3.51	3.39	6.91	16.60
181l	NH_2	H	1.0048	2.0401	3.43	7.00	1.73	3.52	3.40	6.93	16.61
181m	H	Me	0.9956	2.0391	3.52	7.18	1.77	3.61	3.50	7.14	16.91
181n	H	F	0.9897	2.0391	3.57	7.29	1.80	3.67	3.56	7.26	17.45
181o	H	OMe	0.9381	2.0386	3.77	7.70	1.90	3.87	3.76	7.66	17.48
181p	H	OH	0.9346	2.0372	3.47	7.08	1.75	3.56	3.45	7.05	17.88
181q	H	NH_2	0.9021	2.0367	3.64	7.42	1.83	3.73	3.64	7.43	17.91
185	-	-	1.0112	2.0346	3.32	6.75	1.67	3.40	3.32	6.75	17.41
186	-	-	0.9822	2.0368	5.08	10.35	2.56	5.21	4.94	10.06	17.77
187	-	-	0.9124	2.0350	5.56	11.31	2.80	5.69	5.07	10.31	15.17

For angular structures **181** and **185-187**, the spin contaminations of the triplet states are low likewise in linear systems, and the deviation from the expected value of 2.0 is at most 0.042. All the singlet wave functions are unstable and in the BS application the spin contamination is high in a shorter range of values which span from 0.9124 to 1.0147.

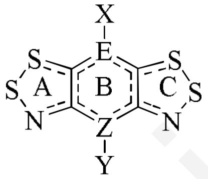
All the studied angular systems are stabilized in triplet ground states. Upon substitution at either the X or Y position the triplet state stabilizes at different degrees depending on substituent and the place of substitution. When EWGs are placed on X position the effect on the singlet-triplet gap was minimal as in linear analogs, with ΔE^3_{ST} taking values between 6.74 (X = C≡N, **181g**) to 7.17 kcal/mol (X = F, **181i**) affecting the parent system by -0.17 to 0.26 kcal/mol respectively. Substitution with electron donating groups (X = EDG) at the same position again did not affect the ΔE^3_{ST} much with ΔE^3_{ST} being affected between -0.69 (X = OMe, **181e**) to 0.28 kcal/mol (X = OH, **181h**). When CH was replaced by N on the C-X position though, structure **186** was stabilized in triplet even more with ΔE_{ST} increasing by 3.15 kcal/mol.

A reverse behavior is observed with substituents attached to the Y position. Electron withdrawing groups help to stabilize the singlet states likewise in linear systems and even then the ΔE_{ST} is positive. ΔE^3_{ST} is taking values between 3.04 kcal/mol (Y = C≡N, **181b**) and 4.99 kcal/mol (Y = Cl, **181d**) being reduced by -3.87 and -1.92 kcal/mol from the parent system respectively. Only exception is **181n** (Y = F) where ΔE^3_{ST} is slightly increased by 0.35 kcal/mol. EDGs on the same position stabilize the triplet more but not with great impact. ΔE^3_{ST} takes values between 7.05 kcal/mol (Y = OH, **181p**) and 7.66 kcal/mol (Y = OMe, **181o**) being affected by 0.14 and 0.75 kcal/mol respectively from the parent system. The replacement of C-Y by N in structure **185** has a slight impact on the singlet-triplet gap and reduces ΔE^3_{ST} by 0.16 kcal/mol. On the other hand, the pyrazino-fused bis(1,2,3-dithiazole) **187** has the most stable triplet singlet state with $\Delta E^3_{\mathrm{ST}} = 10.31$ kcal/mol.

5.3 Aromaticity Considerations

The aromaticity of the central arene has a detrimental role on the ground state multiplicities of structures **180-187**. Therefore the ground state multiplicities and the ΔE_{ST} values were expected to follow trends based on aromaticity indices such as the nucleus independent chemical shifts (NICS) as shown before on linear DTQPs (Chapter 2.3.3).

NICS calculations for structures **180-187** were performed at the B3LYP/6-31G(d) level of theory. To assess the aromaticity of each of the three rings of the linear and angular bis(1,2,3-dithiazoles) **180-187**, diagrams correlating the NICS values (in ppm) versus the distance above each ring centre f(r) (in Å) were constructed (Figures 46-48). In these diagrams negative minimums denote diatropic ring currents, while positive maximums stand for paratropic and when negative NICS values approach zero in an asymptomatic manner with increasing distance, then no ring current is present.[365]



180a (E, Z = CH)
182 (E = CH, Z = N)
183 (E = N, Z = CH)
184 (E, Z = N)

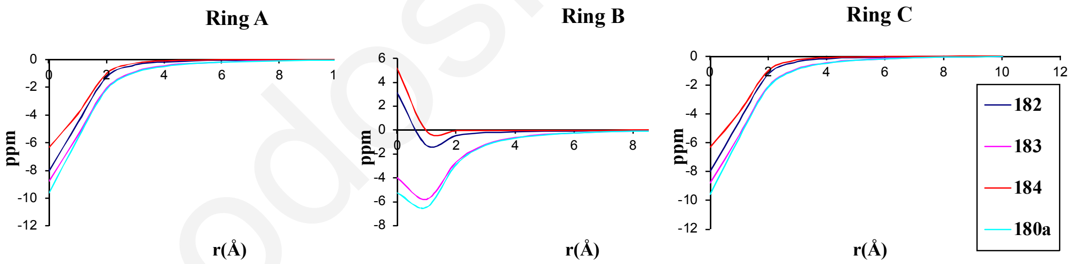
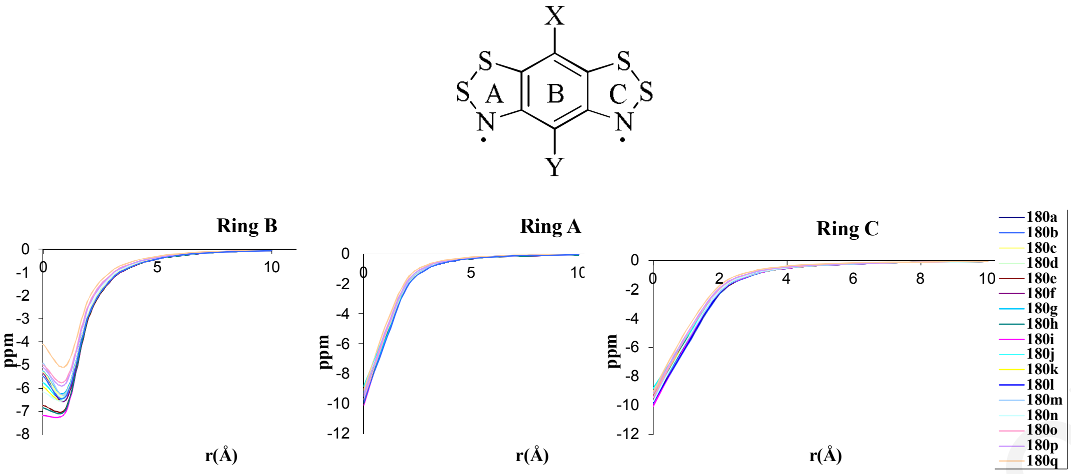


Figure 46. NICS diagram [ppm=f(r)] for structures **180a** and **182-184**.



Figre 47. NICS diagram [ppm=f(r)] for structures **180a-q**.

The outer 1,2,3-dithiazoles (rings A and C) for all linear studied structures, have negative NICS values which become asymptomatic to zero on going from 0 to 10 Å above the ring centre (Figures 45 and 46). These values are compared to the ones of the monocyclic 1,2,3-dithiazolyl and benzo-fused 1,2,3-dithiazolyl calculated at the same level of theory (Figure 47). The 1,2,3-dithiazole rings are non-aromatic, in line with their 7π electron system. The fused benzene ring has a NICS(1) value of -8.77 ppm and is formally more aromatic than benzene (-4.1 ppm).

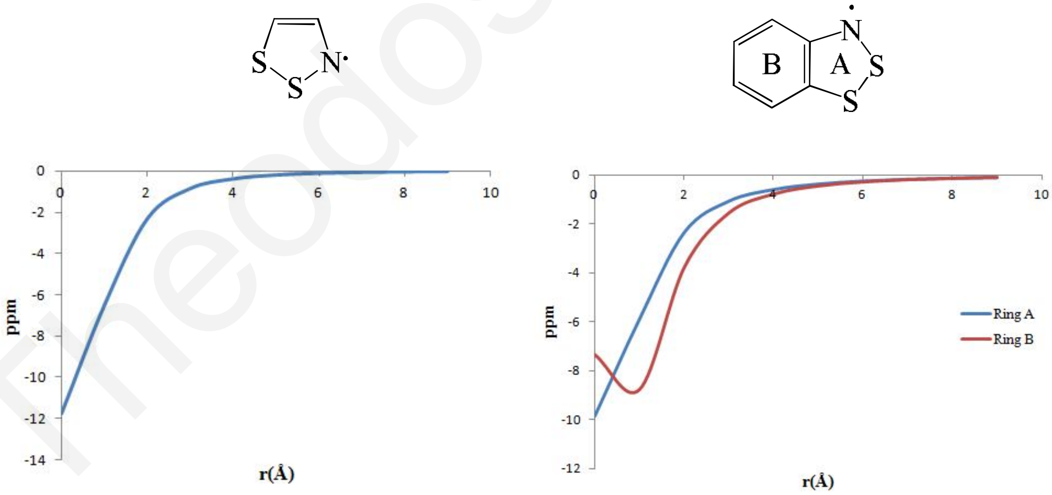


Figure 48. NICS diagram [ppm = f(r)] for the monocyclic and benzo-fused 1,2,3-dithiazolyls.

Structures **180a** and **183**, as already discussed in Section 5.2.1., have a degenerate singlet-triplet diradical ground state. Their central arene rings (ring B) have negative NICS(1) values at *ca.* -6 ppm and a minimum in the [ppm = f(r)] diagram indicative of diatropic ring currents and therefore aromatic character. In contrast, the central rings of structures **182** (pyrido) and **184** (pyrazino), which have singlet ground states with ΔE^3_{ST} of -5.82 and -6.35 kcal/mol, respectively, have weakly positive NICS(0) values, very weakly negative NICS(1) values and an asymptomatic zero at higher distances, characteristic of non-aromatic rings. This result was in agreement with their zwitterionic biscyanine ground states and the loss of aromaticity in the central arene rings.

NICS calculations verify the importance of the pyridyl nitrogen position on the ground state multiplicity of structures **182** and **183**. Placing the nitrogen at the centre of the positive cyanine did not alter the aromatic character of the central ring (*c.f.*, **183**), however, when nitrogen was at the centre of the negative cyanine (*c.f.*, **182**) the central arene becomes non-aromatic. Substitution at the central fused benzene of structure **180** did not affect the non-aromaticity of the peripheral dithiazoles and interestingly, it did not cause significant changes to the aromatic character of the central ring (Figure 47). Structure **180b** (Y = C≡N) with a zwitterionic singlet ground state (ΔE^3_{ST} = -3.11 kcal/mol) has a central ring (-6.33 ppm) more aromatic than the corresponding ring (-5.02 ppm) of **180q** (Y = NH_2) which has a triplet ground state ΔE^3_{ST} = 5.98 kcal/mol, while theoretically it should be vise versa. The result above indicates that indeed there is no obvious relationship between the NICS and the ΔE_{ST} values and that NICS calculations provide only qualitative results as Fleischhauer *et al.* [161]had also previously observed.

NICS calculations on the angular analogs were performed as well and are shown in Figures 49 and 50, Similarly to their linear analogs, the outer 1,2,3-dithiazoles (rings A and C) for all angular structures, have negative NICS values which become asymptomatic to zero on going from 0 to 10 Å above the ring centre indicating no ring current. On the contrary, the central arene rings (ring B) of all the studied angular systems have negative NICS(1) values at *ca.* -6 ppm and a minimum in the [ppm = f(r)] diagram indicative of diatropic ring currents and therefore aromatic character.

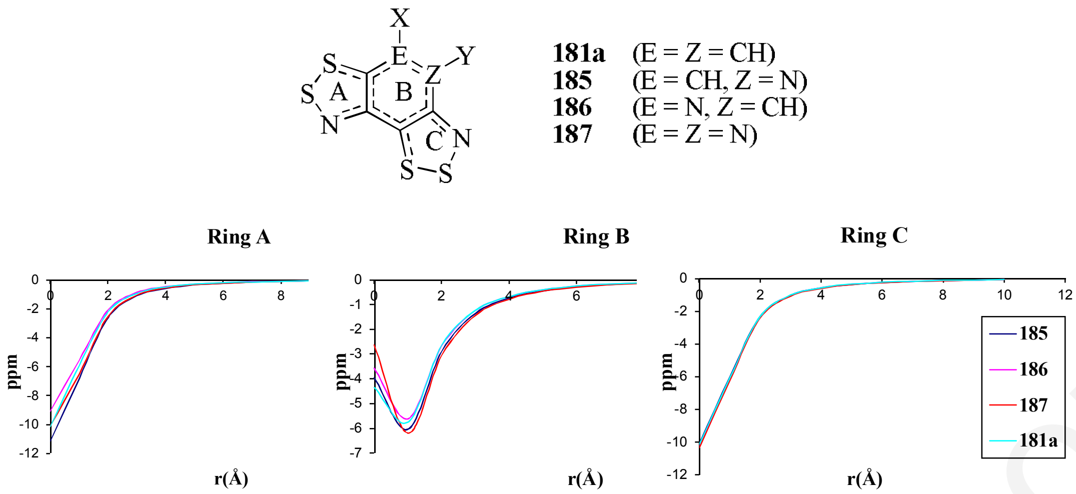


Figure 49. NICS diagram [ppm = f(r)] for structures **181a** and **185-187**.

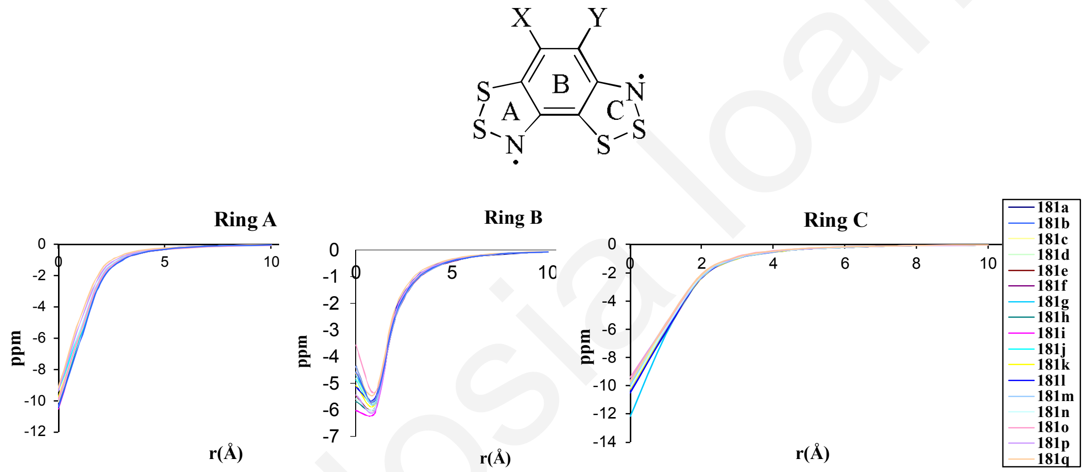
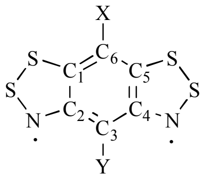


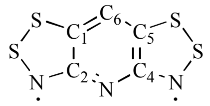
Figure 50. NICS diagram [ppm = f(r)] for structures **181a-q**.

It was previously shown that the lateral C-C bond lengths, which connect the two cyanine units, gave a good indication to whether the central ring is aromatic or non-aromatic.[154,155,157,159-161,163,170,175,366,367] In the charge separated zwitterionic ground states of polyazaacenes the lateral C-C bong lengths were longer and had significant σ character reflecting the conversion of the arene to an anti-quinoid structure in which resonance stabilization was mainly within the two separate cyanine units. In contrast, for structures with triplet ground states these C-C bonds were shorter and had bond lengths typical of aromatic benzene C-C bonds. For structures **180** and **182-184** the lateral C-C bond lengths of the ground states along with the dipole moments are presented in Table 33. Structures **182** and **184** with the zwitterionic single ground states have lateral C-C bond length of *ca.* 1.47 Å and dipole moments of 4 - 5 D indicating the charge redistribution and the formation of the cyanines. In contrast, structure **180b**, which had the largest dipole moment (5.9 D) and a singlet ground state had shorter lateral C-C bonds (1.44 Å) compared to structures **182** and **184**. This was in agreement with its NICS(1) value of -6.33 ppm, that indicated a more aromatic character for the central arene. For structure **180q**, which has the triplet state with the largest $\Delta E^3{}_{ST}$ (5.98 kcal/mol), the lateral C-C bond lengths were the shortest (1.43 Å) and closer to the expected 1.4 Å of aromatic benzene. The dipole moment of **180q** is 0.65 D demonstrating that this structure did not possess a charge separated ground state.

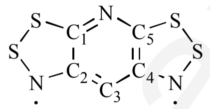
Table 33. Ground state C$_1$-C$_2$ and C$_4$-C$_5$ bond lenghts (Å) and dipole moments (D).



180a-q



182



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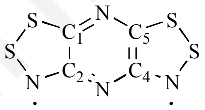


184

#	X	Y	C$_1$-C$_2$ (E)	C$_4$-C$_5$ (E)	Dipole Moment (D)
180a	H	H	1.441	1.441	1.81
180b	H	CN	1.439	1.439	5.90
180c	H	Br	1.441	1.441	2.66
180d	H	Cl	1.441	1.441	2.92
180e	OMe	H	1.439	1.439	2.54
180f	Me	H	1.439	1.439	2.40
180g	CN	H	1.438	1.438	2.03
180h	OH	H	1.441	1.436	2.21
180i	F	H	1.440	1.440	0.65
180j	Br	H	1.441	1.441	1.03
180k	Cl	H	1.441	1.441	0.68
180l	NH$_2$	H	1.437	1.437	3.03
180m	H	Me	1.441	1.439	1.35
180n	H	F	1.439	1.439	2.91
180o	H	OMe	1.442	1.436	1.29
180p	H	OH	1.430	1.440	2.10
180q	H	NH$_2$	1.434	1.434	0.65
182	-	-	1.477	1.477	5.49
183	-	-	1.442	1.442	0.20
184	-	-	1.472	1.472	4.04

5.4 Molecular Orbital Analysis

Other factors which influence the singlet-triplet energy gaps and hence the ground state multiplicities of these structures are the SOMO-SOMO energy splitting (ΔE_{SS}) and their topological distributions. Haas and Zilberg rationalized the origins of the zwitterionic ground states of 1,2,4,5-tetrasubstituted benzenes in terms of the molecular orbitals of the 1,2,4,5-tetramethylenebenzene (TMB), a diradical for which no classical Kekulé structure can be written.[368]

The correlation diagram of TMB is constructed by the molecular orbitals of two pentadienyl radicals containing 5π electrons each.[128,369] The π orbitals are connected *via* σ bonds to form the TMB electronic system. The two non-bonding molecular orbitals maybe chosen so that they are disjoint *i.e.*, do not have atoms in common and the unpaired electrons can be confined to different sets of atoms so that the coulombic repulsion energy from the electrons of opposite spins is minimized. These two orbitals have the same energy as there is no π electron density on the atoms that connect the two 5π electron radical fragments. TMB a formally 10π aromatic molecule, decomposes into two separated 5π electron radical units with relatively long lateral C-C bonds connecting the two fragments.

When the two bonded fragments are nonequivalent the energy of the frontier orbitals change. The molecular orbitals of the benzo-fused bis(1,2,3-dithiazoles) can be constructed based on the TMB approach using two nonequivalent fragments; one 11π sulfur-substituted radical fragment (S) and one 5π imino-substituted radical (N). The two non-bonding molecular orbitals and the antibonding molecular orbital are depicted in Figure 51.

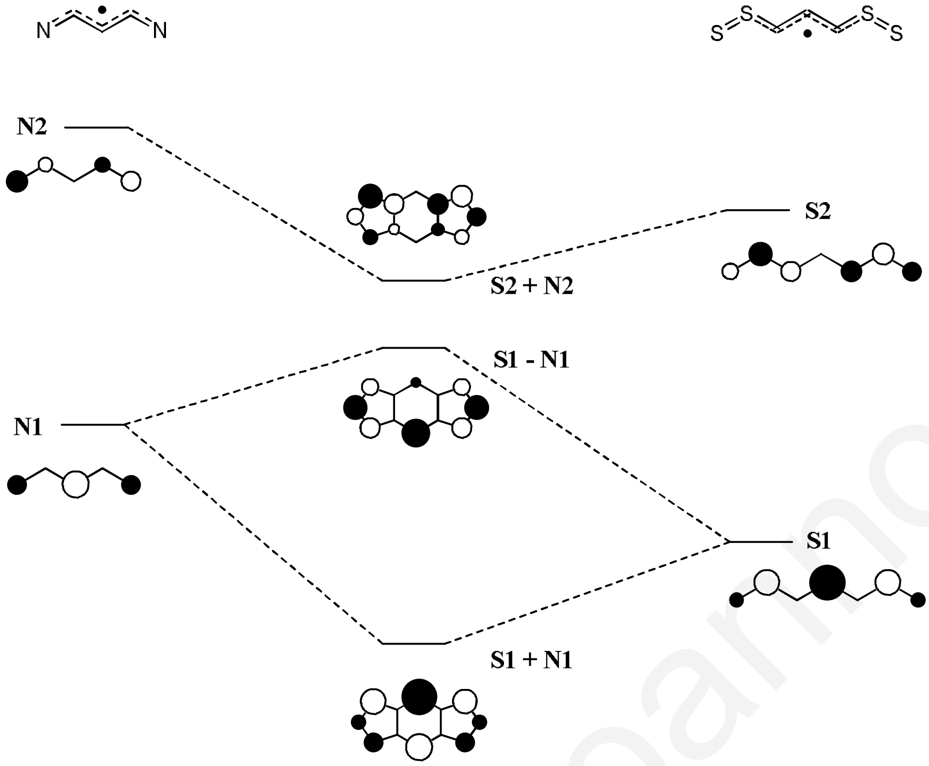
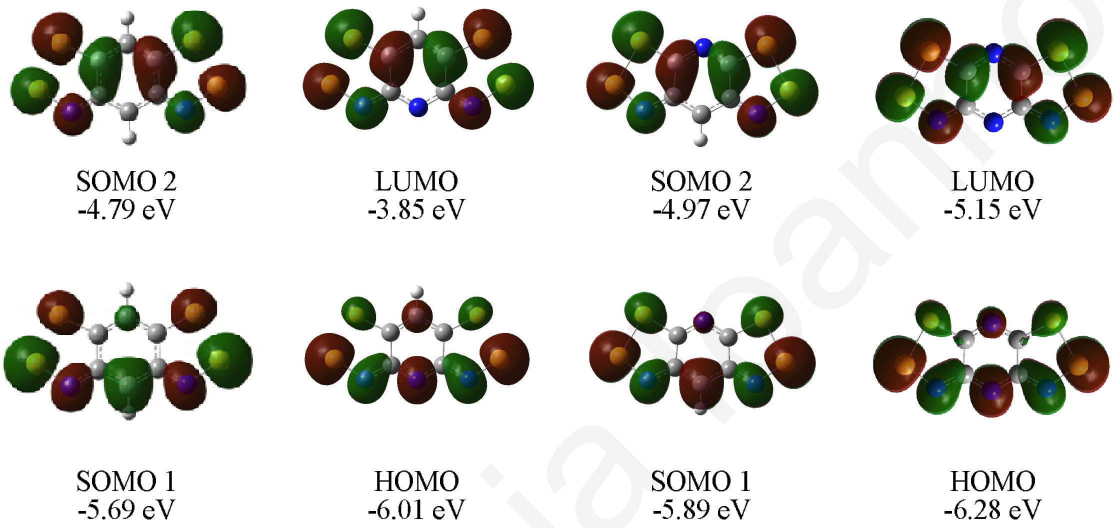


Figure 51. Qualitative correlation diagram of the benzo-fused bis(1,2,3-dithiazole) **180a** constructed by the two non-equivalent 11π and 5π radical fragments.

The S1 - N1 molecular orbital has mostly N1 character with large atomic coefficients on the imino 5π radical fragment. The antibonding orbital S2 + N2 is close in energy to the out-of-phase non-bonding orbital S1 - N1 and has more S2 character with larger coefficients on the sulfur 11π radical fragment. The near degeneracy of these two orbitals can lead to a triplet ground state. A transfer of an electron from the donor 11π sulfur-substituted radical fragment (S) to the acceptor 5π imino-substituted radical (N) subunit results in a 10π positive and 6π negative cyanines.

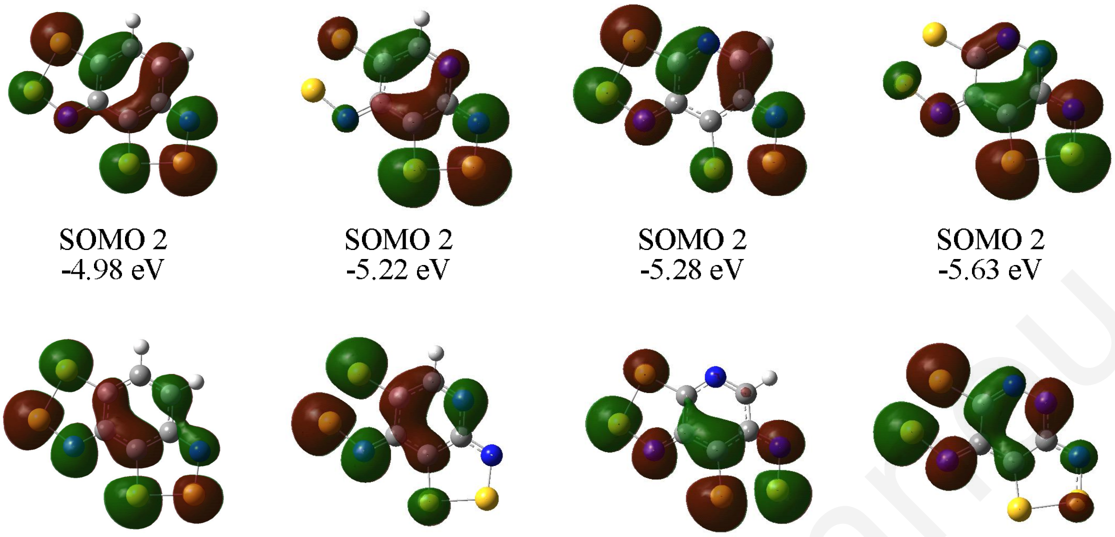
From the calculated frontier orbitals of the ground state structures **180a** and **182-184** at the B3LYP/6-31G(d) level of theory (Figure 51) the SOMO 1 / HOMO is the S1 - N1 non-bonding molecular orbital and the SOMO 2 / LUMO is the antibonding S2 + N2 molecular orbital. It should be noted that the SOMO 1 / HOMO has a large atomic coefficient at the centre of the negative 6π cyanine, as such, substituents directly attached to this position can significantly alter the energy of this orbital. For example, the introduction of the electronegative pyrido nitrogen on this position (structure **182**), stabilizes this orbital and opens up the energy gap of the frontier orbitals leading to pairing of electrons and therefore singlet ground state. In contrast, SOMO 2 / LUMO has a node at the centre of the positive 10π cyanine and therefore any substituent at this position does not affect significantly its energy. For structures with zwitterionic ground states such as **180b** the two electrons are paired in a doubly occupied S1 - N1 orbital which has nodes over the lateral C-C bonds. However, promotion of an electron from the S1 - N1 orbital (HOMO) to the S2 + N2 orbital (LUMO) supplies the lateral C-C bonds with some π-bonding character (smaller bond lengths) as is evident from the atomic coefficients over these bonds (Figures 51 and 52).



180a **182** **183** **184**

Figure 52. Frontier orbitals of ground state structures **180a** and **182-184** calculated at the B3LYP/6-31G(d) level of theory.

In the linear structures SOMOs were identical among the systems, but this was not observed in the angular analogs. Only the SOMOs of structures **185** and **187** are similar. SOMO 1 of structure **181a** has some atomic coefficient at carbon C_5 that can be substituted by the Y substituent but there is a node at the carbon C_6 that X substituent can be placed. This explains why Y substitution indeed affects the energy gap with EDGs stabilizing the triplet more and EWGs destabilizing it. SOMO 2 has similar atomic coefficient on both positions with some more on carbon C_5.



SOMO 2 -4.98 eV | SOMO 2 -5.22 eV | SOMO 2 -5.28 eV | SOMO 2 -5.63 eV

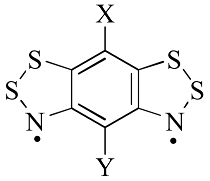
SOMO 1 -5.22 eV | SOMO 1 -5.61 eV | SOMO 1 -5.44 eV | SOMO 1 -5.91 eV

181a **185** **186** **187**

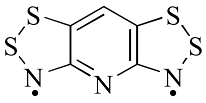
Figure 53. SOMO orbitals of structures **181a** and **185-187** calculated at the B3LYP/6-31G(d) level of theory.

According to Hund's rule the ΔE_{ST} should be inverse correlated to the energy gap of the two SOMOs (ΔE_{SS}). The energy levels ($^{1}E_{S}$ and $^{2}E_{S}$) and energy gaps (ΔE_{SS}) of the two SOMOs for the triplet states of structures **180** and **182-184** are presented in Table 34.[129]

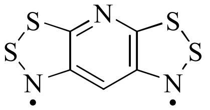
Table 34. Energy levels (^1E_S and ^2E_S) and the energy gaps (ΔE_{SS}) of the SOMOs for the triplet states of molecules **180** and **182**-**184** at the B3LYP/6-31G(d) level of theory.



180a-q



182



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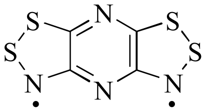

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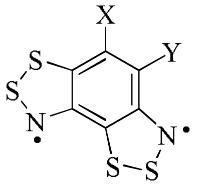
#	X	Y	^1E_S (au)	^2E_S (au)	ΔE_{SS} (eV)	ΔE^3_{ST} (kcal/mol)
180a	H	H	-0.20906	-0.17591	0.90	0.28
180b	H	CN	-0.22492	-0.18924	0.97	-3.11
180c	H	Br	-0.21168	-0.17959	0.87	-0.28
180d	H	Cl	-0.21277	-0.18035	0.88	-0.17
180e	OMe	H	-0.20785	-0.17524	0.89	0.49
180f	Me	H	-0.20641	-0.17356	0.89	0.57
180g	CN	H	-0.22268	-0.19011	0.89	0.71
180h	OH	H	-0.20924	-0.17705	0.88	0.75
180i	F	H	-0.21366	-0.18185	0.87	0.80
180j	Br	H	-0.21321	-0.18098	0.88	0.93
180k	Cl	H	-0.21412	-0.18196	0.88	0.96
180l	NH_2	H	-0.20539	-0.17379	0.86	0.96
180m	H	Me	-0.20420	-0.17273	0.86	1.11
180n	H	F	-0.21062	-0.18080	0.81	1.84
180o	H	OMe	-0.19302	-0.17048	0.61	3.38
180p	H	OH	-0.19982	-0.17601	0.65	4.11
180q	H	NH_2	-0.18348	-0.16858	0.41	5.98
182	-	-	-0.22102	-0.18166	1.07	-5.82
183	-	-	-0.21645	-0.18278	0.92	-0.07
184	-	-	-0.23085	-0.18935	1.13	-6.35

Hoffmann provided a rough empirical criterion based on extended Hückel calculations on benzynes and diradicals which suggests that if $\Delta E_{SS} < 1.5$ eV, the two nonbonding electrons will prefer to occupy different degenerate orbitals with a parallel-spin configuration to minimize their electrostatic repulsion leading to triplet states. We previously showed that triplet states for polyazaacenes require $\Delta E_{SS} < 1.3$ eV[170] while Schreiner suggested $\Delta E_{SS} < 0.9$ eV for the ground state triplets for related compounds.[367] Structure **180a** with a $\Delta E_{SS} = 0.9$ eV and degenerate singlet and triplet states ($\Delta E^3_{ST} = 0.28$ kcal/mol) was in agreement with Schreiner's observation. A SOMO-SOMO splitting of 0.9 eV is the limit where the singlet and triplet states are isoenergetic. ΔE_{SS} of less than 0.9 eV would favor a triplet state as for example in structure **180q**

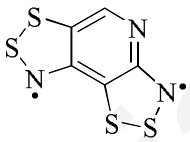
(ΔE_{SS} = 0.41 eV and $\Delta E^3{}_{ST}$ = 5.98 kcal/mol) and ΔE_{SS} of more than 0.9 eV would lead to singlet ground states as in structure **182** (ΔE_{SS} = 1.07 eV and $\Delta E^3{}_{ST}$ = - 5.82 kcal/mol).

For comparison on the studied angular analogs, the maximum ΔE_{SS} observed was 0.66 eV (Table 35). What is strange though is that ΔE_{SS} does not decrease accordingly to $\Delta E^3{}_{ST}$ in every case. For instance structures **181b-d** have ΔE_{SS} in the range 0.19-0.23 eV and $\Delta E^3{}_{ST}$ in range 3.04-4.99 kcal/mol but **181p-q** with larger $\Delta E^3{}_{ST}$ (7.05-7.43 kcal/mol) have also larger ΔE_{SS} (0.53-0.66 eV) when it was expected to be lower. Despite the non-linearity between ΔE_{SS} and $\Delta E^3{}_{ST}$, all the angular systems have very low ΔE_{SS} values and this may justify this observation. Structure **186** for example has the lowest ΔE_{SS} (0.15 eV) and one of the largest $\Delta E^3{}_{ST}$ (10.06 kcal/mol) as expected but its ΔE_{SS} does not differ much from structures **181g** (0.18 eV) or **181b** (0.19 eV) that have lower $\Delta E^3{}_{ST}$ values 6.74 and 3.04 kcal/mol, respectively.

Table 35. Energy levels (^1E_S and ^2E_S) and the energy gaps (ΔE_{SS}) of the SOMOs for the triplet states of molecules **181** and **185-187** at the B3LYP/6-31G(d) level of theory.



181a-q



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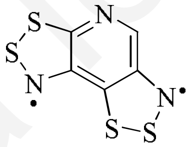

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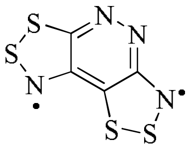

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Structures	X	Y	^1E_S (au)	^2E_S (au)	ΔE_{SS} (eV)	$\Delta E^3{}_{ST}$ (kcal/mol)
181a	H	H	-0.19219	-0.18332	0.24	6.91
181b	H	CN	-0.20814	-0.20129	0.19	3.04
181c	H	Br	-0.19688	-0.18881	0.22	4.22
181d	H	Cl	-0.19774	-0.18939	0.23	4.99
181e	OMe	H	-0.18813	-0.17783	0.28	6.22
181f	Me	H	-0.18977	-0.18076	0.25	6.63
181g	CN	H	-0.20671	-0.20027	0.18	6.74
181h	OH	H	-0.19019	-0.18083	0.25	7.19
181i	F	H	-0.19784	-0.18892	0.24	7.17
181j	Br	H	-0.19743	-0.19020	0.20	6.98
181k	Cl	H	-0.19837	-0.19096	0.20	6.91
181l	NH_2	H	-0.18832	-0.17754	0.29	6.93
181m	H	Me	-0.18919	-0.17962	0.26	7.14
181n	H	F	-0.19643	-0.18601	0.28	7.26
181o	H	OMe	-0.19064	-0.17703	0.37	7.66
181p	H	OH	-0.19569	-0.17604	0.53	7.05
181q	H	NH_2	-0.18506	-0.16075	0.66	7.43
185	-	-	-0.20678	-0.19207	0.40	6.75
186	-	-	-0.20018	-0.19484	0.15	10.06
187	-	-	-0.21773	-0.20708	0.29	10.31

5.5 Mulliken Charge Distribution

The Mulliken charge distribution of the singlet and triplet states of the linear benzo-fused system **180a** is shown in Figure 54. The electronegative nitrogen atoms are strongly negative but more so in the singlet state structure (-0.577 *vs* -0.531). Furthermore, while the electropositive sulfur atoms are positive in both singlet and triplet states there are interesting differences. The sulfur atoms next to the nitrogen atoms are the most positive and also almost equal in value between singlet and triplet structures (0.302 *vs* 0.306), however, by comparison the sulfurs bound to carbon are significantly less positive and as expected that of the singlet state was more positive than that of the triplet structure (0.116 *vs* 0.077). These charge distributions are in agreement with the zwitterioninc biscyanine state proposed for the singlet states. If the total charges on the S-C-C-C-S and the N-C-C-C-N fragments are compared for both singlet and triplet states we obtain -0.185_{SCCCS} (singlet) *vs* -0.297_{SCCCS} (triplet) compared to -0.742_{NCCCN} (singlet) *vs* -0.658_{NCCCN} (triplet) which correlates to a comparative charge separation between the SCCCS and NCCCN fragments of 0.557 and 0.361 between the singlet and triplet states, respectively.

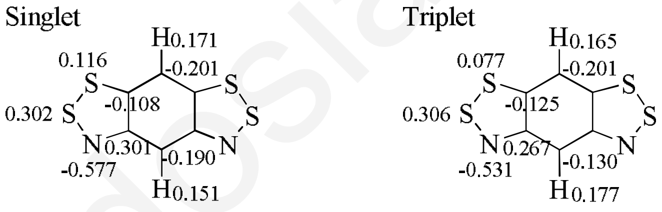
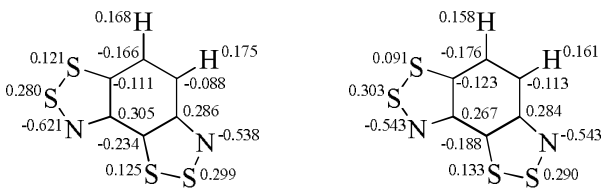


Figure 54. Mulliken charge distribution on singlet and triplet state of linear system **180a**.

On the angular parent system **181a** (Figure 55) the positive charged sulfur atoms and negative charged nitrogen atoms in the singlet are increased and reduced symmetrically in the triplet (*e.g.*, one nitrogen reduced and the other increased in charge). There is no clear polarization in the angular motif as observed with the linear analog.

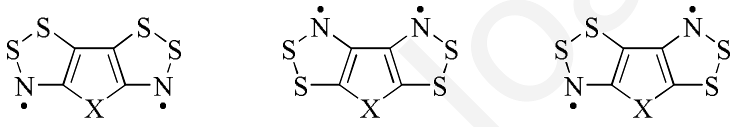


Singlet Triplet

Figure 55. Mulliken charge distribution on singlet and triplet state of angular system **181a**.

5.6 Replacing the Central 6-Membered Arene by a 5-Membered Arene

Replacing the central 6-membered arene with a 5-membered one, afforded the corresponding symmetrical (**188a-d** and **189a-d**) and asymmetrical (**190a-d**) bisdithiazole analogs where X = NH, O, S and SO_2 (Figure 56).



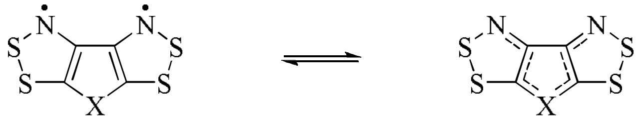
188a-d **189a-d** **190a-d**

a (X = NH); **b** (X = O); **c** (X = S); **d** (X = SO_2)

Figure 56. Bisdithiazole analogs with 5-membered central rings.

The geometry optimisation [UB3LYP/6-31G(d)] of structures **188a-d** (triplet state) and **190a-d** (singlet state) were unsatisfactory affording in both cases one imaginary frequency, which could not be overcome. As such, meaningful ΔE_{ST} data or other properties could not be calculated. Nevertheless, the geometry optimisations on structures **189a-d** were successful (Table 36).

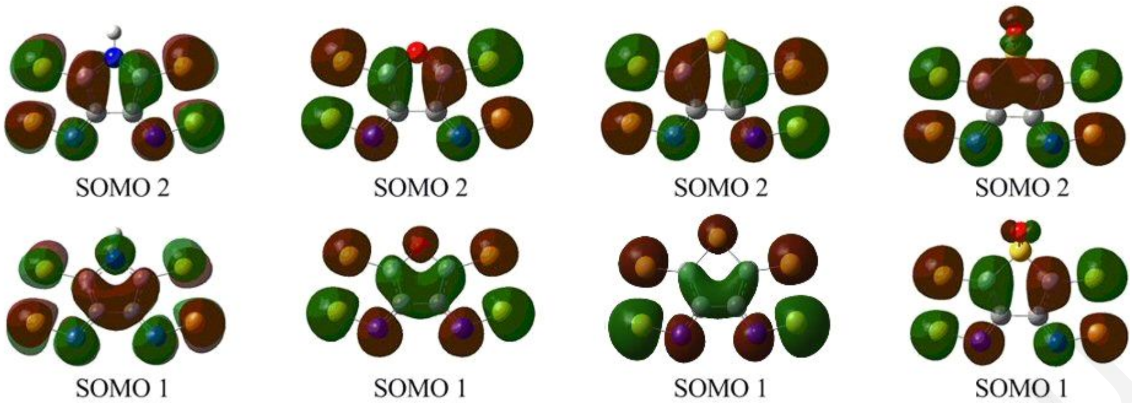
Table 36. Computational values at the B3LYP/6-31G(d) level of theory for NICS(0) (ppm), NICS(1) (ppm), J and ΔE_{ST} (kcal/mol) values for the central arene of structures **189a-d**, in order of increasingly positive ΔE_{ST}.



X	NICS(0)	NICS(1)	J^1	ΔE^1_{ST}	J^2	ΔE^2_{ST}	J^3	ΔE^3_{ST}	ΔE^U_{ST}
SO_2	-0.8	-1.5	-2.35	-4.75	-1.18	-2.39	-2.18	-4.42	5.71
NH	-7.5	-5.9	0.73	1.46	0.36	0.73	0.70	1.42	10.49
S	-6.3	-4.8	-0.02	-0.05	-0.01	-0.02	-0.02	-0.05	13.09
O	-6.2	-5.0	0.78	1.57	0.39	0.79	0.79	1.60	14.94

Interestingly, little correlation with the aromaticity of the central arene was observed. The degree of aromaticity of the central arenes follows the series thiophene [X = S, 43 (84-117 kJ/mol)] > pyrrole [X = NH, 40.5 (59-130 kJ/mol)] > furan [X = O, 27.2 (34-96 kJ/mol)] based on experimental resonance energies,[370] and pyrrole (I_A 85) > thiophene (I_A 81.5) > furan (I_A 53) based on Bird's aromaticity[371] indices and pyrrole (-12.5) > thiophene (-11.1) > furan (-10.5) based on NICS(1).[273] Clearly the computed ΔE_{ST} values followed none of the above trends, with the preference for the triplet ground state favored in the order furan > thiophene > pyrrole. As such, the least aromatic heteroarene furan **189b** (X = O) gave the largest ΔE_{ST}, however, the non aromatic thiophene-1,1-dioxide (**189d**, X = SO_2) did not follow this trend and gave the least positive ΔE_{ST} value (5.71 kcal/mol).

The SOMOs of the systems **189a-c (**X = NH, O and S) (Figure 57) are very similar and differ from those of **189d** (X = SO_2) which has the lower ΔE_{ST} and least aromaticity in the central ring. The lower SOMO of **189a-c**, presents nodal points between the two carbons nearby the heteroatom while that picture is presented at the higher SOMO of system **189d**, X = SO_2.

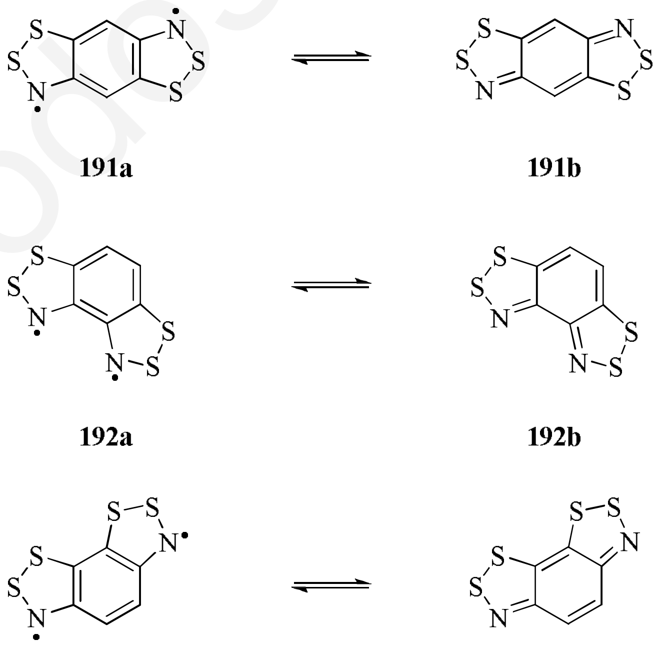


189a, X=NH **189b**, X=O **189c**, X=S **189d**, X=SO_2

Figure 57. SOMOs of system **189a-d** (X = NH, O, S and SO_2)

5.7 The Analogous Quinoid Structures

As expected, linear and angular dithiazolobenzodithiazoles where the spin carriers are *ortho* or *para* orientated prefer the corresponding quinoid structures. The singlet ground state was most favored with structures **191** and **193** where the spin carriers are *para* orientated (Figure 58) where ΔE_{ST} reaches -18.54 and -16.73 kcal/mol, respectively. The spin coupling constants (*J*) and the singlet-triplet energy gaps (ΔE_{ST}) are given in Table 37. The frontier molecular orbitals HOMO and LUMO of the three systems are shown in Figure 59.



191a **191b**

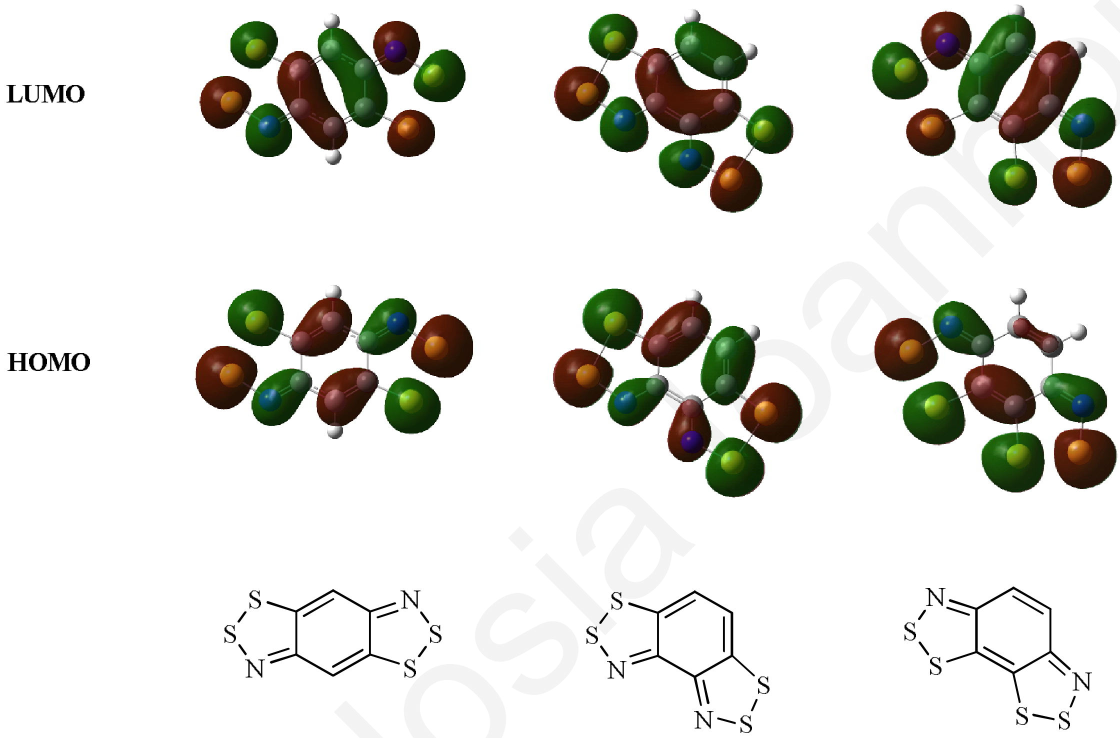
192a **192b**

193a **193b**

Figure 58. The *ortho*- and *para*-oriented spin carriers analogs **191-193**.

Table 37. Computational values at the B3LYP/6-31G(d) level of theory for J and ΔE_{ST} (kcal/mol) values for the central arene of structures **191-193**.

Structures	J^1	ΔE^1_{ST}	J^2	ΔE^2_{ST}	J^3	ΔE^3_{ST}	$\Delta E^{\mathrm{U}}_{\mathrm{ST}}$
191	-18.41	-37.02	-9.22	-18.54	-9.22	-18.54	-18.54
192	-8.64	-17.41	-4.33	-8.73	-4.46	-8.99	-8.73
193	-16.58	-33.38	-8.31	-16.73	-8.31	-16.73	-16.73

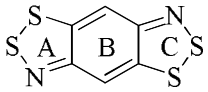


191 **192** **193**

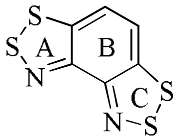
Figure 59. HOMO and LUMO orbitals of systems **191-193**.

NICS calculations gave NICS(0) and NICS(1) values for the three rings of systems **191-193** (Table 38). Unlike the *meta* oriented spin carrier analogs **180a** and **181a**, molecules **191-193** have no ring current in the central rings, supporting the quinoid structures.

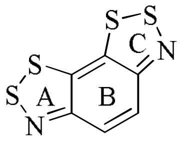
Table 38. NICS(0) and (1) of systems **191-193** [B3LYP/6-31G(d)].



191



192



193

	Ring A		Ring B		Ring C	
	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)
191	-8.63	-5.00	-0.60	-3.65	-8.66	-5.02
192	-7.91	-4.31	-1.33	-3.44	-7.88	-4.31
193	-8.96	-4.81	-1.00	-3.88	-8.90	-4.78

5.8 Summary

The singlet and triplet states of the substituted benzo **180a** (X = Y = CH), pyrido **182** (X = CH, Y = N), **183** (X = N, Y = CH) and pyrazino **184** (X = Y = N) linear fused bis(1,2,3-dithiazoles) as well as their corresponding angular analogs **181a** and **185-187** have been studied using DFT calculations in combination with the BS approach and spin-projected methods. The calculations show that the multiplicity of these molecules is determined by their ability to form zwitterionic independent cyanines by sacrificing the central arene aromaticity. NICS calculations show that the pyrido and pyrazino rings in molecules **182** and **184** readily sacrifice their aromaticity to access the “double-barreled” biscyanine avoiding in this way their overall 4n π antiaromaticity and a triplet ground state. Indeed strategic substitution on the linear and angular systems **180** and **181** can affect their ground state multiplicity and therefore their electronic properties.

CHAPTER 6

Experimental

Sections **Page**

6.1 General Methods and Materials

DCM was freshly distilled from CaH_2 under argon. Reactions were protected from atmospheric moisture by $CaCl_2$ drying tubes. Anhydrous Na_2SO_4 was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus or a TA Instruments DSC Q1000 with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 °C/min. Solvents used for recrystallization are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation "inf". IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike *Miracle* Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (at 300 and 75 MHz, respectively) and 500 machine (at 500 and 125 MHz, respectively). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GCMS with direct inlet probe. High resolution (EI) mass spectra were recorded on an Autospec 'Q' machine. 3-Fluoro-4-nitroanisole (**95b**),[297] 1,3-dichloro-2,4-dinitrobenzene (**133**),[310-312] *N*-phenyl-1,2-benzenediamine **134a**,[155] *N*-butyl-1,2-benzenediamine **134c**[155] and 2,4-dichloro-1,3-dinitro-5-trifluoromethylbenzene (**169**)[342] were prepared according to literature procedures.

6.2 Compounds Related to Chapter 3

6.2.1 Substituted 2-halonitrobenzenes

6.2.1.1 3-Chloro-4-nitrobenzonitrile ***95f***

To a suspension of 4-amino-3-chlorobenzonitrile **102** (1.5 g, 9.86 mmol) in concentrated HCl (3.8 mL) and water (3.8 mL) at *ca.* 0 °C, an aqueous solution of $NaNO_2$ (1.6 equiv.) (1.1 g, 15.80 mmol, in 5.6 mL of water) was added. The mixture was stirred (10 min) and then added to a suspension of $NaNO_2$ (4.9 g, 0.07 mol) and freshly prepared Cu_2O (0.5 g, 6.41 mmol)[299,300] in H_2O at *ca.* 0 °C. After stirring for 30 min at *ca.* 0 °C and then 30 min at *ca.* 20 °C, the reaction mixture was extracted (DCM), washed with brine and dried (Na_2SO_4). Dry flash chromatography (hexane / DCM, 8 : 2) gave 3,4-dichlorobenzonitrile **104** as colorless needles (traces); mp 64-65 °C (from *n*-pentane) (lit.,[372] 71.8-72.1 °C from petroleum ether); (Found: C, 49.01; H, 1.64; N, 8.09. $C_7H_3Cl_2N$ requires C, 48.88; H, 1.76; N, 8.14%); ν_{max}(cm^{-1}) 3272w (Ar NH), 3092w (Ar CH), 2955w, 2922w, 2852w, 2234m (C≡N), 1910w, 1779w, 1653w, 1647w, 1601w, 1587w, 1540w, 1506w, 1487w, 1462s, 1419w, 1380m, 1261w, 1201m, 1148s, 1131m, 1051w, 1041s, 889ss, 865m, 855w, 822s, 791w; δ_H (300 MHz; $CDCl_3$) 7.74 (1H, d, *J* 1.8, Ar *H*), 7.59-7.48 (2H, m, Ar *H*); δ_C (75 MHz; $CDCl_3$) 138.2 (*C*≡N), 133.9 (Ar *C*), 133.6 (Ar *C*H), 131.4 (Ar *C*H), 131.0 (Ar *C*H), 116.7 (Ar *C*), 111.9 (Ar *C*); δ_C (75 MHz; $CDCl_3$, DEPT-135) 133.6 (Ar *C*H), 131.4 (Ar *C*H), 131.0 (Ar *C*H); *m/z* (EI) 175 (M^++4, 10%), 173 (M^++2, 60), 171 (M^+, 100), 136 (27), 109 (7), 100 (37), 85 (9), 75 (19), 62 (6), 50 (28). Further elution (hexane / DCM, 6 : 4) gave the title compound **95f** (1.3 g, 70%) as colorless plates; mp 77-78 °C (from *n*-pentane) (lit.,[298] oil; lit.,[373] mp 85-86 °C); (Found C, 45.95; H, 1.55; N, 15.26. $C_7H_3ClN_2O_2$ requires C, 46.05; H, 1.66; N, 15.34%); ν_{max}(cm^{-1}) 3100w (Ar NH), 3079w, 3038w, 2239m (C≡N), 1596w, 1581w, 1569m, 1559w, 1533s, 1506w, 1474w, 1457w, 1388m, 1363s, 1341w, 1294w, 1266m, 1199w, 1142w, 1055m, 899m, 890m, 852s, 818m, 751m; δ_H (300 MHz; $CDCl_3$) 7.96 (1H, d, *J* 8.3, Ar *H*), 7.88 (1H, s, Ar *H*), 7.44 (1H, dd, *J* 8.4, 1.4, Ar *H*); δ_C (75 MHz; $CDCl_3$) 150.2 (*C*≡N), 135.3 (Ar *C*H), 131.3 (Ar *C*H), 128.2 (Ar *C*), 126.1 (Ar *C*H), 117.1 (Ar *C*), 115.6 (Ar *C*); δ_C (75 MHz; $CDCl_3$, DEPT-135) 135.3 (Ar *C*H), 131.3 (Ar *C*H), 126.1 (Ar *C*H).

6.2.2 Substituted 2-Nitrodiphenylamines

Synthesis of 2-nitrodiphenylamines **94b-k** follow the typical procedure described for 1-*N*-(*p*-tolyl)-2-nitrobenzeneamine **94a** and quantities of products **94b-k** are based on the same mol scale of typical procedure described for product **94a**.

*6.2.2.1 1-*N*-(*p*-Tolyl)-2-nitrobenzeneamine **94a**; typical procedure:*

To a stirred mixture of 2-fluoronitrobenzene **95a** (1 mL, 9.49 mmol) and *p*-toluidine (1.93 g, 18.98 mmol) at *ca*. 20 ^{o}C, potassium fluoride (0.5 g, 9.49 mmol) was added in one portion. The reaction mixture then was heated at *ca*. 180 ^{o}C for 48 h before being allowed to cool to *ca.* 20 ^{o}C. The mixture was then dissolved in dichloromethane and extracted with aqueous hydrochloric acid (5-10%) to remove unreacted amine. The organic layer was separated, dried ($MgSO_4$), filtered (fluted filter paper) and the volatiles removed *in vacuo*. Dry flash chromatography gave the title compound **94a** (1.9 g, 87%) as orange needles; mp 66-67 ^{o}C (from *n*-hexane) (lit.,[374] 68 ^{o}C from MeOH); (Found C, 68.52; H, 5.33; N, 12.14. $C_{13}H_{12}N_2O_2$ requires C, 68.41; H, 5.30; N, 12.27%); λ_{max}(DCM)/nm 205 (log ε 3.88), 262 (3.96), 434 (3.60); ν_{max}(cm^{-1}) 3335w (Ar NH), 1618m, 1609m, 1570m, 1504s, 1441w, 1422m, 1352s, 1325m, 1256s, 1223s, 1163w, 1146m, 1111w, 1078m, 1043m, 1016w, 951w, 895w, 849m, 802m, 775w, 766w, 735s, 692w; δ_H (300 MHz; $CDCl_3$) 9.46 (1H, s, N*H*), 8.21 (1H, d, *J* 8.6, Ar *H*), 7.34 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.21-7.13 (5H, m, Ar *H*), 6.73 (1H, dd, *J* 7.8, 7.8, Ar *H*), 2.38 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 143.6 (Ar *C*), 135.8 (Ar *C*), 135.7 (Ar *C*), 135.6 (Ar *C*H), 132.7 (Ar *C*), 130.3 (Ar *C*H), 126.6 (Ar *C*H), 124.7 (Ar *C*H), 117.0 (Ar *C*H), 115.9 (Ar *C*H), 21.0 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 135.6 (Ar *C*H), 130.3 (Ar *C*H), 126.6 (Ar *C*H), 124.7 (Ar *C*H), 117.0 (Ar *C*H), 115.9 (Ar *C*H), 21.0 (*C*H$_3$); *m/z* (EI) 228 (M$^+$, 100%), 211 (12), 194 (26), 183 (20), 181 (31), 180 (38), 167 (23), 152 (7), 140 (4), 91 (8), 77 (9), 65 (14), 51 (6).

*6.2.2.2 5-Methoxy-2-nitro-1-*N*-(*p*-tolyl)-benzeneamine **94b***

Orange plates (1.8 g, 75%); mp 85-86 ^{o}C (from *n*-hexane); (Found: C, 65.23; H, 5.50; N, 10.94. $C_{14}H_{14}N_2O_3$ requires C, 65.11; H, 5.46; N, 10.85%); λ_{max}(DCM)/nm 265 (log ε 4.02), 477 (3.60); ν_{max}(cm^{-1}) 3343w (Ar NH), 3116w (Ar CH), 1572m, 1505s, 1467w, 1454w, 1443w, 1408m, 1339m, 1324w, 1307w, 1272s, 1222s, 1180w, 1140s, 1111w, 1069m, 1034s, 1017m, 854m, 821s, 811s, 790m; δ_H (300 MHz; $CDCl_3$) 9.72 (1H, s, N*H*), 8.16 (1H, d, *J* 9.5, Ar *H*), 7.24-7.15 (4H, m, Ar *H*), 6.48 (1H, d, *J* 2.6, Ar *H*), 6.30 (1H, dd, *J* 9.5, 2.6, Ar *H*), 3.72 (3H, s, OC*H*$_3$), 2.38 (3H, s, C*H*$_3$); δ_C (75 MHz; CDCl$_3$) 165.5 (Ar *C*), 146.1 (Ar *C*), 135.8 (Ar *C*), 135.6 (Ar *C*), 130.3 (Ar *C*H), 128.9 (Ar *C*H), 127.0 (Ar *C*), 124.9 (Ar *C*H), 106.3 (Ar *C*H), 97.0 (Ar *C*H), 55.6 (*C*H$_3$), 20.9 (*C*H$_3$); δ_C (75 MHz; CDCl$_3$, DEPT-135) 130.3 (Ar *C*H), 128.9 (Ar *C*H), 124.9 (Ar *C*H), 106.3 (Ar *C*H), 97.0 (Ar *C*H), 55.6 (*C*H$_3$), 20.9 (*C*H$_3$); *m/z* (EI) 258 (M$^+$, 100%), 241 (10), 224 (30), 212 (11), 197 (13), 181 (16), 168 (15), 154 (7), 106 (4), 91 (8), 65 (11).

*6.2.2.3 4-Methoxy-2-nitro-1-*N*-(*p*-tolyl)-benzeneamine* ***94c***

Red cubes (0.4 g, 17%); mp 86-87 °C (from *n*-hexane) (lit.,[375] 85-86 °C); (Found C, 65.15; H, 5.39; N, 10.87. C$_{14}$H$_{14}$N$_2$O$_3$ requires C, 65.11; H, 5.46; N, 10.85%); λ_{max}(DCM)/nm 204 (log ε 4.02), 266 (4.18), 477 (3.72); ν_{max}(cm^{-1}) 3343w (Ar NH), 3115w (Ar CH), 1572m, 1506s, 1466w, 1443w, 1408m, 1339m, 1310w, 1273s, 1221s, 1138m, 1069m, 1034m, 1016w, 935w, 874w, 853m, 810m, 791m; δ_H (300 MHz; CDCl$_3$) 9.34 (1H, s, N*H*), 7.61 (1H, d, *J* 2.9, Ar *H*), 7.21-7.02 (6H, m, 6H), 3.81 (3H, s, OC*H*$_3$), 2.36 (3H, s, C*H*$_3$); δ_C (75 MHz; CDCl$_3$) 150.8 (Ar *C*), 138.8 (Ar *C*), 136.4 (Ar *C*), 135.1 (Ar *C*), 132.3 (Ar *C*), 130.2 (Ar *C*H), 126.4 (Ar *C*H), 124.1 (Ar *C*H), 117.7 (Ar *C*H), 106.6 (Ar *C*H), 55.8 (O*C*H$_3$), 20.9 (*C*H$_3$); δ_C (75 MHz; CDCl$_3$, DEPT-135) 130.2 (Ar *C*H), 126.4 (Ar *C*H), 124.1 (Ar *C*H), 117.7 (Ar *C*H), 106.6 (Ar *C*H), 55.8 (O*C*H$_3$), 20.9 (*C*H$_3$); *m/z* (EI) 258 (M$^+$, 100%), 243 (11), 224 (23), 211 (29), 197 (16), 196 (32), 181 (9), 168 (10), 154 (9), 91 (10), 65 (8); (Found: M$^+$, 258.1007. C$_{14}$H$_{14}$N$_2$O$_3$ requires *M*, 258.1004).

*6.2.2.4 5-Methyl-2-nitro-*N*-(*p*-tolyl)-benzeneamine* ***94d***

Orange plates (1.9 g, 84%); mp 92-93°C (from *n*-hexane) (lit.,[376] 80 °C from EtOH); (Found: C, 69.38; H, 5.73; N, 11.67. C$_{14}$H$_{14}$N$_2$O$_2$ requires C, 69.41; H, 5.82; N, 11.56%); λ_{max}(DCM)/nm 273 (log ε 3.97), 433 (3.60); ν_{max}(cm^{-1}) 3351m (Ar NH), 3032w (Ar CH), 2916w, 2862w, 1623s, 1610m, 1575s, 1539w, 1517m, 1507s, 1487s, 1444w, 1411m, 1379w, 1338s, 1325s, 1261s, 1221s, 1168m, 1157m, 1104w, 1076s, 1017m, 961w, 941w, 853w, 831w, 818s; δ_H (300 MHz; CDCl$_3$) 9.51 (1H, s, N*H*), 8.09 (1H, d, *J* 8.7, Ar *H*), 7.25-7.15 (4H, m, Ar *H*), 6.92 (1H, s, Ar *H*), 6.54 (1H, d, *J* 8.7, Ar *H*), 2.39 (3H, s, C*H*$_3$), 2.25 (3H, s, C*H*$_3$); δ_C (75 MHz; CDCl$_3$) 147.8 (Ar *C*), 144.2 (Ar *C*), 136.4 (Ar *C*), 136.1 (Ar *C*), 131.3 (Ar *C*), 130.7 (Ar *C*H), 127.0 (Ar *C*H), 125.3 (Ar *C*H), 119.2 (Ar *C*H), 115.7 (Ar *C*H), 22.4 (*C*H$_3$), 21.4 (*C*H$_3$); δ_C (75 MHz; CDCl$_3$, DEPT-135) 130.7 (Ar *C*H), 127.0 (Ar *C*H), 125.3 (Ar *C*H), 119.2 (Ar *C*H), 115.7 (Ar *C*H), 22.4 (*C*H$_3$), 21.4 (*C*H$_3$); *m/z* (EI) 242 (M$^+$, 100%), 225 (13), 208 (30), 197 (18), 196 (11), 194 (23), 181 (16), 152 (3), 91 (6), 65 (8); (Found: M$^+$, 242.1060. $C_{14}H_{14}N_2O_2$ requires *M*, 242.1055).

*6.2.2.5 4-Methyl-2-nitro-*N*-(*p*-tolyl)-benzeneamine* **94e**

Red plates (0.8 g, 37%); mp 83-84 °C (from *n*-hexane) (lit.,[377] 85 °C); (Found: C, 69.42; H, 5.86; N, 11.58. $C_{14}H_{14}N_2O_2$ requires C, 69.41; H, 5.82; N, 11.56%); λ_{max}(DCM)/nm 203 (log ε 4.06), 263 (4.01), 450 (3.58); ν_{max}(cm^{-1}) 3358m (Ar NH), 2924w, 1630m, 1610w, 1566m, 1511s, 1429w, 1402m, 1376w, 1339s, 1321w, 1308w, 1263s, 1221s, 1199m, 1151s, 1108w, 1082w, 1039w, 1020w, 924m, 878w, 844w, 822s, 807s, 786w, 765m; δ_H (300 MHz; $CDCl_3$) 9.35 (1H, s, N*H*), 7.99 (1H, s, Ar *H*), 7.22-7.07 (6H, m, Ar *H*), 2.37 (3H, s, C*H*$_3$), 2.28 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 141.5 (Ar *C*), 137.1 (Ar *C*H), 136.2 (Ar *C*), 135.2 (Ar *C*), 132.6 (Ar *C*), 130.2 (Ar *C*H), 126.8 (Ar *C*), 125.7 (Ar *C*H), 124.3 (Ar *C*H), 116.0 (Ar *C*H), 20.9 (*C*H$_3$), 20.0 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 137.1 (Ar *C*H), 130.2 (Ar *C*H), 125.7 (Ar *C*H), 124.3 (Ar *C*H), 116.0 (Ar *C*H), 20.9 (*C*H$_3$), 20.0 (*C*H$_3$); *m/z* (EI) 242 (M$^+$, 100%), 225 (11), 208 (32), 197 (22), 194 (37), 181 (24), 171 (3), 168 (4), 152 (7), 149 (6), 127 (3), 125 (4), 123 (3), 111 (4), 109 (3), 108 (3), 104 (6), 91 (11), 83 (9), 77 (12), 69 (13), 67 (5), 65 (17), 63 (7), 55 (10), 51 (6); (Found: M$^+$, 242.1060. $C_{14}H_{14}N_2O_2$ requires *M*, 242.1055).

*6.2.2.6 5-Cyano-2-nitro-1-*N*-(*p*-tolyl)-benzeneamine* **94f**

Orange plates (1.5 g, 64%); mp 139-140 °C (from *n*-hexane); (Found: C, 66.40; H, 4.29; N, 16.48. $C_{14}H_{11}N_3O_2$ requires C, 66.40; H, 4.38; N, 16.59%); λ_{max}(DCM)/nm 205 (log ε 4.08), 262 (4.11), 442 (3.61); ν_{max}(cm^{-1}) 3317m (Ar NH), 2236w (C≡N), 1616m, 1606m, 1587m, 1569s, 1512s, 1482s, 1445w, 1412m, 1406m, 1339s, 1322m, 1313w, 1258s, 1223s, 1211m, 1182m, 1168m, 1151m, 1065s, 1018w, 980m, 955w, 867m, 879w, 845m, 839m, 826s, 814s; δ_H (500 MHz; $CDCl_3$) 9.43 (1H, s, N*H*), 8.28 (1H, d, *J* 9.0, Ar *H*), 7.36 (1H, d, *J* 1.5, Ar *H*), 7.29-7.26 (2H, m, Ar *H*), 7.14 (2H, d, *J* 8.0, Ar *H*), 6.93 (1H, d, *J* 8.8, 2.0, Ar *H*), 2.41 (3H, s, C*H*$_3$); δ_C (125 MHz; $CDCl_3$) 143.7 (Ar *C*), 137.3 (Ar *C*), 134.4 (Ar *C*), 134.1 (Ar *C*), 130.8 (Ar *C*H), 127.7 (Ar *C*H), 125.3 (Ar *C*H), 120.6 (Ar *C*H), 118.9 (Ar *C*H), 118.5 (Ar *C*), 117.2 (Ar *C*), 21.0 (*C*H$_3$); *m/z* (EI) 253 (M$^+$, 100%), 236 (13), 219 (25), 208 (33), 206 (39), 205 (55), 192 (33), 177 (7), 164 (8), 151 (12), 103 (15), 89 (19), 65 (46), 51 (19); (Found M$^+$, 253.0848. $C_{14}H_{11}N_3O_2$ requires *M*, 253.0851).

Further elution on column chromatography (hexane / DCM, 4 : 6) gave 4-nitro-*N*-*p*-tolyl-3-(*p*-tolylamino)benzamide **106** as red crystals (trace); mp 211-212 °C (from *n*-hexane); (Found: C, 69.89; H, 5.24; N, 11.58. $C_{21}H_{19}N_3O_3$ requires C, 69.79; H, 5.30; N, 11.63%); 3340w(Ar NH), 3292w, 1658s, 1616m, 1601s, 1576s, 1533s, 1516s, 1508s, 1479s, 1436m, 1405m, 1336s, 1329s, 1305w, 1276m, 1261s, 1241w, 1229m, 1197m, 1184w, 1153w, 1109w, 1066m, 1020m, 978w, 938w, 888m, 876w, 841m, 818s, 806m, 775w; δ_H (300 MHz; DMSO-d_6) 10.33 (1H, s, N*H*), 9.45 (1H, s, N*H*), 8.23 (1H, d, *J* 8.8, Ar *H*), 7.60-7.56 (3H, m, Ar *H*), 7.34-7.22 (5H, m, Ar *H*), 7.13 (2H, d, *J* 8.5, Ar *H*), 2.32 (3H, s, CH_3), 2.26 (3H, s, CH_3); δ_C (75 MHz; DMSO-d_6) 163.8 (*C*=O), 142.3 (Ar *C*), 141.3 (Ar *C*), 136.2 (Ar *C*), 136.0 (Ar *C*), 134.7 (Ar *C*), 134.0 (Ar *C*), 133.2 (Ar *C*), 130.1 (Ar *C*H), 129.0 (Ar *C*H), 126.6 (Ar *C*H), 124.3 (Ar *C*H), 120.5 (Ar *C*H), 116.2 (Ar *C*H), 115.7 (Ar *C*H), 20.5 (CH_3), 20.5 (CH_3); δ_C (75 MHz; DMSO-d_6, DEPT-135) 130.1 (Ar *C*H), 129.0 (Ar *C*H), 126.6 (Ar *C*H), 124.3 (Ar *C*H), 120.5 (Ar *C*H), 116.2 (Ar *C*H), 115.7 (Ar *C*H), 20.5 (CH_3), 20.5 (CH_3); *m/z* (EI) 361 (M^+, 100%), 255 (49), 253 (10), 227 (14), 221 (5), 208 (8), 205 (6), 192 (4), 181 (34), 152 (4), 91 (6), 77 (5), 65 (4).

*6.2.2.7 4-Cyano-2-nitro-1-*N*-(*p*-tolyl)-benzeneamine* ***94g***

Orange plates (2.2 g, 92%); mp 122-123 °C (from *n*-hexane) (lit.,[378] 128 °C from EtOH); (Found: C, 66.39; H, 4.26; N, 16.49. $C_{14}H_{11}N_3O_2$ requires C, 66.40; H, 4.38; N, 16.59%); λ_{max}(DCM)/nm 228 (log ε 4.01), 260 (4.10), 286 (4.10), 419 (3.96); ν_{max}(cm^{-1}) 3318m (Ar NH), 3300w (Ar CH), 2222m ($C\equiv N$), 1620s, 1607s, 1587w, 1562s, 1530, 1512s, 1439w, 1418m, 1377w, 1358s, 1317w, 1263s, 1225s, 1184s, 1150m, 1069m, 926m, 910m, 870w, 810s, 783w, 766m, 700m; δ_H (300 MHz; $CDCl_3$) 9.78 (1H, s, N*H*), 8.53 (1H, s, Ar *H*), 7.47 (1H, dd, *J* 9.1, 1.9, Ar *H*), 7.29 (1H, s, Ar *H*), 7.16-7.08 (4H, m, Ar *H*), 2.39 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 146.2 (Ar *C*), 137.6 (Ar *C*), 137.2 (Ar *C*H), 134.0 (Ar *C*), 132.0 (Ar *C*H), 131.7 (Ar *C*), 130.7 (Ar *C*H), 125.5 (Ar *C*H), 117.8 (Ar *C*), 116.8 (Ar *C*H), 99.6 (Ar *C*), 21.1 (CH_3); δ_C (75 MHz; $CDCl_3$, DEPT-135) 137.2 (Ar *C*H), 132.0 (Ar *C*H), 130.7 (Ar *C*H), 125.5 (Ar *C*H), 116.8 (Ar *C*H), 21.1 (CH_3); *m/z* (EI) 253 (100%, M^+), 236 (5), 223 (5), 219 (16), 206 (30), 205 (30), 192 (17), 179 (4), 177 (4), 164 (5), 151 (5), 103 (5), 102 (4), 91 (7), 89 (5), 77 (5), 65 (8), 63 (4), 51 (4); (Found M^+, 253.0858. $C_{14}H_{11}N_3O_2$ requires *M*, 253.0851).

*6.2.2.8 5-Trifluoromethyl-2-nitro-*N*-(*p*-tolyl)-benzeneamine* ***94h***

Orange cubes (2.4g, 85%); mp 64-65°C (from *n*-hexane); (Found: C, 56.81; H, 3.71; N, 9.33. $C_{14}H_{11}F_3N_2O_2$ requires C, 56.76; H, 3.74; N, 9.46%); λ_{max}(DCM)/nm 254 (log ε 3.95), 431 (3.52); ν_{max}(cm^{-1}) 3364w (Ar NH), 2926w, 1625w, 1612w, 1586m, 1559w, 1540w, 1512s, 1496s, 1445w, 1420m, 1399w, 1344m, 1331m, 1305m, 1286w, 1256s, 1207m, 1183m, 1175s, 1153m, 1120s, 1112s, 1091w, 1067m, 1017w, 976w, 939w, 883m, 860w, 847m, 828s, 822s, 775w, 762m; δ_H (300 MHz; $CDCl_3$) 9.53 (1H, s, N*H*), 8.31 (1H, d, *J* 8.9, Ar *H*), 7.39 (1H, s, Ar *H*), 7.27 (2H, d, *J* 8.2, Ar *H*), 7.17 (2H, d, *J* 8.3, Ar *H*), 6.94 (1H, dd, *J* 8.9, 1.8, Ar *H*), 2.41 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 143.5 (Ar *C*), 136.7 (q, $^2J_{CF}$ 32.9, Ar *C*), 136.6 (Ar *C*), 134.8 (Ar *C*), 133.9 (Ar *C*), 130.6 (Ar *C*H), 127.7 (Ar *C*H), 124.8 (Ar *C*H), 121.0 (Ar *C*), 113.4 (q, $^3J_{CF}$ 4.1, Ar *C*H), 112.8 (q, $^3J_{CF}$ 3.3, Ar *C*H), 21.0 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 130.6 (Ar *C*H), 127.7 (Ar *C*H), 124.8 (Ar *C*H), 113.4 (q, $^3J_{CF}$ 4.1, Ar *C*H), 112.8 (q, $^3J_{CF}$ 3.3, Ar *C*H), 21.0 (*C*H$_3$); *m/z* (EI) 296 (M$^+$, 100%), 279 (11), 262 (18), 251 (17), 250 (8), 249 (22), 248 (24), 235 (11), 181 (7), 65 (6).

*6.2.2.9 4-Trifluoromethyl-2-nitro-*N*-(*p*-tolyl)-benzeneamine* ***94i***

Orange plates (2.8 g, 99%); mp 111-112 °C (from *n*-hexane) (lit.,[379] 113.5-114 °C); (Found: C, 56.70; H, 3.68; N, 9.37. $C_{14}H_{11}F_3N_2O_2$ requires C, 56.76; H, 3.74; N, 9.46%); λ_{max}(DCM)/nm 254 (log ε 4.03), 418 (3.57); ν_{max}(cm^{-1}) 3351w (Ar NH), 3104w (Ar CH), 2928w, 1640m, 1575m, 1530m, 1516m, 1509m, 1439m, 1413m, 1357m, 1323s, 1260s, 1221m, 1150s, 1108s, 1085s, 1022w, 990w, 944w, 916s, 911m, 862w, 845m, 829m, 807m, 778m, 765m; δ_H (300 MHz; $CDCl_3$) 9.68 (1H, s, N*H*), 8.50 (1H, s, Ar *H*), 7.51 (1H, d, *J* 8.7, Ar *H*), 7.27 (2H, d, *J* 7.8, Ar *H*), 7.17 (3H, d, *J* 8.4, Ar *H*), 2.41 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 145.7 (Ar *C*), 137.0 (Ar *C*), 134.7 (Ar *C*), 131.6 (q, $^3J_{CF}$ 3.1, Ar *C*H), 131.4 (Ar *C*H), 130.6 (Ar *C*H), 125.3 (Ar *C*H), 124.7 (q, $^3J_{CF}$ 4.3, Ar *C*H), 121.6 (Ar *C*H), 118.6 (q, $^2J_{CF}$ 34.3, Ar *C*), 116.6 (Ar *C*H), 21.0 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 131.6 (q, $^3J_{CF}$ 3.1, Ar *C*H), 130.6 (Ar *C*H), 125.3 (Ar *C*H), 124.7 (q, $^3J_{CF}$ 4.3, Ar *C*H), 116.6 (Ar *C*H), 21.0 (*C*H$_3$); *m/z* (EI) 296 (M$^+$, 100%), 279 (13), 262 (21), 251 (20), 250 (9), 249 (24), 248 (28), 235 (10), 181 (6), 180 (7), 115 (6); (Found M$^+$, 296.0768. $C_{14}H_{11}N_2O_2F_3$ requires *M*, 296.0773).

*6.2.2.10 5-Fluoro-2-nitro-*N*-(*p*-tolyl)-benzeneamine* ***94j***

Orange needles (1.9 g, 82%); mp 123-124 °C (from *n*-hexane); (Found: C, 63.32; H, 4.43; N, 11.25. $C_{13}H_{11}FN_2O_2$ requires C, 63.41; H, 4.50; N, 11.38%); λ_{max}(DCM)/nm 269 (log ε 3.81), 416 (3.49); ν_{max}(cm^{-1}) 3329m (Ar NH), 3105w (Ar CH), 1632s, 1612m, 1589m, 1572s, 1510s, 1499s, 1455m, 1443w, 1417m, 1381w, 1343s, 1320m, 1303m, 1252s, 1225s, 1205s, 1133m, 1120m, 1108w, 1078s, 1018w, 997m, 968w, 950w, 843m, 834m, 799m, 776w, 751s, 748s; δ_H (300 MHz; $CDCl_3$) 9.59 (1H, s, N*H*), 8.24 (1H, dd, *J* 9.3, 6.0, Ar *H*), 7.25 (2H, d, *J* 7.8, Ar *H*), 7.15 (2H, d, *J* 8.1, Ar *H*), 6.73 (1H, dd, *J* 11.4, 2.4, Ar *H*), 6.47-6.40 (1H, m, Ar *H*), 2.39 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 168.9 (Ar *C*), 165.5 (Ar *C*), 146.1 (Ar *C*), 136.5 (Ar *C*), 135.1 (Ar *C*), 130.5 (Ar *C*H), 129.7 (Ar *C*H), 125.1 (Ar *C*H), 105.6 (Ar *C*H), 101.2 (Ar *C*H), 21.0 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 130.5 (Ar *C*H), 129.7 (Ar *C*H), 125.1 (Ar *C*H), 105.6 (Ar *C*H), 101.2 (Ar *C*H), 21.0 (*C*H$_3$); *m/z* (EI) 246 (M^+, 100%), 229 (21), 212 (60), 198 (73), 189 (3), 185 (38), 178 (7), 170 (7), 157 (5), 151 (6), 106 (9), 99 (14), 95 (5), 91 (13), 86 (5), 77 (10), 65 (29), 57 (4), 51 (11); (Found: M^+, 246.0805. $C_{13}H_{11}FN_2O_2$ requires *M*, 246.0805). Further elution on column chromatography (hexane / DCM, 4 : 6) gave 2-nitro-*N,N'*-[di-(*p*-tolyl)]benzene-2,4-diamine **105** as orange crystals (3.0 mg, 1%); mp 170-171 °C (from *n*-hexane); *m/z* (EI) 333 (M^+, 17%), 298 (4), 246 (46), 229 (6), 212 (16), 198 (16), 185 (10), 180 (9), 149 (6), 91 (8), 77 (8), 65 (9), 58 (5), 51 (5).

*6.2.2.11 4-Fluoro-2-nitro-*N*-(*p*-tolyl)-benzeneamine* ***94k***

Red cubes (1.8 g, 79%); mp 119-121 °C (from *n*-hexane); (Found: C, 63.43; H, 4.38; N, 11.22. $C_{13}H_{11}FN_2O_2$ requires C, 63.41; H, 4.50; N, 11.38%); λ_{max}(DCM)/nm 257 (log ε 3.93), 449 (3.58); ν_{max}(cm^{-1}) 3347m (Ar NH), 3107w (Ar CH), 2919w, 1589m, 1576m, 1559w, 1511s, 1436w, 1412m, 1346m, 1323w, 1304w, 1263s, 1232s, 1180m, 1127s, 1060m, 981w, 962w, 949s, 883m, 839w, 833w, 821s, 812s, 795m, 766m, 757m; δ_H (300 MHz; $CDCl_3$) 9.33 (1H, s, N*H*), 7.89 (1H, tt, *J* 1.7, 1.7, 8.9, Ar *H*), 7.24 (1H, s, Ar *H*), 7.21 (1H, s, Ar *H*), 7.15 (2H, d, *J* 1.6, Ar *H*), 7.13 (2H, d, *J* 1.8, Ar *H*), 2.38 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 154.9 (Ar *C*), 151.7 (Ar *C*), 140.7 (Ar *C*), 135.8 (Ar *C*), 131.7 (Ar *C*), 130.4 (Ar *C*H), 124.6 (Ar *C*H), 124.2 (Ar *C*H), 117.6 (Ar *C*H), 111.7 (Ar *C*H), 20.9 (*C*H$_3$); δ_C(75 MHz; $CDCl_3$, DEPT-135) 130.4 (Ar *C*H), 124.6 (Ar *C*H), 124.2 (Ar *C*H), 117.6 (Ar *C*H), 111.7 (Ar *C*H), 20.9 (*C*H$_3$); *m/z* (EI) 246 (M^+, 100%), 229 (10), 212 (26), 201 (22), 200 (14), 199 (45), 198 (51), 185 (31), 170 (6), 99 (8), 65 (14); (Found M^+, 246.0810. $C_{13}H_{11}FN_2O_2$ requires *M*, 246.0805).

6.2.3 Substituted *N*-(*p*-Tolyl)-1,2-benzenediamines

Synthesis of *N*-(*p*-tolyl)-1,2-benzenediamines **93b-k** follow the typical procedure described for 1-*N*-(*p*-tolyl)-1,2-benzenediamine **93a** and quantities of products **93b-k** are based on the same mol scale of typical procedure described for product **93a**.

*6.2.3.1 1-*N-*(*p*-Tolyl)-1,2-benzenediamine* ***93a****; typical procedure:*

1-*N*-tolyl-2-nitrobenzeneamine **94a** (100 mg, 0.44 mmol) was dissolved in EtOH (20 mL) in a hydrogenation flask and 5% Pd/C (100 mg) was added. The flask was attached to a Parr hydrogenator, evacuated, and flushed with hydrogen twice. Then the mixture was shaken under hydrogen atmosphere at a pressure of 2 bar for 1 h. The hydrogenation was judged complete after the pressure of the hydrogen stayed stable, the red color of the reagent was gone and there was no more starting material according to TLC. TLC at the end of the reaction showed only a colorless product that became red after a while. The mixture was filtered through Celite® directly into a flask containing ice-cold water. The title compound **93a** was separated as colorless plates and kept in the fridge (66 mg, 76%); mp 73-74 °C (from water) (lit.,[380] 74 °C from water); (Found: C, 78.69; H, 7.23; N, 14.06. $C_{13}H_{14}N_2$ requires C, 78.75; H, 7.12; N, 14.13%); λ_{max}(DCM)/nm 235 (log ε 3.89), 275 (3.73); ν_{max}(cm^{-1}) 3430m and 3339m (Ar NH), 2918w, 1653m, 1611s, 1591m, 1556w, 1539w, 1516s, 1500s, 1441m, 1398m, 1378w, 1304s, 1259m, 1219w, 1181w, 1157w, 1139m, 1124m, 1030w, 928m, 888w, 865w, 835w, 809s, 787w, 777w, 771w, 757s, 745s; δ_H (300 MHz; $CDCl_3$) 7.13-6.99 (4H, m, Ar *H*), 6.83-6.94 (4H, m, Ar *H*), 3.82 (3H, s, N*H*$_2$ & N*H*), 2.30 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 142.6 (Ar *C*), 141.2 (Ar *C*), 129.8 (Ar *C*H), 129.4 (Ar *C*), 128.8 (Ar *C*), 125.0 (Ar *C*H), 123.8 (Ar *C*H), 119.1 (Ar *C*H), 116.1 (Ar *C*H), 115.7 (Ar *C*H), 20.5 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$; Dept-135) 129.8 (Ar *C*H), 125.0 (Ar *C*H), 123.8 (Ar *C*H), 119.1 (Ar *C*H), 116.1 (Ar *C*H), 115.7 (Ar *C*H), 20.5 (*C*H$_3$); *m/z* (EI) 198 (M^+, 91%), 183 (85), 182 (36), 181 (18), 169 (7), 154 (7), 145 (7), 132 (10), 119 (19), 107 (38), 106 (27), 98 (74), 91 (100), 80 (72), 65 (56), 53 (12); (Found: M^+, 198.1164. $C_{13}H_{14}N_2$ requires *M*, 198.1157).

*6.2.3.2 5-Methoxy-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93b***

Colorless plates (81 mg, 81%); mp 82-83 °C (from water); (Found: C, 73.76; H, 7.12; N, 12.23. $C_{14}H_{16}N_2O$ requires C, 73.66; H, 7.06; N, 12.27%); λ_{max}(DCM)/nm 237 (log ε 3.98), 296 (3.63); v_{max}(cm^{-1}) 3430w, 3339m and 3329w (Ar NH), 2918w, 2864w, 1653m, 1611s, 1591m, 1576w, 1559w, 1539w, 1519s, 1516s, 1500s, 1441m, 1398m, 1378w, 1304s, 1259m, 1181m, 1157w, 1139m, 1124m, 1030w, 928w, 835w, 809s, 757s; δ_H (300 MHz; $CDCl_3$) 7.08 (2H, d, *J* 8.1, Ar *H*), 6.82-6.73 (4H, m, Ar *H*), 6.54 (1H, dd, *J* 8.5, 2.8, Ar *H*), 5.30 (1H, s, N*H*), 3.70 (3H, s, OC*H*$_3$), 3.31 (2H, s N*H*$_2$), 2.31 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 153.5 (Ar *C*), 141.6 (Ar *C*), 132.8 (Ar *C*), 131.9 (Ar *C*), 129.8 (Ar *C*H), 129.4 (Ar *C*), 117.5 (Ar *C*H), 116.8 (Ar *C*H), 108.7 (Ar *C*H), 107.2 (Ar *C*H), 55.5 (O*C*H$_3$), 20.5 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 129.8 (Ar *C*H), 117.5 (Ar *C*H), 116.8 (Ar *C*H), 108.7 (Ar *C*H), 107.2 (Ar *C*H), 55.5 (O*C*H$_3$), 20.5 (*C*H$_3$); *m/z* (EI) 228 (M^+, 100%), 213 (77), 197 (4), 185 (10), 169 (8), 144 (3), 137 (2), 118 (11), 106 (4), 91 (12), 68 (7), 65 (9), 52 (5).

*6.2.3.3 4-Methoxy-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93c***

Colorless plates (96 mg, 96%); mp 74-76 °C (from water); (Found: C, 73.76; H, 7.11; N, 12.22. $C_{14}H_{16}N_2O$ requires C, 73.66; H, 7.06; N, 12.27%); λ_{max}(DCM)/nm 227 (log ε 3.79), 275 (3.70); v_{max}(cm^{-1}) 3359w (Ar NH), 2918w, 2833w, 1610m, 1596m, 1511s, 1484m, 1452m, 1436w, 1396m, 1312w, 1275m, 1244m, 1214m, 1195m, 1158s, 1111w, 1039m, 1010w, 965w, 810s; δ_H (300 MHz; $CDCl_3$) 7.03 (3H, d, *J* 7.5, Ar *H*), 6.59 (2H, d, *J* 8.1, Ar *H*), 6.36-6.28 (2H, m, Ar *H*), 4.97 (1H, s, N*H*), 3.90 (2H, s, N*H*$_2$), 3.81 (3H, s, OC*H*$_3$), 2.29 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 158.3 (Ar *C*), 144.5 (Ar *C*), 144.3 (Ar *C*), 129.7 (Ar *C*H), 127.9 (Ar *C*H), 127.7 (Ar *C*), 121.3 (Ar *C*), 114.2 (Ar *C*H), 103.9 (Ar *C*H), 101.1 (Ar *C*H), 55.2 (O*C*H$_3$), 20.4 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135); 129.7 (Ar *C*H), 127.9 (Ar *C*H), 114.2 (Ar *C*H), 103.9 (Ar *C*H), 101.1 (Ar *C*H), 55.2 (O*C*H$_3$), 20.4 (*C*H$_3$); *m/z* (EI) 228 (M^+, 100%), 213 (66), 197 (4), 185 (7), 169 (6), 153 (3), 142 (5), 132 (3), 118 (7), 106 (3), 91 (8), 77 (3), 65 (7).

*6.2.3.4 5-Methyl-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93d***

Colorless plates (78 mg, 84%); mp 103-104 °C (from water) (lit.,[381] 103 °C from EtOH); (Found: C, 79.30; H, 7.48; N, 13.02. $C_{14}H_{16}N_2$ requires C, 79.21; H, 7.60; N, 13.20%); λ_{max}(DCM)/nm 237 (log ε 3.94), 274 (3.73), 301 (3.66); v_{max}(cm^{-1}) 3416w, 3330m and

3312w(Ar NH), 3020w (Ar CH), 2916w, 2864w, 1873w, 1616m, 1595w, 1509s, 1488m, 1387w, 1377w, 1308s, 1269w, 1250m, 1182m, 1154m, 1124m, 1113w, 950w, 933w, 888w, 850w, 809s, 785m; δ_H (300 MHz; $CDCl_3$) 7.05 (2H, d, *J* 8.3, Ar *H*), 6.94 (1H, s, Ar *H*), 6.82-6.69 (4H, m, Ar *H*), 5.08 (1H, s, N*H*), 3.18 (2H, s, N*H*$_2$), 2.29 (3H, s, C*H*$_3$), 2.23 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 142.6 (Ar *C*), 138.3 (Ar *C*), 129.7 (Ar *C*H), 129.6 (Ar *C*), 128.7 (Ar *C*), 128.6 (Ar *C*), 125.2 (Ar *C*H), 123.8 (Ar *C*H), 116.2 (Ar *C*H), 115.8 (Ar *C*H), 20.5 (*C*H$_3$), 20.4 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 129.7 (Ar *C*H), 125.2 (Ar *C*H), 123.8 (Ar *C*H), 116.2 (Ar *C*H), 115.8 (Ar *C*H), 20.5 (*C*H$_3$), 20.4 (*C*H$_3$); *m/z* (EI) 212 (M$^+$, 100%), 197 (42), 121 (5), 106 (13), 98 (12), 91 (12), 77 (14), 65 (7); (Found: M$^+$, 212.1315. $C_{14}H_{16}N_2$ requires *M*, 212.1313).

*6.2.3.5 4-Methyl-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93e***

Colorless plates (72 mg, 77%); mp 102-103 °C (from water) (lit.,[382] 109 °C from petroleum ether); (Found: C, 79.30; H, 7.67; N, 13.11. $C_{14}H_{16}N_2$ requires C, 79.21; H, 7.60; N, 13.20%); λ_{max}(DCM)/nm 238 (log ε 3.94), 270 (3.74); ν_{max}(cm^{-1}) 3413m, 3328m and 3314w (Ar NH), 3027w (Ar CH), 2917w, 2862w, 1868w, 1613m, 1509s, 1448w, 1424w, 1399w, 1375w, 1315s, 1306m, 1269w, 1262m, 1251w, 1179w, 1167w, 1144w, 1123w, 1111w, 941w, 924w, 871m, 828w, 807s, 796m; δ_H (300 MHz; $CDCl_3$) 7.06-7.00 (3H, m, Ar *H*), 6.67-6.59 (4H, m, Ar *H*), 4.05 (3H, s, N*H*, N*H*$_2$), 2.32 (3H, s, C*H*$_3$), 2.30 (3H, s, C*H*$_3$); δ_C (75 MHz; $CDCl_3$) 143.4 (Ar *C*), 141.8 (Ar *C*), 135.4 (Ar *C*), 129.7 (Ar *C*H), 128.2 (Ar *C*), 126.3 (Ar *C*), 125.1 (Ar *C*H), 119.8 (Ar *C*H), 116.7 (Ar *C*H), 115.0 (Ar *C*H), 21.0 (*C*H$_3$), 20.4 (*C*H$_3$); δ_C (75 MHz; $CDCl_3$, DEPT-135) 129.7 (Ar *C*H), 125.1 (Ar *C*H), 119.8 (Ar *C*H), 116.7 (Ar *C*H), 115.0 (Ar *C*H), 21.0 (*C*H$_3$), 20.4 (*C*H$_3$); *m/z* (EI) 212 (M$^+$, 100%), 197 (30), 196 (22), 182 (5), 181 (4), 121 (4), 106 (6), 79 (4), 77 (9), 65 (6); (Found: M$^+$, 242.1316. $C_{14}H_{16}N_2$ requires *M*, 212.1313).

*6.2.3.6 5-Cyano-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93f***

Colorless plates (58 mg, 59%); mp 96-97 °C (from water); (Found: C, 75.28; H, 5.75; N, 18.81. $C_{14}H_{13}N_3$ requires C, 75.31; H, 5.87; N, 18.82%); λ_{max}(DCM)/nm 261 (log ε 4.01); ν_{max}(cm^{-1}) 3416m, 3367m and 3340m (Ar NH), 2916w, 2218s (C≡N), 1631m, 1616m, 1594s, 1578s, 1522s, 1512s, 1489m, 1434m, 1399m, 1352m, 1317s, 1312m, 1288m, 1243m, 1183w, 1167w, 1142m, 1127m, 1114w, 1036w, 961m, 948w, 882m, 854m, 820s, 802s; δ_H (300 MHz; $CDCl_3$) 7.30 (1H, d, *J* 1.8, Ar *H*), 7.22 (1H, dd, *J* 8.2, 1.5, Ar *H*), 7.06 (2H, d, *J* 8.3, Ar *H*), 6.76-6.67 (3H, m, Ar *H*), 5.10 (1H, s, N*H*), 4.15 (2H, s, NH_2), 2.29 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 145.5 (Ar *C*), 141.1 (Ar *C*), 130.2 (Ar *C*), 129.9 (Ar *C*H), 129.5 (Ar *C*), 129.2 (Ar *C*H), 126.5 (Ar *C*H), 120.0 (*C*≡N), 116.6 (Ar *C*H), 115.2 (Ar *C*H), 100.4 (Ar *C*), 20.5 (CH_3); δ_C (75 MHz; $CDCl_3$, DEPT-135) 129.9 (Ar *C*H), 129.2 (Ar *C*H), 126.5 (Ar *C*H), 116.6 (Ar *C*H), 115.2 (Ar *C*H), 20.5 (CH_3); *m/z* (EI) 223 (M^+, 100%), 208 (70), 207 (25), 106 (4), 105 (5), 104 (4), 98 (6), 91 (8), 77 (6), 65 (5).

*6.2.3.7 4-Cyano-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93g***

Colorless plates (73 mg, 74%); mp 160-161 °C (from water) (lit.,[383] 162-163 °C from EtOH); (Found: C, 75.42; H, 5.92; N, 18.90. $C_{14}H_{13}N_3$ requires C, 75.31; H, 5.87; N, 18.82%); λ_{max}(DCM)/nm 228 (log ε 3.99), 295 (3.85), 327 (3.86); ν_{max}(cm^{-1}) 3429w, 3379m and 3352w (Ar NH), 2862w, 2209s (C≡N), 1630m, 1595s, 1576m, 1516s, 1485m, 1437m, 1348m, 1314s, 1289m, 1244m, 1236m, 1182w, 1169w, 1142m, 1123w, 1030w, 1017w, 959m, 858m, 851m, 799s; δ_H (300 MHz; $CDCl_3$) 7.13 (2H, d, *J* 8.1, Ar *H*), 7.05 (2H, d, *J* 8.0, Ar *H*), 6.99 (1H, s, Ar *H*), 6.91 (2H, d, *J* 8.2, Ar H), 5.58 (1H, s, N*H*), 3.69 (2H, s, NH_2), 2.33 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 138.8 (Ar *C*), 137.3 (Ar *C*), 136.8 (Ar *C*), 132.2 (Ar *C*), 130.0 (Ar *C*H), 124.8 (Ar *C*H), 119.9 (*C*≡N), 119.7 (Ar *C*H), 119.4 (Ar *C*H), 116.5 (Ar *C*H), 103.5 (Ar *C*), 20.7 (CH_3); δ_C (75 MHz; $CDCl_3$, DEPT-135) 130.0 (Ar *C*H), 124.8 (Ar *C*H), 119.7 (Ar *C*H), 119.4 (Ar *C*H), 116.5 (Ar *C*H), 20.7 (CH_3); *m/z* (EI) 223 (M^+, 100%), 208 (63), 207 (17), 194 (6), 179 (5), 116 (6), 106 (12), 98 (5), 91 (24), 79 (12), 65 (22), 51 (14); (Found: M^+, 223.1110. $C_{14}H_{13}N_3$ requires *M*, 223.1109).

*6.2.3.8 5-Trifluoromethyl-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93h***

Colorless oil (115 mg, 98%); (Found: C, 63.08; H, 4.94; N, 10.59. $C_{14}H_{13}F_3N_2$ requires C, 63.15; H, 4.92; N, 10.52%); λ_{max}(DCM)/nm 235 (log ε 3.87), 292 (3.68); ν_{max}(cm^{-1}) 3370w (Ar NH), 3024w (Ar CH), 2923w, 2866w, 1624m, 1613m, 1560w, 1539w, 1513s, 1473w, 1456w, 1443m, 1396w, 1328s, 1313m, 1274m, 1247w, 1216w, 1205w, 1162m, 1147s, 1109s, 1072m, 1016w, 932m, 899w, 852w, 813s; δ_H (300 MHz; $CDCl_3$) 7.35 (1H, s, Ar H), 7.23 (1H, d, *J* 7.8, Ar *H*), 7.07 (2H, d, *J* 8.4, Ar H), 6.81 (1H, d, *J* 8.3, Ar *H*), 6.70 (2H, d, *J* 8.3, Ar *H*), 5.10 (1H, s, N*H*), 4.05 (2H, s, NH_2), 2.30 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 144.2 (Ar *C*), 141.6 (Ar *C*), 130.0 (Ar *C*H), 129.8 (Ar *C*), 129.1 (Ar *C*), 124.5 (q, $^1J_{CF}$ 270.9 CF_3), 122.1 (q, $^3J_{CF}$ 4.0, Ar *C*H), 121.0 (q, $^2J_{CF}$ 33.0, Ar *C*), 120.5 (q, $^3J_{CF}$ 3.6, Ar *C*H), 116.2 (Ar *C*H), 115.2 (Ar *C*H), 20.5 (CH_3); δ_C (75 MHz; $CDCl_3$, DEPT-135) 130.0 (Ar *C*H), 122.1 (q, $^3J_{CF}$ 4.0, Ar *C*H), 120.5 (q, $^3J_{CF}$ 3.6, Ar *C*H), 116.2 (Ar *C*H), 115.2 (Ar *C*H), 20.5 (CH_3); *m/z* (EI) 266 (M^+, 100%), 51 (58), 250 (20), 237 (8), 181 (7), 175 (5), 148 (8), 132 (6), 106 (4), 98 (4), 91 (12), 89 (4), 80 (6), 79 (7), 65 (5).

*6.2.3.9 4-Trifluoromethyl-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93i***

Colorless plates (90 mg, 77%); mp 72-74 °C (from water); (lit.,[379] semi-oil); (Found: C, 63.11; H, 4.91; N, 10.53. $C_{14}H_{13}F_3N_2$ requires C, 63.15; H, 4.92; N, 10.52%); λ_{max}(DCM)/nm 228 (log ε 3.92), 282 (3.88); ν_{max}(cm^{-1}) 3479w, 3376m (Ar NH), 2919w, 2867w, 1884w, 1621m, 1610m, 1599m, 1511s, 1479w, 1439m, 1396m, 1337s, 1313w, 1300m, 1284w, 1250s, 1224m, 1209w, 1162w, 1153s, 1109s, 1088m, 1047w, 930m, 871m, 817s, 801m; δ_H (300 MHz; $CDCl_3$) 7.17-7.10 (3H, m, Ar *H*), 7.02 (2H, d, *J* 7.0, Ar *H*), 6.84 (2H, d, *J* 8.3, Ar *H*), 4.15 (3H, s, N*H* and NH_2), 2.33 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 140.3 (Ar *C*), 138.4 (Ar *C*), 134.4 (Ar *C*), 130.8 (Ar *C*H), 129.9 (Ar *C*), 124.4 (q, $^1J_{CF}$ 271.5, CF_3,), 124.8 (q, $^2J_{CF}$ 35.2, Ar *C*), 119.4 (Ar *C*H), 118.0 (Ar *C*H), 116.7 (q, $^3J_{CF}$ 4.0, Ar *C*H), 113.1 (q, $^3J_{CF}$ 4.0, Ar *C*H), 20.6 (CH_3); δ_C (75 MHz; $CDCl_3$, DEPT-135) 130.8 (q, $^3J_{CF}$ 4.0, Ar *C*H), 119.4 (Ar *C*H), 118.0 (Ar *C*H), 116.7 (q, $^3J_{CF}$ 4.0, Ar *C*H), 113.1 (Ar *C*H), 20.6 (CH_3); *m/z* (EI) 266 (M^+, 100%), 251 (63), 250 (21), 122 (4), 106 (4), 91 (7), 79 (5), 65 (5); (Found: M^+, 266.1030. $C_{14}H_{13}F_3N_2$ requires *M*, 266.1031).

*6.2.3.10 5-Fluoro-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93j***

Colorless oil (63 mg, 66%). (Found: C, 72.36; H, 6.26; N, 13.02. $C_{13}H_{13}FN_2$ requires C, 72.20; H, 6.06; N, 13.95%); λ_{max}(DCM)/nm 232 (log ε 3.73), 275 (3.60), 305 (3.47); ν_{max}(cm^{-1}) 3365w (Ar NH), 3030w (Ar CH), 2974w, 2921w, 2868w, 1608m, 1512s, 1480m, 1447m, 1397m, 1373w, 1344w, 1312m, 1302m, 1263m, 1244m, 1211w, 1180w, 1146m, 1108w, 1092w, 1038w, 1010w, 978m, 970m, 933m, 904m, 850m, 809s, 786m; δ_H (300 MHz; $CDCl_3$) 7.13 (2H, d, *J* 8.1, Ar *H*), 6.92-6.84 (3H, m, Ar *H*), 6.77-6.72 (1H, m, Ar *H*), 6.68-6.62 (1H, m, Ar *H*), 5.35 (1H, s, N*H*), 3.46 (2H, s, NH_2) 2.35 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 158.5 (Ar *C*), 155.3 (Ar *C*), 140.8 (Ar *C*), 134.5 (Ar *C*), 130.3 (Ar *C*), 129.9 (Ar *C*H), 117.5 (Ar *C*H), 117.0 (Ar *C*H), 109.0 (Ar *C*H), 106.9 (Ar *C*H), 20.54 (CH_3); δ_C (75 MHz; $CDCl_3$; Dept-135) 129.9 (Ar *C*H), 117.5 (Ar *C*H), 117.0 (Ar *C*H), 109.0 (Ar *C*H), 106.9 (Ar *C*H), 20.5 (CH_3); *m/z* (EI) 216 (M^+, 100%), 201 (58), 200

(36), 185 (5), 137 (6), 125 (10), 107 (17), 98 (28), 91 (28), 77 (20), 65 (28), 63 (16), 57 (9), 51 (20).

*6.2.3.11 4-Fluoro-1-*N*-(*p*-tolyl)-1,2-benzenediamine* ***93k***

Colorless plates (77 mg, 81%); mp 85-86 °C (from water); (Found: C, 72.30; H, 6.00; N, 12.93. $C_{13}H_{13}FN_2$ requires C, 72.20; H, 6.06; N, 12.95%); λ_{max}(DCM)/nm 205 (log ε 3.98), 236 (4.09), 290 (3.78); v_{max}(cm^{-1}) 3421m (Ar NH), 3336m (Ar NH), 3300w, 3061w (Ar CH), 1613m, 1594w, 1506s, 1468w, 1435m, 1398w, 1385w, 1307w, 1284m, 1250s, 1217w, 1207w, 1158s, 1122m, 1110m, 1013w, 974m, 932w, 856s, 841w, 813s, 793m, 770m; δ_H (300 MHz; $CDCl_3$) 7.04-6.99 (3H, m, Ar *H*), 6.59 (2H, d, *J* 8.3, Ar *H*), 6.53-6.40 (2H, m, Ar *H*), 3.90 (3H, s, N*H*, NH_2) 2.28 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 162.8 (Ar *C*), 159.6 (Ar *C*), 143.5 (Ar *C*), 129.8 (Ar *C*H), 128.5 (Ar *C*), 127.3 (Ar *C*H), 124.2 (Ar *C*), 114.7 (Ar *C*H), 105.1 (Ar *C*H), 102.3 (Ar *C*H), 20.4 (*C*H_3); δ_C (75 MHz; $CDCl_3$; Dept-135) 129.8 (Ar *C*H), 127.3 (Ar *C*H), 114.7 (Ar *C*H), 105.1 (Ar *C*H), 102.3 (Ar *C*H), 20.4 (*C*H_3); *m/z* (EI) 216 (100%, M^+), 201 (51), 200 (23), 125 (8), 107 (8), 98 (11), 91 (6), 83 (5), 77 (5), 65 (7), 51 (5); (Found: M^+, 216.1066. $C_{13}H_{13}N_2F$ requires *M*, 216.1063);

6.2.4 Substituted 1,5-Bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzenes

Synthesis of 1,5-Bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzene **92b-k** follow the typical procedure described for 1,5-Bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzene **92a** except when noted and quantities of products **92b-k** are based on the same mol scale of typical procedure described for product **92a**.

*6.2.4.1 1,5-Bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzene* ***92a****; typical procedure:*

To a stirred solution of 1-*N*-(*p*-tolyl)-1,2-benzenediamine **93a** (1.0 g, 5.05 mmol) in EtOH (10 mL) at *ca*. 20 °C, 1,5-difluoro-2,4-dinitrobenzene **56** (0.5 g, 2.53 mmol) was added in one portion. The color of the reaction mixture became orange-red and Hünig's base (0.9 mL, 5.05 mmol) was then added in one portion. A red crystalline precipitate was observed in minutes. The reaction mixture was heated under reflux for 24 h, and then allowed to cool to *ca*. 20 °C. The red precipitate was filtered, washed with hot water and then with cold EtOH and dried. The precipitate often consisted of both mono- and disubstituted products. The *title compound* **92a** was obtained after recrystallisation by EtOH as red plates (1.1 g, 76%); mp 219-220 °C (from EtOH); (Found: C, 68.68; H, 5.09; N, 15.07. $C_{32}H_{28}N_6O_4$ requires C, 68.56; H, 5.03; N, 14.99%); λ_{max}(DCM)/nm 228 (log ε 4.16), 283 (4.32), 331 (4.19), 379 inf (3.94); ν_{max}(cm^{-1}) 3390w, 3373w and 3322m (Ar NH), 1653w, 1620s, 1601s, 1593s, 1565s, 1517s, 1483m, 1472m, 1461m, 1429w, 1408s, 1379w, 1340s, 1322s, 1311m, 1284s, 1247s, 1232m, 1207m, 1188m, 1161w, 1130w, 1120w, 1067m, 1044w, 930w, 897w, 830m, 804m, 753s, 745s; δ_H (300 MHz; DMSO-d_6) 9.39 (2H, s, N*H*), 8.97 (1H, s, Ar *H*), 7.44 (2H, s, N*H*), 7.08-7.03 (6H, m, Ar *H*), 6.97 (4H, d, *J* 8.3, Ar *H*), 6.82-6.77 (2H, m, Ar *H*), 6.70 (4H, d, *J* 8.3, Ar *H*), 5.91 (1H, s, Ar *H*), 2.19 (6H, s, C*H*$_3$); δ_C (75 MHz; DMSO-d_6) 146.8 (Ar *C*), 140.1 (Ar *C*), 140.0 (Ar *C*), 130.0 (Ar *C*), 129.5 (Ar *C*H), 127.7 (Ar *C*H), 127.5 (Ar *C*H), 125.1 (Ar *C*), 124.4 (Ar *C*), 119.8 (Ar *C*H), 119.4 (Ar *C*H), 118.4 (Ar *C*H), 116.5 (Ar *C*H), 95.1 (Ar *C*H), 20.4 (*C*H$_3$); δ_C (75 MHz; DMSO-d_6, DEPT-135) 129.5 (Ar *C*H), 127.7 (Ar *C*H), 127.5 (Ar *C*H), 119.8 (Ar *C*H), 119.4 (Ar *C*H), 118.4 (Ar *C*H), 116.5 (Ar *C*H), 95.1 (Ar *C*H), 20.4 (*C*H$_3$); *m/z* (EI) 560 (M$^+$, 100%), 546 (15), 513 (5), 496 (8), 479 (58), 468 (62), 454 (11), 420 (5), 405 (25), 388 (70), 375 (27), 359 (12), 345 (7), 317 (6), 300 (12), 284 (14), 277 (6), 271 (15), 257 (12), 243 (7), 239 (5), 232 (11), 221 (7), 219 (8), 209 (6), 207 (5), 195 (18), 183 (20), 180 (23), 167 (13), 154 (8), 140 (5), 128 (7), 118 (5), 116 (5), 115 (5), 106 (20), 91 (30), 79 (15), 77 (42), 65 (30), 51 (13); (Found M$^+$, 560.2168. $C_{32}H_{28}N_6O_4$ requires *M*, 560.2172).

*6.2.4.2 1,5-Bis{*N*-[5-methoxy-*N'*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92b***

Red plates (800 mg, 51%); mp 241-242 °C (from EtOH); (Found: C, 65.78; H, 5.99; N, 13.69. $C_{34}H_{32}N_6O_6$ requires C, 65.80; H, 5.20; N, 13.54%) λ_{max} (DCM)/nm 229 (logε 4.18), 281 (4.16), 327 (4.11), 388 inf (3.81); ν_{max}(cm^{-1}) 3414w, 3396w and 3334m (Ar NH), 3001w (Ar CH), 1653w, 1616s, 1608s, 1591m, 1581m, 1565s, 1526s, 1514s, 1481w, 1464m, 1452w, 1436m, 1408m, 1342m, 1342m, 1318s, 1286s, 1244s, 1204s, 1168m, 1149w, 1132w, 1114w, 1072m, 1045m, 1019w, 935w, 901w, 854m, 837m, 821m, 808s, 778m; δ_H (300 MHz; DMSO-d_6) 9.19 (2H, s, N*H*), 8.96 (1H, s, Ar *H*), 7.42 (2H, s, N*H*), 7.01 (4H, d, *J* 7.5, Ar *H*), 6.93 (2H, d, *J* 8.0, Ar *H*), 6.79 (4H, d, *J* 5.9, Ar *H*), 6.55 (2H, s, Ar *H*), 6.36 (2H, d, *J* 8.1, Ar *H*), 5.64 (1H, s, Ar *H*), 3.66 (6H, s, OC*H*$_3$), 2.22 (6H, s, C*H*$_3$); δ_C (75 MHz; DMSO-d_6) 158.9 (Ar *C*), 147.7 (Ar *C*), 141.7 (Ar *C*), 139.4

(Ar *C*), 130.3 (Ar *C*), 129.3 (Ar *C*H), 129.2 (Ar *C*H), 127.4 (Ar *C*H), 124.9 (Ar *C*), 120.0 (Ar *C*H), 118.2 (Ar *C*), 104.7 (Ar *C*H), 100.6 (Ar *C*H), 95.2 (Ar *C*H), 55.0 (O*C*H$_3$), 20.3 (*C*H$_3$); δ_C (75 MHz; DMSO-d_6, DEPT-135); 129.3 (Ar *C*H), 129.2 (Ar *C*H), 127.4 (Ar *C*H), 120.0 (Ar *C*H), 104.7 (Ar *C*H), 100.6 (Ar *C*H), 95.2 (Ar *C*H), 55.0 (O*C*H$_3$), 20.3 (*C*H$_3$); *m/z* (EI) 620 (M$^+$, 100%), 539 (14), 528 (10), 525 (7), 480 (7), 450 (7), 435 (6), 434 (6), 392 (10), 375 (13), 347 (5), 228 (91), 212 (7), 91 (7).

*6.2.4.3 1,5-Bis{*N*-[4-methoxy-*N'*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92c***

Red plates (690 mg, 44%); mp 187-188 °C (from EtOH); (Found: C, 65.72; H, 5.09; N, 13.51. $C_{34}H_{32}N_6O_6$ requires C, 65.80; H, 5.20; N, 13.54%); λ_{max}(DCM)/nm 228 (log ε 4.22), 284 (4.30), 336 (4.19), 383 inf (3.94); ν_{max}(cm^{-1}) 3408m and 3333m (Ar NH), 3028w (Ar CH), 2916w, 2859w, 1627m, 1603s, 1566s, 1518s, 1481m, 1456w, 1406m, 1397m, 1375w, 1323s, 1287s, 1250s, 1200s, 1163w, 1119m, 1069m, 1036w, 936w, 907w, 874m, 833m, 802s, 781w, 745m; δ_H (300 MHz; DMSO-d_6) 9.51 (2H, s, N*H*), 8.96 (1H, s, Ar *H*), 7.19 (2H, s, N*H*), 7.09 (2H, d, Ar *H*), 6.84-6.78 (8H, m, Ar *H*), 6.51 (4H, d, *J* 8.2, Ar *H*), 6.31 (1H, s, Ar *H*), 3.62 (6H, s, OC*H*$_3$), 2.13 (6H, s, C*H*$_3$); δ_C (75 MHz; DMSO-d_6) 155.1 (Ar *C*), 147.1 (Ar *C*), 142.8 (Ar *C*), 132.9 (Ar *C*), 130.2 (Ar *C*H), 130.1 (Ar *C*), 128.6 (Ar *C*H), 125.9 (Ar *C*), 122.1 (Ar *C*H), 117.5 (Ar *C*H), 114.3 (Ar *C*H), 112.1 (Ar *C*H), 96.1 (Ar *C*H), 74.4 (Ar *C*), 56.1 (O*C*H$_3$), 21.1 (*C*H$_3$); δ_C (75 MHz; DMSO-d_6, DEPT-135) 130.2 (Ar *C*H), 128.6 (Ar *C*H), 122.1 (Ar *C*H), 117.5 (Ar *C*H), 114.3 (Ar *C*H), 112.1 (Ar *C*H), 96.1 (Ar *C*H), 56.1 (O*C*H$_3$), 21.1 (*C*H$_3$); *m/z* (EI) 620 (M$^+$, 100%), 528 (17), 480 (9), 450 (26), 435 (8), 310 (7), 106 (7), 91 (6); (Found: M$^+$, 620.2382. $C_{34}H_{32}N_6O_6$ requires *M*, 620.2383).

*6.2.4.4 1,5-Bis{*N*-[5-methyl-*N'*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92d***

Red plates (1.2 g, 84%); mp 254-255 °C (from EtOH); (Found: C, 69.37; H, 5.56; N, 14.33. $C_{34}H_{32}N_6O_4$ requires C, 69.37; H, 5.48; N, 14.28%); λ_{max} (DCM)/nm 228 (log ε 4.22), 284 (4.35), 331 (4.22), 383 inf (3.96); ν_{max}(cm^{-1}) 3398m, 3378m and 3336m (Ar NH), 3091w, 3024w (Ar CH), 2918w, 2862w, 1621s, 1609m, 1593m, 1581m, 1566s, 1521s, 1486m, 1456w, 1436m, 1429m, 1408s, 1374w, 1340m, 1321s, 1287s, 1247s, 1207, 1193m, 1118m, 1070m, 1038w, 1018w 962w, 931w, 904w, 856w, 831w, 810s, 800m, 775w; δ_H (300 MHz; DMSO-d_6) 9.28 (2H, s, N*H*), 8.96 (1H, s, Ar *H*), 7.37 (2H, s, N*H*), 7.00-6.88 (8H, m, Ar *H*), 6.73 (4H, d, *J* 7.8, Ar *H*), 6.61 (2H, d, *J* 7.8, Ar *H*), 5.81 (1H, s, Ar *H*), 2.21 (12H, s, CH_3); δ_C (75 MHz; DMSO-d_6) 147.7 (Ar *C*), 140.2 (Ar *C*), 138.8 (Ar *C*), 138.4 (Ar *C*), 132.1 (Ar *C*), 129.8 (Ar *C*H), 128.9 (Ar *C*H), 127.2 (Ar *C*H), 125.4 (Ar *C*), 122.1 (Ar *C*), 121.0 (Ar *C*H), 120.5 (Ar *C*H), 116.2 (Ar *C*H), 96.4 (Ar *C*H), 21.4 (CH_3), 20.7 (CH_3); δ_C (75 MHz; DMSO-d_6, DEPT-135); 129.8 (Ar *C*H), 128.9 (Ar *C*H), 127.2 (Ar *C*H), 121.0 (Ar *C*H), 120.5 (Ar *C*H), 116.2 (Ar *C*H), 96.4 (Ar *C*H), 21.4 (CH_3), 20.74 (CH_3); *m/z* (EI) 588 (M^+, 100%), 507 (34), 496 (38), 448 (6), 418 (27), 402 (23), 387 (9), 386 (9), 376 (8), 359 (9), 345 (5), 331 (10), 312 (10), 298 (12), 283 (10), 271 (8), 260 (7), 254 (6), 247 (8), 239 (7), 231 (6), 212 (18), 197 (12), 180 (5), 106 (9), 91 (9), 79 (5), 65 (6); (Found 588.2492 $C_{34}H_{32}N_6O_4$ requires 588.2485).

*6.2.4.5 1,5-Bis{*N*-[4-methyl-*N*'-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92e***

Red plates (1.1 g, 74%); mp 197-199 °C (from EtOH); (Found: C, 69.45; H, 5.54; N, 14.15. $C_{34}H_{32}N_6O_4$ requires C, 69.37; H, 5.48; N, 14.28%); λ_{max}(DCM)/nm 228 (log ε 4.10), 278 (4.36), 331 (4.11), 381 inf (3.92); ν_{max}(cm^{-1}) 3409w and 3334m (Ar NH), 3029w (Ar CH), 2916w 2856w, 1628m, 1613m, 1567s, 1516s, 1481m, 1456w, 1448w, 1419w, 1406m, 1397m, 1375w, 1324s, 1287s, 1250m, 1201m, 1162w, 1120w, 1070m, 1036w, 935w, 874w, 833m, 802s; δ_H (300 MHz; DMSO-d_6) 9.42 (2H, s, N*H*), 8.96 (1H, s, Ar *H*), 7.32 (2H, s, N*H*), 7.02-6.87 (10H, m, Ar *H*), 6.61 (4H, d, *J* 8.1, Ar *H*), 6.10 (1H, s, Ar *H*), 2.15 (6H, s, CH_3), 2.15 (6H, s, CH_3); δ_C (75 MHz; DMSO-d_6) 151.8 (Ar *C*), 147.5 (Ar *C*), 141.6 (Ar *C*), 137.9 (Ar *C*), 130.4 (Ar *C*), 130.2 (Ar *C*H), 129.9 (Ar *C*), 128.8 (Ar *C*H), 127.9 (Ar *C*H), 127.6 (Ar *C*H), 125.8 (Ar *C*), 119.2 (Ar *C*H), 118.7 (Ar *C*H), 95.8 (Ar *C*H), 21.1 (CH_3), 21.0 (CH_3); δ_C (75 MHz; DMSO-d_6, DEPT-135) 130.2 (Ar *C*H), 128.8 (Ar *C*H), 127.9 (Ar *C*H), 127.6 (Ar *C*H), 119.2 (Ar *C*H), 118.7 (Ar *C*H), 95.8 (Ar *C*H), 21.1 (CH_3), 21.0 (CH_3)**;** *m/z* (EI) 588 (M^+, 100%), 541 (5), 524 (5), 507 (31), 496 (50), 448 (6), 418 (34), 403 (14), 402 (14), 387 (6), 294 (5), 106 (11), 91 (10), 79 (7), 65 (6); (Found: M^+, 588.2478. $C_{34}H_{32}N_6O_4$ requires *M*, 588.2485).

*6.2.4.6 1,5-Bis{*N*-[5-cyano-*N*'-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92f***

Similar treatment to typical procedure for **92a** but using THF as the solvent (65 °C) instead of EtOH gave the *title compound* as red plates (648 mg, 42%); mp 268-270 °C (from EtOH); (Found: C, 66.71; H, 4.32; N, 18.26. $C_{34}H_{26}N_8O_4$ requires C, 66.88; H, 4.29; N, 18.35%); λ_{max}(DCM)/nm 228 (log ε 4.33), 287 (4.33), 327 (4.21), 381 inf (4.06);

ν_{max}(cm^{-1}) 3335m (Ar NH), 2230m (C≡N), 1623m, 1590m, 1570s, 1525m, 1512m, 1489w, 1472w, 1458w, 1410m, 1363w, 1343m, 1325m, 1291s, 1252m, 1212m, 1192m, 1157w, 1112w, 1067m, 1019w, 976w, 938w, 829m, 814m; δ_H (300 MHz; DMSO-d_6) 9.54 (2H, s, N*H*), 8.97 (1H, s, Ar *H*), 7.85 (2H, s, N*H*), 7.31-7.23 (6H, m, Ar *H*), 7.07 (4H, d, *J* 7.5, Ar *H*), 6.77 (4H, d, *J* 7.4, Ar *H*), 5.70 (1H, s, Ar *H*), 2.24 (6H, s, CH_3); δ_C (75 MHz; DMSO-d_6) 146.4 (Ar *C*), 142.3 (Ar *C*), 139.0 (Ar *C*), 132.7 (Ar *C*), 130.6 (Ar *C*H), 130.3 (Ar *C*), 129.6 (Ar *C*H), 128.1 (Ar *C*H), 126.5 (Ar *C*), 123.2 (Ar *C*H), 121.8 (Ar *C*H), 119.4 (*C*≡N), 118.4 (Ar *C*H), 110.6 (Ar *C*), 97.2 (Ar *C*H), 21.3 (CH_3); δ_C (75 MHz; DMSO-d_6, DEPT-135); 130.6 (Ar *C*H), 129.6 (Ar *C*H), 128.1 (Ar *C*H), 123.2 (Ar *C*H), 121.8 (Ar *C*H), 118.4 (Ar *C*H), 97.2 (Ar *C*H), 21.3 (CH_3); *m/z* (EI) 610 (M$^+$, 100%), 576 (5), 546 (7), 529 (48), 518 (54), 505 (5), 503 (5), 470 (5), 439 (19), 425 (27), 410 (10), 407 (26), 395 (5), 373 (5), 358 (6), 342 (6), 333 (7), 327 (5), 323 (6), 312 (9), 305 (10), 295 (9), 284 (9), 269 (10), 258 (10), 247 (15), 233 (10), 231 (10), 223 (23), 212 (5), 208 (33), 192 (14), 179 (10), 164 (6), 153 (5), 151 (5), 140 (5), 129 (5), 127 (7), 116 (8), 109 (6), 106 (49), 91 (55), 84 (6), 79 (27), 77 (28), 69 (15), 65 (50), 56 (34), 51 (11).

*6.2.4.7 1,5-Bis{*N*-[4-cyano-*N′*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* **92g**

Similar treatment to typical procedure for compound **92a** but using THF as the solvent (65 °C) instead of EtOH gave the *title compound* as red plates (756 mg, 49%); mp 303-305 °C (from EtOH); (Found: C, 66.97; H, 4.33; N, 18.16. $C_{34}H_{26}N_8O_4$ requires C, 66.88; H, 4.29; N, 18.35%); λ_{max}(DCM)/nm 229 (log ε 4.19), 303 (4.50), 388 inf (3.83); ν_{max}(cm^{-1}) 3379w and 3304w (Ar NH), 2220m (C≡N), 1653w, 1623s, 1599s, 1577s, 1569s, 1517s, 1490w, 1472w, 1457w, 1430m, 1399m, 1333s, 1314m, 1287s, 1265m, 1252m, 1235m, 1200m, 1179w, 1117w, 1070m, 891m, 835m, 814m, 807s; δ_H (500 MHz; DMSO-d_6) 9.46 (2H, s, N*H*), 9.00 (1H, s, Ar *H*), 8.10 (2H, s, N*H*), 7.47 (2H, d, *J* 8.5, Ar *H*), 7.41 (2H, s, Ar *H*), 7.15 (4H, d, *J* 7.5, Ar *H*), 6.84 (2H, d, *J* 8.5, Ar *H*), 6.74 (4H, d, *J* 8.0, Ar *H*), 5.33 (1H, s, Ar *H*), 2.27 (6H, s, CH_3); δ_C (125 MHz; DMSO-d_6) 146.6 (Ar *C*), 146.1 (Ar *C*), 136.8 (Ar *C*), 133.2 (Ar *C*), 133.0 (Ar *C*H), 132.4 (Ar *C*H), 129.7 (Ar *C*H), 127.0 (Ar *C*H), 125.4 (Ar *C*), 123.6 (Ar *C*), 122.9 (Ar *C*H), 119.1 (*C*≡N), 112.7 (Ar *C*H), 98.5 (Ar *C*), 95.4 (Ar *C*H), 20.5 (CH_3); *m/z* (EI) 610 (M$^+$, 100%), 546 (6), 530 (12), 518 (27), 516 (18), 440 (16), 425 (14), 305 (9), 257 (6), 223 (6), 220 (12), 208 (7), 205 (7), 192 (5), 106 (18), 91 (13), 79 (6), 77 (5), 65 (10); (Found: M$^+$, 610.2068. $C_{34}H_{26}N_8O_4$ requires *M*, 610.2077).

*6.2.4.8 1,5-Bis{*N*-[5-trifluoromethyl-*N'*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitrobenzene* ***92h***

Similar treatment to typical procedure for compound **92a** but using THF as the solvent (65 ^{o}C) instead of EtOH gave the *title compound* **92h** as red plates (704 mg, 40%); mp 246-247 ^{o}C (from EtOH); (Found: C, 58.57; H, 3.78; N, 11.92. $C_{34}H_{26}F_6N_6O_4$ requires C, 58.62; H, 3.76; N, 12.06%); λ_{max}(DCM)/nm 230 (log ε 4.31), 283 (4.49), 326 (4.41), 380 inf (4.14); ν_{max}(cm^{-1}) 3423w, 3413w and 3313m (Ar NH), 1623m, 1606m, 1595m, 1573s, 1560w, 1539w, 1525m, 1513m, 1490w, 1495w, 1456w, 1441m, 1416m, 1340m, 1332m, 1311w, 1290s, 1251m, 1228w, 1192m, 1165s, 1109s, 1077m, 1065m, 944m, 926w, 875m, 856w, 829m, 813s; δ_H (500 MHz; $CDCl_3$) 9.37 (2H, s, N*H*), 9.27 (1H, s, Ar *H*), 7.30 (2H, d, *J* 1.0, Ar *H*), 7.14 (2H, d, *J* 8.5, Ar *H*), 7.07 (4H, d, *J* 8.0, Ar *H*), 7.01 (2H, dd, *J* 8.0, 1.0, Ar *H*), 6.70 (4H, d, *J* 8.5, Ar *H*), 5.89 (1H, s, Ar *H*), 5.72 (2H, s, N*H*), 2.32 (6H, s, C*H*$_3$); δ_C (125 MHz; $CDCl_3$) 146.9 (Ar *C*), 141.6 (Ar *C*), 137.0 (Ar *C*), 133.9 (Ar *C*), 131.1 (Ar *C*, q, $^{2}J_{CF}$ 32.7), 130.2 (Ar *C*H), 128.8 (Ar *C*H), 127.9 (Ar *C*H), 126.5 (Ar *C*), 125.8 (Ar *C*), 123.5 (Ar *C*, q, $^{1}J_{CF}$ 272.8), 121.4 (Ar *C*H), 116.1 (Ar *C*H), 111.5 (Ar *C*H), 96.9 (Ar *C*H), 20.8 (*C*H$_3$); δ_C (75 MHz; DMSO-d_6, DEPT-135); 129.5 (Ar *C*H), 128.4 (Ar *C*H), 127.1 (Ar *C*H), 121.1 (Ar *C*H), 114.7 (Ar *C*H), 110.1 (Ar *C*H), 95.9 (Ar *C*H), 20.4 (*C*H$_3$); *m/z* (EI) 696 (M$^+$, 100%), 677 (9), 661 (5), 632 (10), 615 (30), 604 (56), 556 (5), 526 (21), 511 (18), 495 (5), 348 (27), 339 (7), 327 (5), 307 (6), 300 (9), 263 (18), 258 (5), 256 (5), 251 (12), 106 (17), 91 (16), 79 (8), 77 (5), 65 (13).

*6.2.4.9 1,5-Bis{*N*-[4-trifluoromethyl-*N'*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitrobenzene* ***92i***

Red plates (1.3 g, 73%); mp 185-187 ^{o}C (from EtOH); (Found: C, 58.58; H, 3.75; N, 11.86. $C_{34}H_{26}F_6N_6O_4$ requires C, 58.62; H, 3.76; N, 12.06%); λ_{max}(DCM)/nm 228 (log ε 4.20), 287 (4.37), 322 (4.29), 388 inf (3.89); ν_{max}(cm^{-1}) 3396m and 3316m (Ar NH), 1622m, 1609m, 1592w, 1584w, 1570m, 1523m, 1515m, 1489w, 1471w, 1437m, 1408m, 1338s, 1320s, 1282, 1245m, 1230m, 1209m, 1185w, 1163m, 1118m, 1102s, 1075m, 1069m, 937w, 932w, 892m, 871w, 829m, 801m, 780w, 771w, 746m, 711m; δ_H (500 MHz; DMSO-d_6) 9.44 (2H, s, N*H*), 9.02 (1H, s, Ar *H*), 7.86 (2H, s, N*H*), 7.33-7.31 (4H, m, Ar *H*), 7.02 (4H, d, *J* 8.0, Ar *H*), 6.95 (2H, d, *J* 8.5, Ar *H*), 6.71 (4H, d, *J* 8.5, Ar *H*), 5.56 (1H, s, Ar *H*), 2.24 (6H, s, C*H*$_3$); δ_C (125 MHz; DMSO-d_6) 146.9 (Ar *C*), 145.0 (Ar *C*), 137.8 (Ar *C*), 132.3 (Ar *C*), 129.5 (Ar *C*H), 127.1 (Ar *C*H), 125.8 (Ar *C*H), 125.4 (Ar

C), 125.1 (Ar *C*H), 124.2 (Ar *C*, q, $^{1}J_{CF}$ 270.4), 123.4 (Ar *C*H), 122.2 (Ar *C*H), 117.9 (Ar *C*, q, $^{2}J_{CF}$ 32.7), 113.1 (Ar *C*H), 94.9 (Ar *C*H), 20.4 (CH_3); *m/z* (EI) 696 (M$^+$, 100%), 677 (12), 659 (7), 649 (5), 630 (97), 615 (10), 604 (35), 584 (8), 564 (7), 552 (25), 545 (4), 526 (28), 511 (25), 495 (6), 429 (5), 421 (5), 419 (5), 352 (5), 348 (18), 339 (6), 327 (6), 301 (7), 263 (19), 258 (5), 251 (16), 180 (5), 106 (27), 91 (32), 79 (14), 77 (9), 65 (18).

*6.2.4.10 1,5-Bis{*N*-[5-fluoro-*N′*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92j***

Red needles (1.2 g, 79%); mp 240-241 °C (from EtOH); (Found: C, 64.52; H, 4.31; N, 14.09. $C_{32}H_{26}F_2N_6O_4$ requires C, 64.42; H, 4.39; N, 14.09%); λ_{max}(DCM)/nm 228 (log ε 4.22), 277 (4.32), 323 (4.26), 393 inf (3.88); ν_{max}(cm^{-1}) 3401m, 3378w and 3317m (Ar NH), 1610s, 1586m, 1569s, 1521s, 1511s, 1486m, 1472w, 1465w, 1446m, 1436w, 1414s, 1345s, 1327m, 1314m, 1308m, 1287s, 1244s, 1209m, 1190w, 1177w, 1161m, 1121w, 1096w, 1068m, 989m, 846w, 830m, 815s, 796m; δ_H (300 MHz; DMSO-d_6) 9.28 (2H, s, N*H*), 8.98 (1H, s, Ar *H*), 7.64 (2H, s, N*H*), 7.07-6.99 (6H, m, Ar *H*), 6.78 (4H, d, *J* 8.2, Ar *H*), 6.65 (2H, dd, *J* 11.5, 2.6, Ar *H*), 6.55 (2H, ddd, *J* 8.3, 8.2, 2.6, Ar *H*), 5.51 (1H, s, Ar *H*), 2.24 (6H, s, CH_3); δ_C (75 MHz; DMSO-d_6) 163.3 (Ar *C*), 160.1 (Ar *C*), 147.4 (Ar *C*), 143.2 (Ar *C*), 138.5 (Ar *C*), 131.6 (Ar *C*H), 130.5 (Ar *C*H), 129.6 (Ar *C*H), 125.2 (Ar *C*), 121.1 (Ar *C*H), 120.6 (Ar *C*), 105.0 (Ar *C*H), 100.7 (Ar *C*H), 95.2 (Ar *C*H), 20.4 (CH_3); δ_C (75 MHz; DMSO-d_6, DEPT-135); 131.6 (Ar *C*H), 130.5 (Ar *C*H), 129.6 (Ar *C*H), 121.1 (Ar *C*H), 105.0 (Ar *C*H), 100.7 (Ar *C*H), 95.2 (Ar *C*H), 20.4 (CH_3); *m/z* (EI) 596 (M$^+$, 100%), 532 (7), 515 (42), 504 (35), 500 (5), 456 (6), 426 (15), 411 (18), 394 (7), 381 (6), 363 (5), 335 (10), 319 (7), 306 (5), 289 (6), 277 (5), 275 (5), 250 (6), 239 (5), 237 (5), 216 (27), 213 (12), 201 (20), 185 (7), 130 (6), 106 (19), 91 (27), 79 (11), 77 (9), 65 (19); (Found: M$^+$, 596.1977. $C_{32}H_{26}F_2N_6O_4$ requires *M*, 596.1984).

*6.2.4.11 1,5-Bis{*N*-[4-fluoro-*N′*-(*p*-tolyl)-1,2-benzenediamino]}-2,4-dinitro-benzene* ***92k***

Red plates (1.0 g, 69%); mp 200-202 °C (from EtOH); (Found: C, 64.36; H, 4.22; N, 13.94. $C_{32}H_{26}F_2N_6O_4$ requires C, 64.42; H, 4.39; N, 14.09%); λ_{max}(DCM)/nm 223 (log ε 4.46), 277 (4.47), 321 (4.33), 396 inf (4.47); ν_{max}(cm^{-1}) 3379w, 3366w and 3312m (Ar NH), 1630m, 1601m, 1568s, 1516s, 1490m, 1482m, 1434m, 1429m, 1407m, 1395m, 1340m, 1326s, 1287s, 1273s, 1262s, 1233m, 1206m, 1196m, 1159m, 1152m, 1120w, 1102m, 1068m, 982w, 973w, 924w, 974m, 865m, 829m, 802s, 780m, 769w, 744m, 705m; δ_H (300 MHz; DMSO-d_6) 9.49 (2H, s, N*H*), 8.97 (1H, s, Ar *H*), 7.40 (2H, s, N*H*), 7.08-6.93 (10H, m, Ar *H*), 6.64 (4H, d, *J* 7.5, Ar *H*), 5.97 (1H, s, Ar *H*), 2.18 (6H, s, CH_3); δ_C (75 MHz; DMSO-d_6) 157.4 (Ar *C*), 154.3 (Ar *C*), 146.0 (Ar *C*), 140.4 (Ar *C*), 136.4 (Ar *C*), 129.4 (Ar *C*H), 127.5 (Ar *C*), 127.4 (Ar *C*H), 125.2 (Ar *C*), 118.7 (Ar *C*H), 118.6 (Ar *C*H), 118.4 (Ar *C*H), 114.0 (Ar *C*H), 95.7 (Ar *C*H), 20.3 (CH_3); δ_C (75 MHz; DMSO-d_6, DEPT-135) 129.4 (Ar *C*H), 127.4 (Ar *C*H), 118.7 (Ar *C*H), 118.6 (Ar *C*H), 118.4 (Ar *C*H), 114.0 (Ar *C*H), 95.7 (Ar *C*H), 20.3 (CH_3); *m/z* (EI) 596 (M^+, 100%), 532 (5), 515 (10), 504 (44), 456 (6), 426 (45), 411 (25), 395 (8), 335 (7), 319 (6), 305 (6), 298 (12), 289 (6), 277 (7), 254 (5), 250 (8), 243 (6), 239 (8), 224 (5), 213 (16), 198 (14), 185 (9), 106 (30), 91 (31), 83 (5), 79 (17), 65 (22), 57 (7).

*6.2.4.12 4-(5-Ethoxy-2,4-dinitrophenylamino)-3-(*p*-tolylamino)benzonitrile* ***107a***

As in typical procedure for compound **92a**, treatment of 5-cyano-1-*N*-(*p*-tolyl)-1,2-benzenediamine **93f** with 1,5-difluoro-2,4-dinitrobenzene **56** gave the *title compound* **107a** as yellow-orange plates (668 mg, 61%); mp 228-229 °C (from EtOH); (Found: C, 61.07; H, 4.36; N, 16.08. $C_{22}H_{19}N_5O_5$ requires C, 60.97; H, 4.42; N, 16.16%); ν_{max}(cm^{-1}) 3328w (Ar NH), 3304w (Ar CH), 2239w (C≡N), 1622s, 1597w, 1574s, 1568s, 1543w, 1529m, 1511s, 1505m, 1494w, 1471w, 1452w, 1432m, 1415m, 1400m, 1375w, 1350m, 1336m, 1309m, 1289s, 1262s, 1243s, 1216w, 1185w, 1126w, 1114w, 1070m, 1027m, 980w, 940w, 910w, 887m, 854w, 829m, 817s, 770m, 7766w, 749m; *m/z* (EI) 433 (M^+, 100%), 399 (5), 387 (35), 372 (8), 358 (5), 342 (5), 340 (4), 324 (6), 312 (10), 296 (23), 282 (15), 267 (24), 256 (6), 244 (6), 231 (5), 223 (12), 208 (16), 205 (11), 192 (8), 179 (5), 106 (23), 91 (20), 79 (12), 77 (11), 65 (19), 53 (7).

*6.2.4.13 3-(5-Ethoxy-2,4-dinitrophenylamino)-4-(*p*-tolylamino)benzonitrile* ***107b***

As in typical procedure for compound **92a**, treatment of 4-cyano-1-*N*-(*p*-tolyl)-1,2-benzenediamine **93g** with 1,5-difluoro-2,4-dinitrobenzene **56** gave the *title compound* **107b** as red plates (657 mg, 60%); mp 205-207 °C (from EtOH); ν_{max}(cm^{-1}) 3324m (Ar NH), 2216m, 1653w, 1619m, 1600m, 1580s, 1570m, 1539m, 1515s, 1490w, 1481w, 1473w, 1457w, 1448w, 1428m, 1401m, 1387w, 1363w, 1354m, 1330s, 1314m, 1299s, 1291s, 1275m, 1262m, 1248s, 1204w, 1181w, 1157w, 1118w, 1113w, 1066m, 1053m, 1037w, 1032w, 1017w, 1006w, 958w, 923w, 908w, 885w, 847w, 832m, 818m, 804w,792w, 775w, 767w, 742w; *m/z* (EI) 433 (M^+, 69%), 407 (100), 387 (17), 373 (10), 358 (12), 344 (5), 326 (8), 312 (18), 298 (16), 282 (10), 269 (14), 267 (13), 244 (5), 223

(31), 208 (27), 203 (5), 197 (5), 192 (8), 179 (6), 164 (5), 106 (40), 102 (5), 91 (35), 81 (6), 77 (20), 69 (5), 65 (32), 57 (8), 55 (9), 51 (9).

6.2.4.14 N-*(5-Ethoxy-2,4-dinitrophenyl)*-N′-p-*tolyl-4-trifluoromethyl-benzene-1,2-diamine* ***107c***

As in typical procedure for compound **92a**, treatment of 5-trifluoromethyl-1-*N*-(*p*-tolyl)-1,2-benzenediamine **93h** with 1,5-difluoro-2,4-dinitrobenzene **56** gave the *title compound* **107c** as red plates (446 mg, 37%); *m/z* (EI) 476 (M^+, 100%), 431 (60), 339 (7), 311 (67), 251 (69), 106 (37), 91 (15), 79 (17), 65 (23), 51 (63).

6.2.5 Substituted 5,7-Di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides

Synthesis of 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ides **91b-k** follow the typical procedure described for 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **91a** except when noted and quantities of products **91b-k** are based on the same mol scale of typical procedure described for product **91a**.

*6.2.5.1 5,7-Di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91a****; typical procedure:*

To a suspension of 1,5-bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzene **92a** (100 mg, 0.18 mmol) in EtOH (20 mL) in a hydrogenation flask, 5% Pd/C (100 mg) was added. The flask was attached to the hydrogenator, evacuated, and flushed with hydrogen twice. Then the mixture was shaken under hydrogen at a pressure of 3 bar for 5-6 h. The hydrogenation was judged complete after the hydrogen pressure remained stable, the red color of the reagent was gone and there was no more starting material (by TLC). TLC at the end of the reaction showed only a colorless product that became blue on standing. The mixture was filtered (Celite®) and the brown colored filtrate was heated in air atmosphere until a deep green color developed. On standing green colored crystals precipitated which were collected by filtration and recrystallised to afford the *title compound* **91a** as green needles (73 mg, 87%), mp 343.61 °C (from EtOH); (Found: C, 82.61; H, 5.09; N, 11.93. $C_{32}H_{24}N_4$ requires C, 82.73; H, 5.21; N, 12.06%); λ_{max}(DCM)/nm 227 (log ε 3.95), 298 (4.69), 401 (4.23), 423 (4.62), 449 (3.56), 478 (3.68), 512 (3.44), 631 (3.75), 686 (4.08), 757 (4.13); ν_{max}(cm^{-1}) 3042w (Ar CH), 1560m, 1537w, 1505s, 1456m, 1441m, 1370w, 1350m, 1335m, 1308m, 1248m, 1192m, 1175m, 1140m, 1105w, 1028w, 972w, 916w, 824m, 814m, 729s, 721m; δ_H (500 MHz; CD_2Cl_2) 7.24 (4H, d, *J* 8.0, Ar *H*), 7.04 (2H, d, *J* 8.0, Ar *H*), 6.95-6.92 (6H, m, Ar *H*), 6.56 (2H, dd, *J* 7.8, 7.5, Ar *H*), 6.14-6.11 (3H, m, Ar *H*), 4.27 (1H, s, Ar *H*), 3.42 (1H, s, Ar *H*), 2.39 (6H, s, C*H*$_3$); δ_C (125 MHz; CD_2Cl_2) 150.8 (Ar *C*), 144.8 (Ar *C*), 144.1 (Ar *C*), 140.3 (Ar *C*), 134.3 (Ar *C*), 131.6 (Ar *C*H), 130.7 (Ar *C*), 127.7 (Ar *C*H), 127.1 (Ar *C*H), 125.9 (Ar *C*H), 122.8 (Ar *C*H), 116.3 (Ar *C*H), 103.3 (Ar *C*H), 93.0 (Ar *C*H), 21.3 (*C*H$_3$); *m/z* (EI) 464 (M^+, 100%), 450 (23), 373 (39), 357 (13), 277 (8), 262 (8), 232 (26), 169 (3), 105 (37), 91 (7), 77 (33), 65 (11), 51 (17); (Found: M^+, 464.2016. $C_{32}H_{24}N_4$ requires *M*, 464.2001).

*6.2.5.2 3,9-Dimethoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91b***

Similar treatment to typical procedure for compound **91a** but use of acid conditions (drops of HCl in the ethanolic solution) before refluxing followed by basic conditions (sat. NaOH) for the isolation of the *title compound* **91b** as green plates (29 mg, 31%); mp 239.76 °C (from EtOH); (Found: C, 77.89; H, 5.49; N, 10.62. $C_{34}H_{28}N_4O_2$ requires C, 77.84; H, 5.38; N, 10.68%); λ_{max}(DCM)/nm 290 (log ε 4.69), 399 (4.33), 421 (4.72), 477 (3.82), 686 (3.63), 749 (4.03), 825 (4.22); ν_{max}(cm^{-1}) 3186w, 3030w (Ar CH), 2920w, 2862w, 1595m, 1578m, 1528s, 1513s, 1429m, 1410m, 1379w, 1331m, 1308m, 1292m, 1271w, 1231m, 1204m, 1175w, 1136w, 1111w, 1034w, 1011m, 957w, 920w, 858m, 812s, 789w; *m/z* (EI) 525 (M^++1, 100%), 524 (M^+, 90), 510 (62), 509 (62), 493 (28), 492 (31), 401 (33), 262 (38), 247 (32), 216 (58), 184 (33), 127 (30), 111 (30), 103 (39), 97 (48), 95 (41), 91 (69), 85 (37), 83 (42), 81 (39), 77 (58), 71 (46), 69 (53), 67 (28), 65 (34), 57 (95), 56 (26), 55 (42), 51 (37).

*6.2.5.3 2,10-Dimethoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91c***

Green plates (19 mg, 20%); mp 336.33 °C (from EtOH); (Found: C, 77.93; H, 5.29; N, 10.73. $C_{34}H_{28}N_4O_2$ requires C, 77.84; H, 5.38; N, 10.68%); λ_{max}(DCM)/nm 259 (log ε 3.97), 308 (4.68), 414 (4.05), 436 (4.36), 536 (3.57), 605 (3.60), 668 (4.12), 722 (4.36); ν_{max}(cm^{-1}) 3063w (Ar CH), 2993w, 2934w, 2907, 2830w, 1831w, 1622m, 1607w, 1564m, 1506s, 1472s, 1437w, 1424m, 1393w, 1354m, 1329w, 1308m, 1285w, 1262m, 1234s, 1209m, 1182w, 1157m, 1136m, 1119m, 1080w, 1034m, 1024w, 976w, 914w, 855w, 824m, 812m, 801w, 789m; δ_H (500 MHz; CD_2Cl_2) 7.24 (4H, d, *J* 8.0, Ar *H*), 6.99 (4H, d, *J* 8.0, Ar *H*), 6.50 (2H, s, Ar *H*), 6.16 (2H, d, *J* 8.0, Ar *H*), 6.11 (1H, s, Ar *H*), 6.03 (2H, d, *J* 9.0, Ar *H*), 4.22 (1H, s, Ar *H*), 3.71 (1H, s, OCH_3), 2.39 (1H, s, CH_3); δ_C (125 MHz; CD_2Cl_2) 158.9 (Ar *C*), 150.8 (Ar *C*), 145.5 (Ar *C*), 142.8 (Ar *C*), 140.1 (Ar *C*), 134.6 (Ar *C*), 131.5 (Ar *C*H), 127.8 (Ar *C*H), 125.5 (Ar *C*), 117.0 (Ar *C*H), 112.0 (Ar *C*H), 106.7 (Ar *C*H), 103.5 (Ar *C*H), 92.2 (Ar *C*H), 55.7 (OCH_3), 21.3 (CH_3); *m/z* (EI) 524 (M^+, 41%), 481 (6), 433 (3), 390 (3), 262 (10), 241 (7), 211 (3), 142 (3), 91 (7), 69 (3), 65 (6), 64 (4), 57 (4), 55 (6); (Found: M^+, 524.2212. $C_{34}H_{28}N_4O_2$ requires *M*, 524.2212).

*6.2.5.4 3,9-Dimethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **91d***

Green plates (77 mg, 87%); mp 311.27 °C (from EtOH); (Found: C, 82.85; H, 5.59; N, 11.48. $C_{34}H_{28}N_4$ requires C, 82.90; H, 5.73; N, 11.37%); λ_{max}(DCM)/nm 296 (log ε 4.44), 402 (3.98), 424 (4.37), 449 (3.46), 478 (3.55), 510 (3.21), 638 (3.34), 709 (3.73), 779 (3.87); ν_{max}(cm^{-1}) 3048w (Ar CH), 2909w, 1553m, 1531w, 1503s, 1451m, 1368m, 1346m, 1308m, 1287w, 1250m, 1221m, 1209m, 1175m, 1128m, 1109m, 1020m, 945w, 817s, 802m, 727w, 692m; δ_H (500 MHz; CD_2Cl_2) 7.25 (4H, d, *J* 8.0, Ar *H*), 6.96 (4H, d, *J* 8.0, Ar *H*), 6.91 (2H, d, *J* 8.0, Ar *H*), 6.70 (2H, d, *J* 8.0, Ar *H*), 6.15 (1H, s, Ar *H*), 5.93 (2H, s, Ar *H*), 4.25 (1H, s, Ar *H*), 2.41 (1H, s, CH_3), 2.01 (1H, s, CH_3); *m/z* (EI) 492 (M^+, 100%), 401 (21), 385 (6), 311 (4), 246 (25), 238 (4), 231 (3), 193 (3), 91 (6), 64 (6), 51 (2).

*6.2.5.5 2,10-Dimethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **91e***

Green plates (36 mg, 41%); mp 340.07 °C (from EtOH); (Found: C, 83.04; H, 5.68; N, 11.41. $C_{34}H_{28}N_4$ requires C, 82.90; H, 5.73; N, 11.37%); 302 (log ε 4.70), 406 (4.20), 428 (4.56), 454 (3.62), 483 (3.61), 519 (3.56), 626 (3.61), 686 (4.05), 750 (4.23); ν_{max}(cm^{-1}) 3048w, 3026w (Ar CH), 3005w, 2909w, 2853w, 1831w, 1622w, 1572m, 1533w, 1514s, 1468m, 1435w, 1418m, 1381m, 1368m, 1350m, 1327m, 1308m, 1254w, 1233m, 1188m, 1179w, 1152m, 1130w, 1078w, 1030w, 1001w, 835m, 808s, 781s; δ_H (500 MHz; CD_2Cl_2) 7.23 (4H, d, *J* 8.0, Ar *H*), 6.93 (4H, d, *J* 8.0, Ar *H*), 6.84 (2H, s, Ar *H*), 6.39 (2H, dd, *J* 8.5, 1.5, Ar *H*), 6.11 (1H, s, Ar *H*), 6.01 (2H, d, *J* 8.5, Ar *H*), 4.23 (1H, s, Ar *H*), 2.38 (1H, s, CH_3), 2.17 (1H, s, CH_3); δ_C (125 MHz; CD_2Cl_2) 150.7 (Ar *C*), 144.6 (Ar *C*), 143.6 (Ar *C*), 140.1 (Ar *C*), 136.9 (Ar *C*), 134.4 (Ar *C*), 131.5 (Ar *C*H), 128.7 (*C*), 127.8 (Ar *C*H), 125.5 (Ar *C*H), 124.0 (Ar *C*H), 115.9 (Ar *C*H), 103.2 (Ar *C*H), 92.6 (Ar *C*H), 21.3 (Ar CH_3), 21.0 (Ar CH_3); *m/z* (EI) 492 (M^+, 100%), 433 (2), 401 (25), 386 (6), 371 (3), 311 (3), 262 (5), 246 (27), 238 (5), 201 (3), 192 (3), 91 (8), 65 (10).

*6.2.5.6 3,9-Dicyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91f***

Green plates (46 mg, 50%); mp 354.96 °C (from EtOH); (Found: C, 79.42; H, 4.24; N, 16.29. $C_{34}H_{22}N_6$ requires C, 79.36; H, 4.31; N, 16.33%); λ_{max}(DCM)/nm 315 (log ε 4.65), 424 (4.07), 450 (4.58), 502 (3.76), 625 (3.65), 681 (4.12), 744 (4.30); ν_{max}(cm^{-1}) 3023w (Ar CH), 2213s (C≡N), 1617w, 1596w, 1569w, 1559w, 1540s, 1506s, 1490w, 1453s, 1436m, 1430w, 1405w, 1374w, 1353s, 1324w, 1312m, 1257m, 1202w, 1190m, 1127w, 1031w, 1009w, 876m, 861m, 831m, 816s; δ_H (500 MHz; TFA-*d*) 7.74 (2H, dd, *J* 8.8, 1.5 Hz, Ar *H*), 7.65 (2H, d, *J* 8.0 Hz, Ar *H*), 7.48 (1H, s, C *H*), 7.42 (4H, d, *J* 8.5, Hz, Ar *H*), 7.22 (2H, d, *J* 1.5 Hz, Ar *H*), 7.07 (4H, d, *J* 8.5 Hz, Ar *H*), 5.46 (1H, s, C *H*), 2.45 (3H, s, CH_3); δ_C (125 MHz; TFA-*d*) 147.0 (*C*), 145.7 (Ar *C*), 144.6 (Ar *C*), 134.6 (Ar *C*H), 133.8 (Ar *C*H), 133.6 (Ar *C*), 133.3 (Ar *C*), 132.4 (Ar *C*), 126.9 (Ar *C*H), 124.7 (Ar *C*H), 121.5 (Ar *C*H), 115.8 (*C*N), 113.5 (*C*), 99.8 (Ar *C*H), 98.7 (Ar *C*H), 21.0 (Ar CH_3); *m/z* (EI) 514 (M^+, 32%), 424 (5), 407 (3), 258 (7), 249 (3), 107 (3), 105 (3), 97 (3), 91 (13), 84 (3), 81 (3), 77 (3), 71 (3), 65 (15), 51 (5).

*6.2.5.7 2,10-Dicyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91g***

Green plates (35 mg, 38%); mp 390.84 °C (from EtOH); (Found: C, 79.50; H, 4.26; N, 16.27. $C_{34}H_{22}N_6$ requires C, 79.36; H, 4.31; N, 16.33%); λ_{max}(DCM)/nm 228 (log ε 4.19), 315 (4.42), 411 (3.75), 435 (4.14), 461 (2.89), 494 (3.09), 654 (2.94), 721 (3.42), 795 (3.55); ν_{max}(cm^{-1}) 3034w (Ar CH), 2224m (C≡N), 1592w, 1566m, 1508s, 1457m, 1425w, 1410w, 1381w, 1358s, 1320m, 1314m, 1227m, 1195w, 1152w, 1030w, 895w, 872w, 833m, 818s, 801m; δ_H (500 MHz; TFA-*d*) 7.83 (2H, s, Ar *H*), 7.56 (2H, d, *J* 9.0 Hz, Ar *H*), 7.41 (1H, d, *J* 8Hz, Ar *H*), 7.36 (1H, s, C *H*), 7.06 (4H, d, *J* 8.0 Hz, Ar *H*), 6.94 (2H, d, *J* 9.0 Hz, Ar *H*), 5.51 (1H, s, C *H*), 2.44 (3H, s, CH_3); δ_C (125 MHz; TFA-*d*) 147.5 (*C*), 145.6 (Ar *C*), 144.3 (Ar *C*), 135.9 (Ar *C*), 134.0 (Ar *C*H), 133.7 (Ar *C*H), 132.6 (Ar *C*), 130.8 (Ar *C*), 126.9 (Ar *C*H), 124.7 (Ar *C*H), 121.4 (Ar *C*H), 115.7 (*C*N), 114.1 (*C*), 100.8 (Ar *C*H), 97.6 (Ar *C*H), 21.0 (Ar CH_3); *m/z* (EI) 514 (M$^+$, 13%), 416 (88), 401 (24), 367 (25), 263 (18), 242 (89), 199 (9), 184 (3), 152 (15), 139 (19), 128 (9), 124 (86), 121 (13), 109 (23), 107 (24), 103 (14), 99 (90), 92 (40), 84 (11), 80 (9), 79 (9), 74 (94), 71 (21), 68 (93), 62 (100), 55 (20), 53 (37).

*6.2.5.8 3,9-Ditrifluoromethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91h***

Green plates (62 mg, 57%); mp 384.80°C (from EtOH); (Found: C, 67.90; H, 3.52; N, 9.23. $C_{34}H_{22}F_6N_4$ requires C, 68.00; H, 3.69; N, 9.33%); λ_{max}(DCM)/nm 304 (log ε 4.77), 408 (4.26), 432 (4.67), 455 (3.66), 487 (3.77), 521 (3.11), 620 (3.72), 679 (4.13), 742 (4.24); ν_{max}(cm^{-1}) 3052w, 3032w (Ar CH), 1626w, 1613w, 1567w, 1509m, 1460w, 1439w, 1401w, 1359m, 1338m, 1322m, 1286s, 1258w, 1246s, 1223w, 1192w, 1171w, 1155m, 1127m, 1104s, 1070s, 1030w, 992m, 986m, 871w, 862w, 825m, 814s; δ_H (500 MHz; TFA-*d*) 7.71 (2H, dd, *J* 9.0, 1.0 Hz, Ar *H*), 7.63 (2H, d, *J* 8.5 Hz, Ar *H*), 7.44 (4H, d, *J* 8.0 Hz, Ar *H*), 7.37 (1H, s, C *H*), 7.09 (6H, d, *J* 8.0 Hz, Ar *H*), 5.45 (1H, s, C *H*), 2.47 (3H, s, CH_3); δ_C (125 MHz; TFA-*d*) 146.6 (*C*), 145.4 (Ar *C*), 144.1 (Ar *C*), 134.4 (Ar *C*, q, $^2J_{C\text{-}F}$ 35.2 Hz), 133.7 (Ar *C*H), 133.0 (Ar *C*H), 132.7 (Ar *C*), 132.3 (*C*), 128.7 (Ar *C*H, q, $^3J_{C\text{-}F}$ 2.5 Hz), 127.0 (Ar *C*H), 123.5 (Ar *C*, q, $^1J_{C\text{-}F}$ 272.9 Hz), 121.0 (Ar *C*H), 117.5 (Ar *C*H, q, $^3J_{C\text{-}F}$ 3.8 Hz), 99.6 (Ar *C*H), 97.6 (Ar *C*H), 21.0 (Ar CH_3); *m/z* (EI) 600 (M$^+$, 100%), 581 (4), 509 (26), 493 (6), 439 (3), 425 (3), 300 (16), 91 (11), 65 (11).

*6.2.5.9 2,10-Ditrifluoromethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91i***

Green plates (54 mg, 50%); mp 257.81°C (from EtOH); (Found: C, 68.10; H, 3.63; N, 9.29. $C_{34}H_{22}F_6N_4$ requires C, 68.00; H, 3.69; N, 9.33%); λ_{max}(DCM)/nm 228 (log ε 4.12), 302 (4.45), 401 (3.85), 424 (4.24), 483 (3.46), 639 (3.13), 705 (3.53), 771 (3.64); ν_{max}(cm^{-1}) 3030w (Ar CH), 1609w, 1576w, 1514s, 1470w, 1422m, 1387w, 1368w, 1356m, 1323s, 1283w, 1248w, 1206m, 1186m, 1161m, 1130m, 1109s, 1069s, 1030w, 957m, 876m, 835m, 806s, 729m, 720m, 679m; δ_H (500 MHz; TFA-*d*) 7.76 (2H, d, *J* 0.5 Hz, Ar *H*), 7.50 (2H, dd, *J* 9.0, 1.5 Hz, Ar *H*), 7.41 (4H, d, *J* 8Hz, Ar *H*), 7.36 (1H, s, C *H*), 7.05 (4H, d, *J* 8.5 Hz, Ar *H*), 6.91 (2H, d, *J* 9.0 Hz, Ar *H*), 5.46 (1H, s, C *H*), 2.44 (3H, s, CH_3); δ_C (125 MHz; TFA-*d*) 146.9 (*C*), 145.3 (Ar *C*), 143.9 (Ar *C*), 135.0 (Ar *C*, q, $^2J_{C\text{-}F}$ 35.2 Hz), 134.7 (Ar *C*), 133.5 (Ar *C*H), 132.9 (*C*), 128.0 (Ar *C*H, q, $^3J_{C\text{-}F}$ 2.5 Hz), 123.4 (Ar *C*, q,

$^1J_{\text{C-F}}$ 181.1 Hz), 120.2 (Ar *C*H), 117.5 (Ar *C*, q, $^3J_{\text{C-F}}$ 3.8 Hz), 99.9 (Ar *C*H), 97.2 (Ar *C*H), 21.0 (Ar *C*H$_3$); *m/z* (EI) 600 (M$^+$, 100%), 509 (26), 493 (8), 425 (3), 419 (4), 300 (20), 91 (17), 89 (5), 65 (23).

*6.2.5.10 3,9-Difluoro-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91j***

Green plates (32 mg, 36%); mp 411.97 °C (from EtOH); (Found: C, 76.87; H, 4.39; N, 11.15. $C_{32}H_{22}F_2N_4$ requires C, 76.79; H, 4.43; N, 11.19%); λ_{max}(DCM)/nm 226 (log ε 3.96), 291 (4.74), 394 (4.40), 416 (4.80), 445 (3.62), 474 (3.82), 506 (3.38), 650 (3.62), 722 (4.07), 793 (4.21); ν_{max}(cm^{-1}) 3050w, 3032w and 3007w (Ar CH), 1622w, 1578m, 1559m, 1547m, 1506s, 1449s, 1441m, 1395w, 1372m, 1350m, 1306m, 1285w, 1269m, 1242s, 1219s, 1188m, 1152m, 1132w, 1105s, 1030w, 999m, 984w, 964w, 877w, 868w, 835s, 802s, 782w, 729m, 710w; δ_{H} (500 MHz; TFA-*d*) 7.45 (2H, q, *J* 4.5 Hz, Ar *H*), 7.40 (4H, d, *J* 8.0 Hz, Ar *H*), 7.21-7.17 (2H, m, Ar *H*), 7.14 (1H, s, C *H*), 7.03 (4H, d, *J* 8.5 Hz, Ar *H*), 6.45 (2H, dd, *J* 8.8, 2.5 Hz, Ar *H*), 5.37 (1H, s, C *H*), 2.44 (3H, s, C*H*$_3$); δ_{C} (125 MHz; TFA-*d*) 165.4 (*C*), 163.4 (Ar *C*), 146.2 (Ar *C*), 145.1 (Ar *C*), 142.3 (Ar *C*), 134.2 (Ar *C*, d, $J_{\text{C-F}}$ 11.7 Hz), 133.5 (Ar *C*H), 133.0 (Ar *C*), 127.5 (*C*), 126.9 (Ar *C*H), 121.9 (Ar *C*H, d, $J_{\text{C-F}}$ 10.1 Hz), 121.0 (Ar *C*H, d, $J_{\text{C-F}}$ 25.1 Hz), 106.5 (Ar *C*H, d, $J_{\text{C-F}}$ 30.2 Hz), 99.5 (Ar *C*H), 96.3 (Ar *C*H), 21.0 (Ar *C*H$_3$); *m/z* (EI) 500 (M$^+$, 100%), 409 (33), 393 (11), 319 (5), 250 (18), 243 (2), 91 (10), 65 (20).

*6.2.5.11 2,10-Difluoro-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide* ***91k***

Green plates (51 mg, 57%); mp 391.31 °C (from EtOH); (Found: C, 76.85; H, 4.35; N, 11.01. $C_{32}H_{22}F_2N_4$ requires C, 76.79; H, 4.43; N, 11.19%); λ_{max}(DCM)/nm 299 (log ε 4.68), 404 (4.10), 426 (4.47), 453 (3.58), 481 (3.55), 518 (3.51), 611 (3.63), 668 (4.05), 727 (4.20); ν_{max}(cm^{-1}) 3036w (Ar CH), 1628w, 1566m, 1508s, 1462m, 1427m, 1391w, 1381w, 1368w, 1346m, 1310m, 1277w, 1237s, 1209w, 1192w, 1179w, 1157w, 1140w, 1107m, 1026w, 984m, 895w, 876m, 853w, 839w, 833m, 826m, 818s, 802m, 789m, 777m, 760w, 727w, 687m; δ_{H} (500 MHz; TFA-*d*) 7.37 (4H, d, *J* 8.5, Ar *H*), 7.18 (1H, s, Ar *H*), 7.14 (2H, dd, *J* 7.5, 2.0, Ar *H*), 7.02-6.99 (6H, m, Ar *H*), 6.76 (2H, dd, *J* 9.5, 4.5, Ar *H*), 5.30 (1H, s, Ar *H*), 2.41 (1H, s, C*H*$_3$); δ_{C} (125 MHz; TFA-*d*) 165.8 (Ar *C*), 145.0 (Ar *C*), 143.6 (Ar *C*), 133.5 (Ar *C*H), 133.2 (Ar *C*), 131.8 (Ar *C*), 131.7 (Ar *C*), 130.0

(*C*≡N), 127.0 (Ar *C*H), 122.1 (Ar *C*H), 120.4 (Ar *C*H), 106.0 (Ar *C*H), 98.8 (Ar *C*H), 97.0 (Ar *C*H), 21.0 (Ar CH_3); *m/z* (EI) 500 (M^+, 100%), 409 (31), 393 (9), 319 (5), 250 (23), 198 (3), 147 (2), 91 (9), 65 (17).

6.3 Compounds related to Chapter 4

6.3.1 *N*-Trifluoromethylphenyl Substituted Benzeneamines

Synthesis of *N*-(*p*-trifluoromethylphenyl) substituted benzeneamines **160** and **161** follow the typical procedure described for 1-*N*-(*p*-tolyl)-2-nitrobenzeneamine **94a** and 1-*N*-(*p*-tolyl)-1,2-benzenediamine **93a** respectively and quantities of products **160** and **161** are based on the same mol scale of the analogous typical procedures.

*6.3.1.1 1-*N*-(p-Trifluoromethylphenyl)-2-nitrobenzeneamine* ***160***

As in typical procedure of 1-*N*-tolyl-2-nitrobenzeneamine **94a**. Orange needles (1.6 g, 59%); mp 96-98 °C (from *n*-hexane); δ_H (300 MHz; $CDCl_3$) 9.47 (1H, s, N*H*), 8.22 (1H, dd, *J* 8.4, 1.5 Hz, Ar *H*), 7.65 (2H, d, *J* 8.4 Hz, Ar *H*), 7.48-7.35 (4H, m, Ar *H*), 6.93-6.87 (1H, m, Ar *H*); δ_C (75 MHz; $CDCl_3$) 142.4 (Ar *C*), 140.9 (Ar *C*), 135.7 (Ar *C*H), 134.5 (Ar *C*), 129.4 (Ar *C*), 126.9 (Ar *C*H, q, $^3J_{C-F}$ 3.8 Hz), 126.7 (Ar *C*H), 126.4 (Ar *C*, q, $^2J_{C-F}$ 32.5 Hz), 122.3 (Ar *C*H), 119.1 (Ar *C*H), 116.5 (Ar *C*H); δ_C (75 MHz; $CDCl_3$, DEPT-135) 135.7 (Ar *C*H), 126.9 (Ar *C*H, q, $^3J_{C-F}$ 3.8 Hz), 126.7 (Ar *C*H), 122.3 (Ar *C*H), 119.1 (Ar *C*H), 116.5 (Ar *C*H); *m/z* (EI) 282 (M^+, 100%), 279 (6), 265 (20), 263 (8), 248 (26), 235 (43), 216 (18), 185 (10), 183 (7), 167 (40), 149 (48), 145 (9), 140 (7), 125 (5), 113 (5), 95 (13), 83 (7), 75 (14), 71 (8), 63 (9), 57 (16), 55 (5).

*6.3.1.2 1-*N*-(*p*-Trifluoromethylphenyl)-1,2-benzenediamine* ***161***

As in typical procedure of 1-*N*-(*p*-tolyl)-1,2-benzenediamine **93a**. White plates (106 mg, 96%) (from *n*-hexane); δ_H (300 MHz; $CDCl_3$) 7.43 (2H, d, *J* 8.4 Hz, Ar H), 7.14-7.09 (2H, m, Ar *H*), 6.85-6.71 (4H, m, Ar H), 5.47 (1H, s, N*H*), 3.64 (2H, s, NH_2); δ_C (75 MHz; $CDCl_3$) 148.5 (Ar *C*), 142.7 (Ar *C*), 127.1 (Ar *C*H), 126.6 (Ar *C*H, q, $^3J_{C-F}$ 3.8 Hz), 126.5 (Ar *C*H), 126.3 (Ar *C*H), 122.9 (Ar *C*H), 120.5 (Ar *C*, q, $^2J_{C-F}$ 32.5 Hz), 119.2 (Ar *C*H), 116.3 (Ar *C*H), 113.7 (Ar *C*H); δ_C (75 MHz; $CDCl_3$, DEPT-135) 127.1 (Ar *C*H), 126.6 (Ar *C*H, q, $^3J_{C-F}$ 3.8 Hz), 126.5 (Ar *C*H), 119.2 (Ar *C*H), 116.3 (Ar *C*H), 113.7 (Ar

*C*H); *m/z* (EI) 252 (M$^+$, 100%), 251 (18), 237 (16), 231 (22), 213 (14), 182 (23), 118 (9), 116 (5), 107 (10), 91 (10), 80 (22), 65 (11), 53 (9).

6.3.2 *N*-Substituted Tetraamino-dinitrobenzenes **132**

Synthesis of 1,3-bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzene **132b** follows the typical procedure described for 1,3-bis[*N*-(phenyl)-1,2-benzenediamino]-2,4-dinitrobenzene **132a** and quantity of product is based on the same mol scale of typical procedure described for product **132a**.

*6.3.2.1 1,3-Bis[*N*-(phenyl)-1,2-benzenediamino]-2,4-dinitrobenzene* ***132a***

Typical procedure: To a stirred solution of the *N*-phenyl-1,2-benzenediamine **134a** (41.8 mg, 0.22 mmol) in EtOH (2 mL) at *ca*. 20°C, 1,3-dichloro-2,4-dinitrobenzene **133** (24.8 mg, 0.11 mmol) was added in one portion. The color of the reaction mixture became orange-red and Hünig's base (36 μL, 0.22 mmol) was then added in one portion. A red crystalline precipitate was observed in minutes time before even the reflux starts. The reaction mixture was heated under reflux (*ca*. 78 °C) for 48 h, and then allowed to cool to *ca*. 20 °C. The red precipitate was filtered, washed with hot water and then with cold EtOH and dried. The precipitate often was consisted of both mono- and di-substituted products. The *title compound* **132a** was obtained after recrystallisation by EtOH as red crystals (24 mg, 42%); mp 200-201 °C (from EtOH); δ_H (500 MHz; DMSO-d_6) 10.19 (1H, s, N*H*), 8.97 (1H, s, N*H*), 8.06 (1H, d, *J* 10.0 Hz, Ar *H*), 7.72 (1H, s, Ar *H*), 7.29-7.15 (8H, m, Ar *H*), 7.06 (1H, t, *J* 7.5, Ar *H*), 7.01-6.92 (6H, m, Ar *H*), 6.89-6.83 (2H, m, Ar *H*), 6.79 (1H, t, *J* 7.0, Ar *H*), 6.22 (1H, d, *J* 10.0 Hz, Ar *H*); δ_C (125 MHz; CDCl$_3$) 147.7 (Ar *C*), 142.3 (Ar *C*), 141.8 (Ar *C*), 141.6 (Ar *C*), 139.8 (Ar *C*), 137.8 (Ar *C*), 131.7 (Ar *C*H), 129.4 (Ar *C*H), 129.4 (Ar *C*H), 128.8 (Ar *C*), 128.7 (Ar *C*H), 127.9 (Ar *C*), 127.3 (Ar *C*H), 127.3 (Ar *C*H), 126.1 (Ar *C*), 124.7 (Ar *C*), 122.6 (Ar *C*H), 121.8 (Ar *C*H), 121.6 (Ar *C*H), 121.2 (Ar *C*H), 120.9 (Ar *C*H), 119.6 (Ar *C*H), 119.1 (Ar *C*H), 118.2 (Ar *C*H), 117.8 (Ar *C*H), 104.7 (Ar *C*H); *m/z* (EI) 532 (M$^+$, 8%), 485 (100), 468 (28), 451 (10), 438 (13), 408 (17), 391 (5), 375 (4), 361 (24), 346 (5), 283 (11), 270 (8), 258 (17), 243 (13), 231 (6), 219 (16), 207 (7), 195 (7), 181 (35), 167 (30), 154 (11), 140 (10), 129 (12), 117 (4), 115 (8), 102 (7), 93 (15), 77 (62), 65 (15), 51 (21).

*6.3.2.2 1,3-Bis[*N*-(*p*-tolyl)-1,2-benzenediamino]-2,4-dinitrobenzene* ***132b***

As in typical procedure of product **132a**. Red crystals (42%); mp 190-191 °C (from EtOH); (Found C, 68.46; H, 4.93; N, 14.90. $C_{32}H_{28}N_6O_4$ requires C, 68.56; H, 5.03; N, 14.9%); *m/z* (EI) 560 (M^+, 9%), 513 (35), 496 (20), 479 (13), 466 (7), 373 (13), 283 (7), 272 (9), 257 (7), 198 (7), 195 (13), 181 (14), 167 (12), 122 (7), 111 (8), 107 (15), 101 (7), 98 (19), 91 (40), 79 (22), 73 (15), 69 (28), 60 (24), 55 (67).

*6.3.2.3 1,3-Bis[*N*-(*n*-butyl)-1,2-benzenediamino]-2,4-dinitrobenzene* ***132c***

To a stirred solution of the *N*-butyl-1,2-benzenediamine **134c** (1.5 g, 8.9 mmol) in EtOH (10 mL) at *ca*. 20°C, 1,3-dichloro-2,4-dinitrobenzene **133** (0.7 g, 2.9 mmol) was added in one portion. The color of the reaction mixture became orange-red and Hünig's base (1.5 mL, 8.9 mmol) was then added in one portion. The reaction mixture was heated under reflux (*ca*. 78 °C) for 30 h, and then allowed to cool to *ca*. 20 °C. Dry flash chromatography (hexane / DCM, 7 : 3) gave 5-butyl-4-chloro-1-nitro-5,10-dihydrophenazine **146** (430 mg, 47%) as purple needles, mp 95-96 °C (from *n*-hexane); (Found C, 60.42; H, 4.92; N, 13.19. $C_{16}H_{16}ClN_3O_2$ requires C, 60.47; H, 5.08; N, 13.22%); λ_{max}(DCM)/nm 251 (log ε 4.57), 272 (3.92), 327 (3.83), 532 (3.69); δ_H (500 MHz; $CDCl_3$) 9.59 (1H, s, N*H*), 7.62 (1H, d, *J* 9.5 Hz, Ar *H*), 6.93 (1H, td, *J* 7.8, 7.5, 1.0 Hz, Ar *H*), 6.87 (1H, td, *J* 7.7, 7.5, 1.0 Hz, Ar *H*), 6.82 (1H, d, *J* 8.0 Hz, Ar *H*), 6.68 (1H, d, *J* 8.0 Hz, Ar *H*), 6.63 (1H, dd, *J* 7.8, 1.0 Hz, Ar *H*), 3.64 (2H, t, *J* 7.5 Hz, CH_2), 1.61-1.55 (2H, m, CH_2), 1.29 (2H, sextet, *J* 7.5 Hz, CH_2), 0.83 (3H, t, *J* 7.5 Hz, CH_3); δ_C (125 MHz; $CDCl_3$) 142.02 (Ar *C*), 135.9 (Ar *C*), 134.7 (Ar *C*), 134.0 (Ar *C*), 130.6 (Ar *C*), 129.6 (Ar *C*), 124.3 (Ar *C*H), 124.1 (Ar *C*H), 121.3 (Ar *C*H), 121.1 (Ar *C*H), 120.3 (Ar *C*H), 115.7 (Ar *C*H), 56.8 (*C*H_2), 29.7 (*C*H_2), 19.9 (*C*H_2), 13.8 (*C*H_3); *m/z* (EI) 319 (M^++2, 10%), 318 (M^++1, 6%), 317 (M^+, 29%), 263 (5), 261 (15), 260 (100), 243 (6), 216 (15), 215 (8), 214 (41), 213 (10), 179 (24), 178 (6), 153 (8), 152 (9), 151 (6), 132 (29), 131 (19), 118 (5), 109 (6), 108 (88), 107 (19), 104 (5), 102 (12), 91 (8), 90 (5), 81 (20), 80 (47), 78 (6), 77 (8), 76 (9), 75 (9), 65 (9), 64 (13), 63 (13), 62 (6), 57 (21), 55 (7), 54 (12), 53 (18), 52 (19), 51 (13). Further elution (hexane / DCM, 6 : 4) gave 5-butyl-dinitro-5,10-dihydrophenazine **148** as blue crystals (trace); *m/z* (EI) 328 (M^+, 82%), 271 (100), 255 (17), 225 (72), 211 (10), 206 (9), 179 (39), 164 (8), 152 (10), 127 (10), 102 (12), 77 (8), 76 (8), 57 (34), 55 (14). Further elution (hexane / DCM, 5 : 5) gave the *title compound* **132c** as red cotton needles (210 mg, 15%); mp 221-222 °C (from EtOH);

(Found C, 63.37; H, 6.41; N, 16.90. $C_{26}H_{32}N_6O_4$ requires C, 63.40; H, 6.55; N, 17.06%); δ_H (500 MHz; $CDCl_3$) 10.14 (1H, s, N*H*), 8.27 (1H, s, N*H*), 8.16 (1H, d, *J* 10.0 Hz, Ar *H*), 7.26 (1H, dt, *J* 14.5, 1.0 Hz, Ar *H*), 7.15 (1H, dt, *J* 14.5, 1.0 Hz, Ar *H*), 7.05 (1H, dd, *J* 8.0, 1.0 Hz, Ar *H*), 6.85 (1H, d, *J* 7.5 Hz, Ar *H*), 6.80-6.71 (3H, m, Ar *H*), 6.64-6.61 (1H, m, Ar *H*), 6.12 (1H, d, *J* 10.0 Hz, Ar *H*), 4.08 (1H, s, N*H*), 3.85 (1H, s, N*H*), 3.24 (2H, t, *J* 7.5 Hz, CH_2), 3.14 (2H, t, *J* 7.5 Hz, CH_2), 1.74 (2H, pentet, *J* 7.0 Hz, CH_2), 1.61-1.48 (4H, m, CH_2), 1.38 (2H, sextet, *J* 8.0 Hz, CH_2), 1.00 (3H, t, *J* 7.5 Hz, CH_3), 0.94 (3H, t, *J* 7.5 Hz, CH_3); δ_C (125 MHz; $CDCl_3$) 148.5 (Ar *C*), 144.6 (Ar *C*), 142.9 (Ar *C*), 142.4 (Ar *C*), 131.7 (Ar *C*H), 129.5 (Ar *C*H), 128.0 (Ar *C*H), 127.9 (Ar *C*H), 127.4 (Ar *C*), 125.3 (Ar *C*), 124.2 (Ar *C*), 121.8 (Ar *C*), 120.5 (Ar *C*H), 117.0 (Ar *C*H), 116.7 (Ar *C*H), 111.9 (Ar *C*H), 111.6 (Ar *C*H), 104.7 (Ar *C*H), 43.5 (CH_2), 43.2 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 20.3 (CH_2), 20.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3); *m/z* (EI) 492 (M^+, 16%), 446 (21), 428 (6), 389 (100), 368 (5), 357 (13), 354 (10), 343 (9), 341 (5), 329 (6), 326 (5), 324 (5), 312 (26), 299 (9), 285 (9), 270 (5), 256 (7), 254 (6), 241 (5), 194 (7), 181 (6), 169 (6), 164 (29), 156 (11), 149 (7), 122 (15), 119 (13), 92 (6), 77 (6), 65 (5), 57 (12).

*6.3.2.4 1,3-Bis[*N*-(*p*-trifluoromethylphenyl)-1,2-benzenediamino]-2,4-dinitrobenzene* ***132d***

To a stirred solution of the *N*-(*p*-trifluoromethylphenyl)-1,2-benzenediamine **161** (10.0 mg, 0.4 mmol) in EtOH (2 mL) at *ca.* 20°C, 1,3-dichloro-2,4-dinitrobenzene **133** (2.4 mg, 0.1 mmol) was added in one portion. The reaction mixture was heated under reflux (*ca.* 78 °C) for 10 d, and then allowed to cool to *ca.* 20 °C. The red precipitate was filtered, washed with hot water and then with cold EtOH and dried. The precipitate often was consisted of both mono- and di-substituted products. The *title compound* **132d** was obtained after recrystallisation by EtOH as red crystals (37 mg, 56%); mp 223-225 °C (from EtOH); (Found C, 57.42; H, 3.22; N, 12.45. $C_{32}H_{22}F_6N_6O_4$ requires C, 57.49; H, 3.32; N, 12.57%); δ_H (500 MHz; $CDCl_3$) 10.18 (1H, s, N*H*), 8.53 (1H, s, N*H*), 8.17 (1H, d, *J* 10.0 Hz, Ar *H*), 7.49 (4H, dd, *J* 19.0, 8.5 Hz, Ar *H*), 7.41 (2H, t, *J* 7.5 Hz, Ar *H*), 7.33-7.29 (2H, m, Ar *H*), 7.16 (2H, t, *J* 7.5 Hz, Ar *H*), 7.08 (2H, d, *J* 8.5 Hz, Ar *H*), 6.96-6.92 (3H, m, Ar *H*), 6.88 (1H, d, *J* 7.5 Hz, Ar *H*), 6.40 (1H, d, *J* 9.5 Hz, Ar *H*), 6.00 (1H, s, N*H*), 5.80 (1H, s, N*H*); δ_C (125 MHz; $CDCl_3$) *one peak missing* 147.0 (Ar *C*), 145.9 (Ar *C*), 145.6 (Ar *C*), 141.1 (Ar *C*), 137.1 (Ar *C*), 135.6 (Ar *C*), 131.8 (Ar *C*H), 130.6 (Ar *C*H), 128.6 (Ar *C*), 128.5 (Ar *C*H), 128.3 (Ar *C*), 127.3 (Ar *C*H), 126.9 (Ar *C*H), 126.7

(Ar *C*H, q, $^3J_{C\text{-}F}$ 3.8 Hz), 125.1 (Ar *C*), 124.4 (Ar *C*, q, $^1J_{C\text{-}F}$ 270.3 Hz), 124.6 (Ar *C*, q, $^1J_{C\text{-}F}$ 270.3 Hz), 124.1 (Ar *C*H), 123.2 (Ar *C*H), 123.2 (Ar *C*, q, $^2J_{C\text{-}F}$ 32.7 Hz), 122.6 (Ar *C*, q, $^2J_{C\text{-}F}$ 32.7 Hz), 121.3 (Ar *C*H), 120.8 (Ar *C*H), 120.2 (Ar *C*H), 116.7 (Ar *C*H), 116.6 (Ar *C*H), 104.7 (Ar *C*H); *m/z* (EI) 668 (M^+, 12%), 621 (6), 602 (17), 588 (6), 582 (7), 572 (62), 565 (5), 443 (8), 427 (31), 417 (6), 415 (5), 400 (8), 399 (4), 342 (9), 338 (5), 314 (6), 300 (5), 287 (7), 283 (10), 271 (6), 259 (5), 257 (21), 249 (12), 222 (5), 218 (5), 216 (7), 214 (5), 208 (5), 183 (40), 167 (18), 161 (5), 154 (11), 145 (23), 142 (6), 140 (8), 127 (7), 114 (5), 102 (5), 95 (9), 92 (5), 80 (5), 77 (13), 69 (7), 65 (8), 57 (10), 55 (8), 51 (9).

6.3.3 Oxy-tetraazapentacene Radicals

Synthesis of oxy-tetraazapentacene radicals follows the typical procedure described for oxy-tetraazapentacene radical **158a** (R = Phenyl).

*6.3.3.1 Oxy-tetraazapentacene radical **158a** (R = Phenyl); typical procedure:*

1,3-Bis[*N*-(phenyl)-1,2-benzenediamino]-2,4-dinitrobenzene **132a** (100 mg) was hydrogenated using Pd/C and H_2 in a Parr hydrogenator apparatus using EtOH (20 mL) and some THF (10 mL) as the solvents. The reaction was monitored by hydrogen uptake and once this had ceased the reaction was considered complete (confirmed by TLC). The reaction mixture was then filtered through Celite® to remove Pd/C and the ethanolic filtrate was then heated under an air atmosphere to give only a black mixture that was difficult to process. To the ethanolic filtrate before heating, acid (*ca.* 1 mL) was added (*e.g.*, HCl, HBr, HI, HBF_4, $HClO_4$ or HPF_6) and the filtrate was heated extensively in the open air using a heat gun until the initially colorless solution became deep lilac. In each case, after the heated ethanolic solution was allowed to cool to *ca.* 20 °C, a crystalline bronze solid precipitated and was isolated by filtration. To a suspension of the salt in EtOH, NaOH (*ca.* 1 equiv. in small pieces) was added and then gentle heating was applied until the NaOH dissolved and the color of the suspension changed from lilac to brown. On cooling, the free base was obtained as brown solid, isolated by filtration and then recrystallized from benzene or toluene (bulk recrystallization) or using DCE/pentane (vapor diffusion).

158a (HBF_4 salt): (Found C, 66.56; H, 3.87; N, 10.46. $C_{30}H_{21}BF_4N_4O$ requires C, 66.69; H, 3.92; N, 10.37%); **158a** (radical): (Found C, 79.76; H, 4.17; N, 12.46. $C_{30}H_{19}N_4O^{\bullet}$ requires C, 79.81; H, 4.24; N, 12.41%); λ_{max}(DCM)/nm 231 (log ε 3.74), 317 (4.14), 424

(4.01), 445 (4.31), 530 (3.34), 569 (3.30), 900 (3.35); ν_{max}(cm^{-1}) 33052w (Ar NH), 1615w, 1589w, 1572w, 1554s, 1533w, 1509m, 1492s, 1473w, 1462w, 1455w, 1439m, 1419w, 1386w, 1333s, 1303w, 1289w, 1278w, 1234m, 1198w, 1153w, 1141w, 1126w, 1071w, 1052w, 1030w, 1001w, 983w, 918w, 846w, 839w, 797m, 783m, 757m, 745s, 729s, 712s; *m/z* (EI) 451 (M$^+$, 100%), 375 (12), 374 (33), 373 (7), 372 (8), 358 (4), 298 (5), 297 (19), 296 (7), 225 (28), 77 (10), 51 (5).

*6.3.3.2 Oxy-tetraazapentacene radical **158c** (R =* n-*Butyl)*

158c (HBF_4 salt): (Found C, 62.48; H, 5.87; N, 11.06. $C_{26}H_{29}BF_4N_4O$ requires C, 62.41; H, 5.84; N, 11.20%); **158c** (radical): 239 (log ε 3.77), 311 (4.15), 418 (4.07), 442 (4.52), 524 (3.37), 562 (3.32), 900 (3.42); ν_{max}(cm^{-1}) 2957w (Ar NH), 2929w, 2863w, 1613w, 1560m, 1513m, 1489m, 1461w, 1443m, 1384w, 1340s, 1309w, 1296w, 1286w, 1253w, 1226m, 1209w, 1187w, 1156w, 1172m, 1130w, 1113w, 1101w, 1097w, 1063w, 1049w, 1032w, 1011w, 963w, 917w, 887w, 849w, 784m; *m/z* (EI) 411 (M$^+$, 100%), 395 (5), 383 (6), 366 (7), 354 (99), 351 (6), 340 (7), 335 (5), 326 (10), 322 (9), 310 (11), 298 (83), 283 (6), 271 (9), 255 (5), 206 (10), 180 (5), 169 (14), 168 (7), 155 (5), 151 (7), 147 (6), 142 (5), 129 (6), 121 (6), 102 (13), 77 (32), 69 (11), 65 (5), 57 (28), 51 (12), 50 (5).

*6.3.3.3 Oxy-tetraazapentacene radical **158d** (R =* p-$C_6H_4CF_3$*)*

158d (radical): 214 (log ε 3.97), 317 (4.10), 426 (4.01), 450 (4.38), 537 (3.44), 576 (3.45), 900 (3.36).

6.3.4 Mono- and Di-substituted Phenylbenzene-1,2-diamines **171** and **170**

*6.3.4.1 N-(3-Chloro-2,6-dinitro-4-(trifluoromethyl)phenyl)-N'-phenylbenzene-1,2-diamine **171***

To a stirred solution of the *N*-Phenyl-1,2-benzenediamine **134a** (3.61 g, 19.6 mmol) in EtOH (10 mL) at *ca.* 20^{o}C, 2,4-dichloro-1,3-dinitro-5-trifluoromethyl-benzene **169** (1.50 g, 4.9 mmol) was added in one portion. The reaction mixture was heated (*ca.* 80 ^{o}C) for 1.5 h, and then allowed to cool to *ca.* 20 ^{o}C. The reaction products were separeted and isolated after column chromatoghraphy (Hexane / DCM). The *title compound* **171** precipitated and was obtained after recrystallisation by EtOH as orange crystals (1.98 g, 89%); mp 135-137 ^{o}C (from EtOH); (Found C, 50.36; H, 2.63; N, 12.23. $C_{19}H_{12}ClF_3N_4O_4$

requires C, 50.40; H, 2.67; N, 12.37%); δ_H (300 MHz; $CDCl_3$) 9.40 (1H, s, N*H*), 8.61 (1H, s, N*H*), 7.30-7.19 (4H, m, Ar *H*), 7.06-6.89 (5H, m, Ar *H*), 5.78 (1H, s, Ar *H*); δ_C (75 MHz; $CDCl_3$) 141.7 (Ar *C*), 141.3 (Ar *C*), 139.7 (Ar *C*), 139.3 (Ar *C*), 133.9 (Ar *C*), 133.0 (Ar *C*), 129.7 (Ar *C*H), 129.5 (Ar *C*H), 127.0 (Ar *C*H), 126.7 (Ar *C*H, q, $^3J_{C\text{-}F}$ 6.3 Hz), 125.2 (Ar *C*H), 122.5 (Ar *C*H), 121.5 (*C*F_3, q, $^1J_{C\text{-}F}$ 273.2 Hz), 121.3 (Ar *C*H), 119.3 (Ar *C*H), 118.2 (Ar *C*H), 117.8 (Ar *C*, q, $^2J_{C\text{-}F}$ 34.7 Hz).

6.3.4.2 N^1,$N^{1'}$*-(2,4-Dinitro-6-(trifluoromethyl)-1,3-phenylene)bis(*N^2*-phenyl-benzene-1,2-diamine)* ***170***

(i) To a stirred solution of the *N*-phenyl-1,2-benzenediamine **134a** (96.8 mg, 0.50 mmol) in EtOH (3 mL) at *ca*. 20°C, 2,4-dichloro-1,3-dinitro-5-trifluoromethyl-benzene **169** (80.1 mg, 0.25 mmol) was added in one portion. The color of the reaction mixture became orange-red and Hünig's (89 μl, 0.50 mmol) was then added in one portion. A red crystalline precipitate was observed in minutes time before even the reflux starts. The reaction mixture was heated under reflux (*ca*. 78 °C) for 48 h, and then allowed to cool to *ca*. 20 °C. Dry flash chromatography (hexane / DCM, 7 : 3) gave the 1-chloro-4-nitro-10-phenyl-2-(trifluoromethyl)-5,10-dihydrophenazine **173** as purple plates (55 mg, 54%), mp 213-214 °C (from *n*-hexane); (Found C, 56.23; H, 2.70; N, 10.27. $C_{13}H_{12}N_2O_2$ requires C, 56.24; H, 2.73; N, 10.36%); λ_{max}(DCM)/nm 254 (log ε 4.57), 326 (3.83), 492 (3.72); δ_H (500 MHz; $CDCl_3$) 9.84 (1H, s, N*H*), 8.24 (1H, s, Ar *H*), 7.36-7.31 (4H, m, Ar *H*), 7.24-7.18 (2H, m, Ar *H*), 7.03-6.97 (2H, m, Ar *H*), 6.82-6.80 (1H, m, Ar *H*); δ_C (125 MHz; $CDCl_3$) 148.3 (Ar *C*), 142.6 (Ar *C*), 134.9 (Ar *C*), 134.1 (Ar *C*H), 133.3 (Ar *C*), 131.0 (Ar *C*), 129.8 (Ar *C*), 129.5 (Ar *C*H), 128.5 (Ar *C*), 125.8 (Ar *C*H), 125.8 (Ar *C*H), 125.5 (Ar *C*H), 123.2 (Ar *C*H), 122.1 (*C*F_3, q, $^1J_{C\text{-}F}$ 271.6 Hz), 121.1 (Ar *C*H, q, $^3J_{C\text{-}F}$ 6.3 Hz), 120.4 (Ar *C*, q, $^2J_{C\text{-}F}$ 32.7 Hz) 116.1 (Ar *C*H); *m/z* (EI) 409 (M^++2, 32%), 408 (M^++1, 18), 407 (M^+, 91), 390 (10), 389 (7), 388 (30), 361 (6), 360 (23), 359 (19), 358 (71), 328 (11), 324 (10), 323 (30), 322 (6), 303 (9), 290 (5), 289 (8), 282 (9), 276 (7), 254 (12), 253 (13), 247 (12), 227 (6), 152 (7), 149 (6), 128 (6), 127 (6), 113 (6), 102 (11), 99 (6), 97 (6), 95 (6), 93 (9), 91 (7), 88 (9), 86 (44), 85 (11), 84 (62), 83 (10), 81 (9), 79 (6), 78 (6), 77 (59), 76 (10), 75 (8), 71 (10), 70 (5), 69 (15), 67 (8), 65 (9), 64 (11), 63 (6), 59 (7), 57 (21), 56 (6), 55 (20), 51 (65), 50 (14). Further elution (hexane / DCM, 6 : 4) gave 1,4-dinitro-10-phenyl-2-(trifluoromethyl)-5,10-dihydrophenazine **176** as purple-blue plates (19 mg, 18%). mp 206-207 °C (from *n*-hexane); λ_{max}(DCM)/nm 254 (log ε 4.71), 308 (3.77), 559

(3.90); δ_H (500 MHz; $CDCl_3$) 10.21 (1H, s, N*H*), 7.82 (1H, d, *J* 0.5 Hz, Ar *H*), 7.49-7.41 (3H, m, Ar *H*), 7.39-7.36 (2H, m, Ar *H*), 6.83 (1H, td, *J* 7.8, 7.8, 1.0 Hz, Ar *H*), 6.75 (1H, td, *J* 8.0, 8.0, 1.5 Hz, Ar *H*), 6.63 (1H, dd, *J* 7.8, 1.0 Hz, Ar *H*), 6.47 (1H, d, *J* 8.0 Hz, Ar *H*); δ_C (125 MHz; $CDCl_3$) 141.3 (Ar *C*), 141.2 (Ar *C*), 137.5 (Ar *C*), 134.1 (Ar *C*), 132.2 (Ar *C*), 130.6 (Ar *C*H), 130.2 (Ar *C*H), 129.1 (Ar *C*H), 128.6 (Ar *C*), 127.6 (Ar *C*), 125.6 (Ar *C*H), 124.9 (Ar *C*H), 121.2 (*C*F_3, q, $^1J_{C\text{-}F}$ 272.9 Hz), 118.3 (Ar *C*H, q, $^3J_{C\text{-}F}$ 6.3 Hz), 117.6 (Ar *C*H), 116.1 (Ar *C*H), 114.4 (Ar *C*, q, $^2J_{C\text{-}F}$ 35.2 Hz); *m/z* (EI) 416 (M^+, 100%), 399 (11), 369 (76), 352 (11), 339 (5), 323 (60), 320 (9), 303 (15), 296 (7), 283 (10), 273 (11), 271 (11), 254 (46), 251 (5), 247 (11), 243 (6), 241 (8), 229 (7), 227 (12), 215 (6), 208 (6), 202 (8), 200 (10), 179 (6), 177 (9), 162 (6), 152 (22), 150 (8), 145 (6), 138 (10), 136 (5), 127 (18), 123 (9), 114 (13), 112 (6), 103 (12), 93 (7), 88 (8), 81 (7), 77 (39), 69 (9), 65 (8), 51 (34). Further elution (hexane / DCM, 5 : 5) gave 1,2-dinitro-5-phenyl-3-(trifluoromethyl)-5,10-dihydrophenazine **177** as blue cubes (trace). λ_{max}(DCM)/nm 251 (log ε 3.80), 320 (2.92), 585 (3.14); *m/z* (EI) 416 (M^+, 100%), 399 (8), 370 (17), 369 (69), 353 (6), 352 (10), 324 (16), 323 (48), 322 (43), 303 (8), 302 (8), 301 (9), 284 (7), 273 (5), 255 (13), 254 (32), 253 (24), 152 (7), 151 (5), 127 (5), 102 (5), 77 (10), 51 (7). Further elution (hexane / DCM, 4 : 6) gave the *title compound* **170** as red plates (9 mg, 3%); mp 90-91 °C (from EtOH); δ_H (500 MHz; DMSO-d_6) 7.48 (1H, s, N*H*), 7.47 (1H, s, N*H*), 7.21 (1H, s, N*H*), 7.48 (1H, s, N*H*), 7.47 (1H, s, Ar *H*), 7.21-7.13 (6H, m, Ar *H*), 7.07-7.04 (1H, m, Ar *H*), 7.00-6.95 (2H, m, Ar *H*), 6.90 (4H, d, *J* 8.0 Hz, Ar *H*), 6.83-6.68 (5H, m, Ar *H*); δ_C (125 MHz; $CDCl_3$) 143.2 (Ar *C*), 142.3 (Ar *C*), 142.0 (Ar *C*), 141.0 (Ar *C*), 138.6 (Ar *C*), 138.5 (Ar *C*), 138.0 (Ar *C*), 131.2 (Ar *C*), 129.6 (Ar *C*), 129.5 (Ar *C*H), 129.4 (Ar *C*H), 129.3 (Ar *C*H), 128.8 (Ar *C*H, q, $^3J_{C\text{-}F}$ 5.0 Hz), 128.2 (Ar *C*H), 127.3 (Ar *C*H), 127.1 (Ar *C*), 123.6 (Ar *C*H), 122.9 (*C*F_3, q, $^1J_{C\text{-}F}$ 272.8 Hz), 122.9 (Ar *C*H), 122.1 (Ar *C*H), 122.0 (Ar *C*H), 121.4 (Ar *C*H), 120.9 (Ar *C*H), 119.2 (Ar *C*H), 119.0 (Ar *C*H), 118.0 (Ar *C*H), 111.0 (Ar *C*, q, $^2J_{C\text{-}F}$ 35.2 Hz); *m/z* (EI) 600 (M^+, 28%), 553 (100), 551 (6), 537 (7), 520 (7), 508 (79), 487 (21), 469 (6), 467 (9), 450 (7), 444 (9), 438 (20), 430 (31), 415 (6), 409 (52), 365 (6), 390 (5), 384 (5), 361 (7), 359 (8), 351 (8), 347 (5), 339 (6), 332 (17), 325 (8), 318 (11), 253 (9), 243 (6), 218 (9), 215 (9), 204 (16), 195 (6), 184 (20), 167 (10), 156 (5), 77 (21).

(ii) To a stirred solution of the *N*-phenyl-1,2-benzenediamine **134a** (2.0 g, 11.0 mmol) at *ca.* 20°C, *N*-(3-chloro-2,6-dinitro-4-(trifluoromethyl)phenyl)-*N'*-phenylbenzene-1,2-diamine **171** (0.5 g, 1.1 mmol) was added in one portion. The reaction mixture was heated (*ca*. 80 ^{o}C) for 3 d, and then allowed to cool to *ca*. 20 ^{o}C. Dry flash chromatography (hexane / DCM, 7 : 3) gave 1-chloro-4-nitro-10-phenyl-2-(trifluoromethyl)-5,10-dihydrophenazine **173** as purple plates (45 mg, 15% based on recovered (33%) starting material **171**). Further elution (hexane / DCM, 4 : 6) gave the *title compound* **170** as red plates (367 mg, 83% based on recovered (33%) starting material **171**).

APPENDIX

Sections **Page**

I Computational Parameters

Computational Parameters related to Chapter 2

Table 39. Computational output parameters for singlet **TAP 51a** (X = NO_2, Y = NH_2, Z = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H13N9O4|GAUSSIAN|15-N
ov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization||0,1|
C,-1.2231569641,0.9381401015,-0.0000000987|C,-0.0000004303,1.613503911
8,-0.0000007105|C,1.2231560555,0.9381398563,-0.0000009917|C,1.20053638
69,-0.5312144982,-0.0000010937|C,-0.0000006345,-1.2598895314,-0.000001
3733|C,-1.2005375394,-0.5312142771,-0.0000002645|N,-2.4110115686,-1.15
04863616,0.0000006073|N,-2.3764150786,1.6293346155,0.0000005433|C,-3.5
541924861,0.9646687355,0.0000012914|C,-3.6217130914,-0.4685741299,0.00
00014246|H,-2.469737504,-2.1591810209,0.0000010329|C,-4.7680640944,1.6
695475119,0.0000013666|C,-4.8330360283,-1.1268038687,0.0000026039|C,-6
.0205536693,1.0382067275,0.0000009091|C,-6.031946391,-0.4007120602,0.0
000024252|H,-4.7125769427,2.7536510875,0.0000007392|H,-4.8987390571,-2
.2090828576,0.0000038359|N,2.4110103181,-1.1504868178,-0.0000008007|N,
2.3764142313,1.6293341624,-0.0000012004|C,3.6217118076,-0.4685748275,-
0.0000007379|C,3.5541915521,0.9646680267,-0.0000010699|H,2.4697360501,
-2.1591814908,0.0000000895|C,4.8330347473,-1.1268049444,0.0000001388|C
,4.7680634351,1.6695464349,-0.0000020544|C,6.0319445648,-0.4007131592,
-0.0000016339|C,6.0205526324,1.0382049472,-0.0000038747|H,4.7125769099
,2.7536500568,-0.0000030363|H,4.8987377379,-2.2090839461,0.0000024228|
H,-0.0000003306,2.6959944552,-0.0000006179|N,-7.2461372716,-1.16809149
03,0.0000065496|O,-7.1648657279,-2.4035316815,0.0000153588|O,-8.344402
9641,-0.5733579817,0.0000013306|N,7.2461385112,-1.1680919278,0.0000047
25|O,8.3444065611,-0.5733584552,0.0000169337|O,7.1648745571,-2.4035346
024,0.0000444824|N,7.1575166369,1.7796494388,-0.0000087664|N,-7.157516
09,1.7796534102,-0.0000018364|H,7.097963289,2.7852320522,0.0000008041|
H,8.0498728636,1.3065889816,-0.0000114755|H,-8.0498732133,1.3065947407
,-0.0000004405|H,-7.0979603257,2.7852358991,0.0000057163|N,-0.00000077
47,-2.6573212423,-0.0000019122|H,0.8417196316,-3.2031645809,-0.0000137
428|H,-0.8417213015,-3.2031644,-0.000010623||Version=IA32W-G09RevC.01|
State=1-A|HF=-1487.2147954|S2=0.|S2-1=0.|S2A=0.|RMSD=8.553e-009|RMSF=2
.088e-005|Dipole=-0.000019,-0.2876257,-0.0000399|Quadrupole=-37.913782
9,26.4583219,11.4554609,0.0000633,-0.0004342,0.0003102|PG=C01 [X(C18H1
```

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3N9O4)]||@
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Table 40. Computational output parameters for triplet **TAP 51a** (X = NO_2, Y = NH_2, Z = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H13N9O4(3)|GAUSSIAN|1
7-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization||0
,3|C,-1.221679925,0.9713276247,-0.0000191114|C,-0.0000056648,1.6605780
487,-0.0000280319|C,1.2216697687,0.9713301147,-0.000016088|C,1.2058145
239,-0.4629792264,-0.0000078307|C,-0.0000029046,-1.1903289882,-0.00003
26822|C,-1.2058219286,-0.4629822652,-0.0000139935|N,-2.4430293979,-1.0
934765397,0.0000094576|N,-2.3743825746,1.7048480434,-0.0000200466|C,-3
.55284577,1.0484011686,-0.000007335|C,-3.6334225237,-0.3923215134,0.00
00128475|H,-2.5106826971,-2.0997471201,0.0000510279|C,-4.7562345281,1.
7764856023,-0.0000079664|C,-4.8630808902,-1.0190335306,0.0000354664|C,
-6.0198691795,1.1704141683,0.0000107191|C,-6.0506222126,-0.2674638543,
0.0000343694|H,-4.6775649869,2.8591319322,-0.000022952|H,-4.952585467,
-2.098978519,0.000052301|N,2.4430235626,-1.0934703335,0.0000244597|N,2
.3743716891,1.7048519541,-0.0000158552|C,3.633414363,-0.3923147775,0.0
000290999|C,3.5528347347,1.0484075391,0.0000063997|H,2.5106791863,-2.0
997408666,0.0000793229|C,4.8630739792,-1.0190267513,0.0000712661|C,4.7
562243061,1.7764903311,-0.000008174|C,6.0506159706,-0.267461769,0.0000
748107|C,6.0198579269,1.170418127,0.0000101736|H,4.6775557004,2.859136
7763,-0.0000540862|H,4.9525763097,-2.098971235,0.0001201327|H,-0.00000
67588,2.7433363837,-0.0000361894|N,-7.2791960818,-1.0118181869,0.00005
54966|O,-7.2192706213,-2.2490733232,0.000073123|O,-8.3677890964,-0.396
4290894,0.0000554374|N,7.2792123539,-1.0118293486,0.0001660157|O,8.367
8514574,-0.3964842956,0.000137231|O,7.2193534714,-2.2491049459,0.00013
48506|N,7.1440590843,1.9317916251,-0.000069409|N,-7.1440728852,1.93178
34114,0.0000056912|H,7.0675350814,2.9361831851,-0.0000947583|H,8.04379
94878,1.4726597866,-0.0001829238|H,-8.0438129824,1.4726502658,0.000023
4744|H,-7.0675513959,2.9361750204,-0.0000022094|N,-0.0000012523,-2.583
0360319,-0.0000584825|H,0.8435296213,-3.1262508083,-0.0003343108|H,-0.
843530854,-3.1262527887,-0.0003077382||Version=IA32W-G09RevC.01|State=
3-A|HF=-1487.19502|S2=2.048355|S2-1=0.|S2A=2.001395|RMSD=9.316e-009|RM
SF=3.304e-005|Dipole=-0.0002563,0.1267662,-0.0004518|Quadrupole=-39.62
33418,28.3980905,11.2252513,0.0014422,-0.0019555,0.0019539|PG=C01 [X(C
18H13N9O4)]||@
```

Table 41. Computational output parameters for singlet **TAP 51b** (E = C≡N).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C19H11N5|GAUSSIAN|18-Nov
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|C,
-1.0471077946,-1.2472899664,0.|C,-1.7332163248,0.0000002175,0.|C,-1.04
71075413,1.2472901849,0.|C,0.4138205278,1.2045835685,0.|C,1.1158903234
,0.0000000963,0.|C,0.4138202033,-1.2045832921,0.|N,1.0565311433,-2.396
160505,0.|N,-1.7101398944,-2.4038631472,0.|C,-1.0160362812,-3.57539388
32,0.|C,0.4047053971,-3.6237502309,0.|H,2.0703838426,-2.3957462151,0.|
C,-1.7061707632,-4.8107090776,0.|C,1.1050657111,-4.8341666405,0.|C,-1.
0136806039,-6.0095501539,0.|C,0.3940646025,-6.0273837432,0.|H,-2.79066
51241,-4.7749542336,0.|H,-1.561222809,-6.947666694,0.|H,0.9283044848,-
6.9725201228,0.|H,2.1934877849,-4.8330818741,0.|N,1.0565316274,2.39616
0969,0.|N,-1.7101397685,2.4038636591,0.|C,0.4047059016,3.6237509758,0.
|C,-1.0160360429,3.5753946911,0.|H,2.0703844174,2.3957467018,0.|C,1.10
50662167,4.8341675963,0.|C,-1.7061706879,4.8107100463,0.|C,0.394064957
7,6.0273848352,0.|H,0.9283048561,6.9725212739,0.|C,-1.0136803774,6.009
5512495,0.|H,-1.5612226134,6.9476678335,0.|H,-2.7906651761,4.774955116
5,0.|H,2.193488359,4.8330828433,0.|H,2.2044682444,0.0000000842,0.|C,-3
.1567409347,0.0000004978,0.|N,-4.3215258636,0.0000005291,0.||Version=I
A32W-G09RevC.01|State=1-A'|HF=-1004.4023837|S2=0.|S2-1=0.|S2A=0.|RMSD=
4.434e-009|RMSF=6.297e-005|Dipole=4.7395257,-0.0000033,0.|Quadrupole=-
8.2501597,17.4438831,-9.1937234,0.0000098,0.,0.|PG=CS [SG(C19H11N5)]||
@
```

Table 42. Computational output parameters for triplet **TAP 51b** (E = C≡N).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C19H11N5(3)|GAUSSIAN|18-
Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
|C,-1.2449785837,0.4337597588,0.|C,0.0000000041,1.127429038,0.|C,1.244
9786928,0.4337597831,0.|C,1.2078526816,-0.9953774762,0.|C,0.0000000569
,-1.6920381325,0.|C,-1.2078525756,-0.9953774413,0.|N,-2.4314840308,-1.
6509200177,0.|N,-2.3968899524,1.1517240218,0.|C,-3.5720022475,0.462518
7009,0.|C,-3.6343165045,-0.9675089068,0.|H,-2.4448938954,-2.6615954153
,0.|C,-4.7929073116,1.1775469444,0.|C,-4.8646044883,-1.628349275,0.|C,
-6.0103129258,0.5144881613,0.|C,-6.0469129996,-0.8889921004,0.|H,-4.73
05463538,2.260958425,0.|H,-6.937033551,1.0804295257,0.|H,-7.0003535972
```

```
,-1.4091608971,0.|H,-4.8934609428,-2.7159556996,0.|N,2.4314841123,-1.6
509200252,0.|N,2.3968900023,1.1517240706,0.|C,3.6343166041,-0.96750883
87,0.|C,3.572002311,0.4625188086,0.|H,2.4448940611,-2.6615954304,0.|C,
4.864604727,-1.6283492028,0.|C,4.7929073512,1.1775470936,0.|C,6.046913
2548,-0.8889918863,0.|H,7.0003538932,-1.4091606366,0.|C,6.0103130174,0
.5144884145,0.|H,6.9370335994,1.0804298318,0.|H,4.7305463379,2.2609585
537,0.|H,4.8934612612,-2.7159556509,0.|H,0.0000000524,-2.780706365,0.|
C,0.0000000012,2.5543631225,0.|N,-0.0000000427,3.7181251436,0.||Versio
n=IA32W-G09RevC.01|State=3-A'|HF=-1004.3781486|S2=2.046511|S2-1=0.|S2A
=2.001412|RMSD=6.142e-009|RMSF=4.211e-005|Dipole=0.,-3.9445704,0.|Quad
rupole=16.7660309,-6.8856502,-9.8803806,0.0000005,0.,0.|PG=CS [SG(C19H
11N5)]||@
```

Table 43. Computational output parameters for singlet **TAP 51c** (Z = NO_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H11N5O2|GAUSSIAN|27-N
ov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|
C,-0.0005736253,-1.424317927,-0.0000016537|C,1.1941025693,-0.696104200
4,-0.0000084258|C,1.2390062164,0.7022954348,-0.0000021727|C,-0.0210080
171,1.4422952606,0.000008671|C,-1.2774579588,0.7445417947,0.0000136324
|C,-1.2654385125,-0.6926179549,0.0000112387|N,-2.387572961,-1.42240991
77,0.0000196396|N,0.0185662973,-2.7730569819,-0.0000081277|C,-1.146443
381,-3.4568637106,-0.0000017584|C,-2.4115980826,-2.8047511823,0.000012
6679|H,-3.2549860437,-0.8773618817,0.0000349333|C,-1.1525194664,-4.877
2909265,-0.0000090357|C,-3.6204673201,-3.5148391936,0.0000206193|C,-2.
344021516,-5.5750946082,-0.0000017563|C,-3.5851391359,-4.8995167016,0.
0000127398|H,-0.1921356294,-5.3823661532,-0.0000204589|H,-2.3300915404
,-6.6614924023,-0.0000074054|H,-4.5120661257,-5.4643301907,0.000018173
3|H,-4.5651633016,-2.9760593529,0.0000324943|N,0.0609645668,2.77835486
02,0.0000173217|N,2.4220144027,1.350338494,-0.0000078178|C,1.251934755
4,3.4805175879,0.0000126167|C,2.442858945,2.701045679,-0.0000008556|H,
-0.8407843518,3.2644915428,0.0000290579|C,1.274039284,4.8823382396,0.0
000207626|C,3.6758162272,3.4063594661,-0.0000067984|C,2.496295841,5.53
40033986,0.0000143733|H,2.5309411362,6.6189033221,0.0000201623|C,3.695
7905955,4.7870148037,0.0000009078|H,4.6479598694,5.3103000104,-0.00000
35927|H,4.5885981127,2.8196167542,-0.0000174717|H,0.3396602559,5.43881
85994,0.000031775|H,2.1294909887,-1.2413296616,-0.0000182309|N,-2.5008
463968,1.4578000792,0.0000156849|O,-3.5918453133,0.8392379875,-0.00009
16722|O,-2.4998788238,2.7119590221,-0.0001391476||Version=IA32W-G09Rev
```

```
C.01|State=1-A|HF=-1116.6714749|S2=0.|S2-1=0.|S2A=0.|RMSD=4.575e-009|R
MSF=4.741e-005|Dipole=-0.5940511,0.3459298,0.0001677|Quadrupole=-4.876
2536,12.0360974,-7.1598438,14.9319992,-0.0008941,0.0005975|PG=C01 [X(C
18H11N5O2)]||@
```

Table 44. Computational output parameters for triplet **TAP 51c** (Z = NO_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H11N5O2(3)|GAUSSIAN|2
8-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0
,3|C,1.2347014143,-1.0743827863,0.0000408631|C,0.0000284922,-1.7457816
372,0.0000277282|C,-1.2346564406,-1.0744035603,0.0000039533|C,-1.23975
81896,0.356860766,0.0000352281|C,0.0000047587,1.0767679276,0.000007854
7|C,1.2397767784,0.3568813897,-0.0000150178|N,2.4707122041,0.961193219
1,-0.0000903692|N,2.3696550355,-1.8316982637,0.0000731238|C,3.56411857
97,-1.1801416706,0.0000486505|C,3.6547978213,0.2440487522,-0.000040967
7|H,2.4694318887,1.9770517584,-0.0002409589|C,4.7690747761,-1.92155311
26,0.0000879536|C,4.895385678,0.8852759085,-0.0000934176|C,5.998254910
7,-1.2797910545,0.0000418542|C,6.0629546043,0.1230208035,-0.0000496509
|H,4.6884353265,-3.0038316609,0.0001521273|H,6.9144386896,-1.862897182
6,0.0000732242|H,7.0267151094,0.623483322,-0.0000875344|H,4.941441769,
1.9715075836,-0.0001638555|N,-2.4707067262,0.9611473053,0.0000750652|N
,-2.3695952161,-1.8317423245,-0.0000289113|C,-3.6547784201,0.243978931
2,0.0000240759|C,-3.5640715081,-1.1802095508,-0.0000322792|H,-2.469450
7701,1.9770054445,0.000197748|C,-4.8953786633,0.8851819398,0.000041187
3|C,-4.7690132607,-1.9216444746,-0.0000792865|C,-6.0629329882,0.122904
1101,-0.0000047879|H,-7.0267031591,0.6233480669,0.0000063726|C,-5.9982
059625,-1.279906342,-0.0000667633|H,-6.9143783828,-1.863030343,-0.0001
024968|H,-4.6883529539,-3.0039214074,-0.0001215368|H,-4.9414565399,1.9
714126899,0.0000868426|H,0.0000370046,-2.829579871,0.0000323799|N,0.00
00043944,2.5058528314,0.0000025552|O,1.0805832413,3.1303094242,-0.0002
096163|O,-1.0805652955,3.1303200677,0.0001716626||Version=IA32W-G09Rev
C.01|State=3-A|HF=-1116.649498|S2=2.046469|S2-1=0.|S2A=2.001397|RMSD=6
.829e-009|RMSF=1.925e-005|Dipole=0.0000075,0.2151295,-0.0000117|Quadru
pole=20.0257067,-12.1997737,-7.825933,0.0002022,-0.0003708,0.0000497|P
G=C01 [X(C18H11N5O2)]||@
```

Table 45. Computational output parameters for singlet **TAP 51d** (X = NO_2, Y = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|RB3LYP|6-31G(d)|C18H12N8O4|GAUSSIAN|12-N
ov-2012|0||# opt rb3lyp/6-31g(d) geom=connectivity||Optimization Singl
et||0,1|C,1.232543866,1.1044674773,-0.0000001625|C,0.000000093,1.77149
35425,0.0000001504|C,-1.232543518,1.1044672139,0.0000000122|C,-1.20366
53694,-0.3652300144,-0.0000004151|C,0.0000004358,-1.068470643,-0.00000
04744|C,1.203666106,-0.3652298141,-0.0000003981|N,2.3978729301,-0.9960
009367,-0.0000006848|N,2.3882273236,1.7889555923,-0.0000002671|C,3.560
0222951,1.109119346,-0.0000006954|C,3.616064712,-0.3258491813,-0.00000
07976|H,2.4143003478,-2.0100401172,-0.0000006503|H,0.0000005801,-2.156
8822699,-0.0000007237|C,4.779606672,1.8028681566,-0.0000007116|C,4.821
8075892,-0.9942982948,-0.0000009122|C,6.0270218308,1.1607662421,-0.000
0014335|C,6.025872971,-0.2778941034,-0.0000014096|H,4.7336816374,2.887
3931799,-0.0000005373|H,4.8771537295,-2.0769587165,-0.0000006777|N,-2.
3978719226,-0.9960013945,-0.0000009028|N,-2.3882269919,1.7889550354,0.
0000001407|C,-3.6160637319,-0.3258499896,-0.0000009814|C,-3.5600216686
,1.1091185891,-0.0000004199|H,-2.4142990562,-2.0100405272,-0.000001099
7|C,-4.8218062887,-0.9942996354,-0.0000015612|C,-4.7796061186,1.802867
2085,-0.0000001276|C,-6.0258712502,-0.2778949963,-0.0000022432|C,-6.02
70206579,1.1607644564,-0.0000015389|H,-4.7336816109,2.8873922043,0.000
0004598|H,-4.8771524213,-2.0769599213,-0.0000017303|H,0.0000000119,2.8
547561875,0.0000004183|N,7.2350666275,-1.0557799549,-0.000000896|O,7.1
4372454,-2.2896859353,0.0000025868|O,8.3370509806,-0.4690621044,0.0000
069647|N,-7.2350681049,-1.0557748938,-0.0000026433|O,-8.3370473541,-0.
4690474285,0.0000104438|O,-7.1437344735,-2.2896815525,0.0000031596|N,-
7.1693860145,1.8932926736,-0.0000031523|N,7.1693845108,1.8932985006,-0
.0000024086|H,-7.1175702244,2.8993437953,-0.0000010175|H,-8.0583664229
,1.4139389778,-0.0000225612|H,8.0583666991,1.4139483201,-0.0000159595|
H,7.1175645316,2.8993494759,-0.0000021222||Version=IA32W-G09RevC.01|St
ate=1-A|HF=-1431.8825016|RMSD=7.606e-009|RMSF=3.297e-006|Dipole=-0.000
004,0.2656831,-0.000036|Quadrupole=-33.6250024,21.4462187,12.1787837,0
.0001578,0.0000863,-0.0000161|PG=C01 [X(C18H12N8O4)]||@
```

Table 46. Computational output parameters for triplet **TAP 51d** (X = NO_2, Y = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H12N8O4(3)|GAUSSIAN|1
3-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization Si
nglet||0,3|C,-1.23177263,0.8944351876,-0.0000148687|C,-0.0000015373,1.
5740763655,-0.0000184336|C,1.2317696671,0.8944355875,-0.0000156084|C,1
.2069460669,-0.5409212803,-0.0000098239|C,-0.0000012115,-1.2413513507,
```

```
-0.0000061919|C,-1.2069487041,-0.5409218824,-0.000008993|N,-2.42736082
2,-1.1828290107,-0.0000034205|N,-2.3856346761,1.6227896917,-0.00001604
45|C,-3.5586032015,0.950186868,-0.0000116276|C,-3.6266597703,-0.492288
8433,-0.0000044984|H,-2.4526641995,-2.1942485448,0.0000023115|H,-0.000
0009873,-2.3296280138,0.0000005474|C,-4.7672040271,1.667502271,-0.0000
078179|C,-4.8503778947,-1.1285044047,-0.0000007299|C,-6.0267707838,1.0
504939708,0.0000015123|C,-6.0444605111,-0.3862342655,0.0000000611|H,-4
.6979779586,2.7507822439,-0.0000074181|H,-4.9300635727,-2.2090150765,-
0.0000010197|N,2.4273584559,-1.1828278882,-0.0000046442|N,2.3856317661
,1.6227901368,-0.0000170989|C,3.6266569639,-0.4922879539,-0.0000059612
|C,3.5585999883,0.9501876553,-0.0000137675|H,2.4526622068,-2.194247447
3,0.0000008181|C,4.8503752368,-1.1285039644,-0.0000046451|C,4.76720134
58,1.6675020729,-0.0000077453|C,6.0444586087,-0.3862357483,-0.00000487
3|C,6.0267675595,1.0504931131,0.0000024832|H,4.6979758715,2.7507820885
,-0.0000029854|H,4.9300596422,-2.2090144357,-0.0000096053|H,-0.0000016
958,2.657969392,-0.0000225708|N,-7.2678761272,-1.1409534762,-0.0000045
92|O,-7.197879244,-2.3769220819,0.0000075419|O,-8.3605109159,-0.533439
1461,0.0000140728|N,7.2678816756,-1.1409587747,-0.00002115|O,8.3605303
805,-0.5334577535,0.0000002151|O,7.1979075684,-2.3769340304,-0.0000098
353|N,7.1558730234,1.8039235861,0.0000304621|N,-7.1558766714,1.8039235
619,0.0000177828|H,7.0865968785,2.8088733571,0.0000368897|H,8.05248625
28,1.3386059193,0.0001000179|H,-8.0524900299,1.3386059593,0.0000628583
|H,-7.0866009868,2.8088733451,0.000021396||Version=IA32W-G09RevC.01|St
ate=3-A|HF=-1431.8599304|S2=2.047976|S2-1=0.|S2A=2.001391|RMSD=6.893e-
009|RMSF=3.119e-005|Dipole=-0.0000828,0.788442,0.0000736|Quadrupole=-3
5.5911118,23.3954743,12.1956375,0.0004757,0.0004256,0.0003484|PG=C01 [
X(C18H12N8O4)]||@
```

Table 47. Computational output parameters for singlet **TAP 51e** (Y = NH_2, Z = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H15N7|GAUSSIAN|20-Nov
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization||0,1|C,
1.2277238271,-0.5730008689,0.0000003588|C,-0.0000000587,-1.2446208479,
0.000005454|C,-1.2277239428,-0.5730008947,0.0000226128|C,-1.2027227673
,0.8929158749,0.0000328823|C,-0.0000000953,1.617240949,0.0000327116|C,
1.2027226094,0.8929159255,0.0000173949|N,2.4132173393,1.5167686734,0.0
000178633|N,2.3850124003,-1.2593406089,-0.0000174741|C,3.5641076051,-0
.5843780375,-0.0000184207|C,3.627896081,0.8390414108,0.0000007982|H,2.
4649684969,2.5252740234,0.0000334187|C,4.7856968201,-1.2908282437,-0.0
```

```
000363414|C,4.8532763172,1.5073710674,0.0000024901|C,6.0152544014,-0.6
299202669,-0.0000362562|C,6.0398663462,0.7884810316,-0.0000151756|H,4.
73322854,-2.3757413383,-0.0000515747|H,4.8792952553,2.5963431109,0.000
0180671|N,-2.4132174749,1.5167685879,0.0000400517|N,-2.3850124815,-1.2
593406415,0.0000286302|C,-3.6278961487,0.8390413102,0.0000435399|C,-3.
5641076378,-0.5843780933,0.0000412926|H,-2.4649686231,2.5252739267,0.0
000418208|C,-4.8532763654,1.5073709469,0.0000459388|C,-4.7856968241,-1
.2908283068,0.0000421355|C,-6.0398663378,0.7884809254,0.0000477361|C,-
6.0152543652,-0.6299203596,0.0000519264|H,-4.7332285085,-2.3757413843,
0.0000436415|H,-4.879295297,2.5963429791,0.000044676|H,-0.0000000325,-
2.3274339788,-0.0000040708|N,-7.2008984526,-1.3350118029,0.0001296814|
N,7.200898469,-1.3350117269,-0.0000676813|H,-7.2030624359,-2.341020776
6,-0.0003565425|H,-8.0888248289,-0.8629698872,-0.0004190385|H,8.088825
0346,-0.8629698571,0.0000325491|H,7.203062542,-2.3410208175,0.00000751
18|H,6.9920797402,1.312297382,-0.0000156746|H,-6.9920797413,1.31229723
2,0.000061372|N,-0.0000001329,3.0205673005,0.0000469916|H,0.8425603354
,3.5640630604,0.000035101|H,-0.8425606164,3.5640630213,0.0001069325||V
ersion=IA32W-G09RevC.01|State=1-A|HF=-1078.1889615|S2=0.|S2-1=0.|S2A=0
.|RMSD=6.010e-009|RMSF=2.833e-005|Dipole=-0.0000008,2.7197182,-0.00051
45|Quadrupole=26.2268056,-0.8258197,-25.4009859,-0.0000048,0.0118751,0
.0023805|PG=C01 [X(C18H15N7)]||@
```

Table 48. Computational output parameters for triplet **TAP 51e** (Y = NH$_2$, Z = NH$_2$).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H15N7(3)|GAUSSIAN|25-
Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
|C,-0.8315801555,-1.2251618579,0.|C,-1.5159101378,-0.0000007816,0.|C,-
0.8315805075,1.2251604661,0.|C,0.5995662005,1.207807224,0.|C,1.3218057
346,-0.0000000104,0.|C,0.5995667427,-1.2078082149,0.|N,1.2371183765,-2
.4491638237,0.|N,-1.5690619727,-2.3791506762,0.|C,-0.9020990019,-3.560
4307796,0.|C,0.5291914314,-3.6398525389,0.|H,2.2424918615,-2.514106151
1,0.|C,-1.6345868609,-4.7690994829,0.|C,1.1605569732,-4.8840009223,0.|
C,-1.0036066993,-6.0126840335,0.|C,0.4127753408,-6.0579119063,0.|H,-2.
7178301641,-4.6894186192,0.|H,0.9206258803,-7.0191371839,0.|H,2.247915
062,-4.9385857555,0.|N,1.2371182454,2.4491623748,0.|N,-1.5690622431,2.
3791493855,0.|C,0.5291914089,3.6398511613,0.|C,-0.9020991043,3.5604294
439,0.|H,2.242491944,2.5141038953,0.|C,1.1605571012,4.8839994476,0.|C,
-1.6345868289,4.7690982521,0.|C,0.4127755505,6.0579104801,0.|H,0.92062
61726,7.019135709,0.|C,-1.0036065066,6.0126827236,0.|H,-2.7178301445,4
```

```
.6894175189,0.|H,2.2479152064,4.9385841998,0.|H,-2.5990282807,-0.00000
08824,0.|N,2.7196596133,0.0000024422,0.|H,3.2600004777,0.8447411652,0.
|H,3.2600039342,-0.84473387,0.|N,-1.7310588972,7.1860337214,0.|N,-1.73
10592226,-7.1860349533,0.|H,-1.2750294038,8.0821862982,0.|H,-2.7368192
77,7.1691918196,0.|H,-1.2750298279,-8.0821875803,0.|H,-2.7368196011,-7
.1691929447,0.||Version=IA32W-G09RevC.01|State=3-A'|HF=-1078.171166|S2
=2.046638|S2-1=0.|S2A=2.001394|RMSD=9.186e-009|RMSF=6.460e-005|Dipole=
2.2553044,0.0000007,0.|Quadrupole=-0.8562449,27.2583728,-26.4021278,0.
0000035,0.,0.|PG=CS [SG(C18H15N7)]||@
```

Table 49. Computational output parameters for singlet **TAP 51f** (X = NO_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H10N6O4|GAUSSIAN|11-N
ov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization Singl
et||0,1|C,0.0193875588,-1.4360639692,-0.0000004546|C,1.2174941665,-0.7
096856313,-0.000000181|C,1.2591058229,0.69079795,-0.0000005574|C,-0.02
0782744,1.4046568268,-0.0000007238|C,-1.2352015925,0.7199566007,-0.000
0009279|C,-1.2325084931,-0.6741812244,-0.0000006177|N,-2.3818931668,-1
.3874765134,-0.0000008946|N,0.0231123377,-2.7817380812,-0.0000001871|C
,-1.1542886611,-3.4438312189,-0.0000004873|C,-2.4195085935,-2.77698758
79,-0.0000006589|H,-3.2648568639,-0.8884016065,-0.0000015354|H,-2.1753
499771,1.2679560344,-0.0000016205|C,-1.1727987767,-4.8650037026,-0.000
0006829|C,-3.6228949845,-3.4723333648,-0.0000012544|C,-2.3595442804,-5
.5662149519,-0.0000014099|C,-3.578201601,-4.8625866097,-0.0000016064|H
,-0.2154530507,-5.3747275198,-0.0000005778|H,-2.3804384059,-6.64879342
18,-0.0000022429|H,-4.5828018204,-2.9674138067,-0.0000021218|N,0.03345
50814,2.7562979532,-0.0000011064|N,2.4318626174,1.3507171911,-0.000000
3964|C,1.2239835646,3.473792143,-0.0000009788|C,2.4277411204,2.7015036
438,-0.0000008044|H,-0.8359411439,3.2786492508,-0.0000017536|C,1.23599
04743,4.8635765779,-0.0000016796|C,3.6552346606,3.4179765011,-0.000001
1137|C,2.4677273617,5.5098164258,-0.000002161|C,3.680546172,4.79617160
84,-0.0000019464|H,4.6122414742,5.3478568326,-0.0000028675|H,4.5705530
171,2.8361504236,-0.0000010077|H,0.3235904339,5.4499988981,-0.00000255
59|H,2.1533279955,-1.2551702855,0.0000002477|N,-4.833824809,-5.6002226
926,-0.0000046492|O,-5.8843156721,-4.9489954726,0.0000100296|O,-4.7779
466432,-6.8324474834,0.0000102312|N,2.4907897399,6.9658953251,-0.00000
54033|O,3.5905319838,7.524525127,0.0000122611|O,1.406441277,7.55903627
12,0.000012221||Version=IA32W-G09RevC.01|State=1-A|HF=-1321.1666753|S2
=0.|S2-1=0.|S2A=0.|RMSD=8.059e-009|RMSF=1.044e-005|Dipole=-0.7926772,0
```

```
.4620373,-0.0000314|Quadrupole=7.4311193,-32.4325073,25.0013879,-35.19
29941,0.0000533,-0.000079|PG=C01 [X(C18H10N6O4)]||@
```

Table 50. Computational output parameters for triplet **TAP 51f** (X = NO_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H10N6O4(3)|GAUSSIAN|1
4-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization Tr
iplet||0,3|C,1.2300554497,1.0361999622,-0.0000004918|C,-0.0000001082,1
.7172571099,-0.0000008891|C,-1.230055641,1.0361999131,0.0000006683|C,-
1.2060743447,-0.3953981289,0.0000027018|C,-0.000000069,-1.0966559328,0
.0000033773|C,1.2060741906,-0.3953980964,0.0000017292|N,2.4297430712,-
1.0416962795,0.0000019898|N,2.3881631051,1.7638238548,-0.0000024132|C,
3.5555203026,1.0858560276,-0.0000020053|C,3.6276119739,-0.3515526923,0
.0000002598|H,2.4530119472,-2.0530580024,0.0000033939|H,-0.0000000528,
-2.1848346909,0.0000048953|C,4.7799408055,1.808536836,-0.0000040769|C,
4.8532537947,-1.0075329977,0.0000005867|C,5.9981061821,1.1609613053,-0
.0000038309|C,6.0206637421,-0.2431434822,-0.0000014884|H,4.7149754399,
2.8912158098,-0.0000058803|H,6.9347247542,1.7036923755,-0.0000054144|H
,4.9248780311,-2.0892003026,0.0000023279|N,-2.429743222,-1.0416963394,
0.0000037594|N,-2.3881633309,1.7638237533,-0.0000000887|C,-3.627612144
8,-0.351552819,0.0000028562|C,-3.5555204985,1.0858559347,0.0000010167|
H,-2.4530120638,-2.0530580626,0.000004766|C,-4.853253977,-1.0075331469
,0.0000034648|C,-4.7799409987,1.808536789,-0.0000000965|C,-6.020663824
8,-0.2431434958,0.0000021682|C,-5.9981064042,1.1609612878,0.0000003694
|H,-6.9347250361,1.7036922325,-0.0000007744|H,-4.7149755599,2.89121575
91,-0.00000156|H,-4.924878381,-2.0892004247,0.0000046771|H,-0.00000012
79,2.8012180041,-0.0000026292|N,7.3048292825,-0.9346247255,-0.00000119
47|O,7.2919967374,-2.1700761162,-0.0000026767|O,8.3292139114,-0.246817
1133,-0.0000070634|N,-7.3048291053,-0.9346245492,0.0000016948|O,-8.329
2135417,-0.2468165789,-0.0000187704|O,-7.2919962852,-2.1700759777,-0.0
000153588||Version=IA32W-G09RevC.01|State=3-A|HF=-1321.1455077|S2=2.04
9088|S2-1=0.|S2A=2.001539|RMSD=5.889e-009|RMSF=5.641e-006|Dipole=-0.00
00002,-0.4850993,0.0000251|Quadrupole=-52.2256139,28.516664,23.7089499
,0.0000039,-0.0002279,-0.0000781|PG=C01 [X(C18H10N6O4)]||@
```

Table 51. Computational output parameters for singlet **TAP 51g** (X = C≡N, Y = OMe).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C22H14N6O2|GAUSSIAN|01-D
ec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|
C,-0.866697265,1.2328007805,0.0001152974|C,-1.5334988095,0.0000129711,
0.0000000895|C,-0.8667138211,-1.2327840232,-0.0001151545|C,0.600929209
8,-1.2037158821,-0.0001154998|C,1.3043414994,-0.0000063042,0.000000010
4|C,0.6009451436,1.2037126835,0.0001155608|N,1.235777312,2.3973885324,
0.0002322782|N,-1.548313729,2.3914739704,0.0002231217|C,-0.8625161879,
3.5594057013,0.0003408545|C,0.566357679,3.6166055504,0.0003482678|H,2.
2496840628,2.4087988432,0.0002393022|H,2.3928947631,-0.0000135512,-0.0
000000182|C,-1.5514862817,4.7873202425,0.0003940409|C,1.2359626059,4.8
26699968,0.0004900893|C,-0.8986885343,6.0164091439,0.000504321|C,0.531
5346352,6.0481142022,0.0006036775|H,-2.6350609302,4.771447759,0.000319
0256|H,2.3223307926,4.8559263181,0.0005621712|N,1.2357462046,-2.397399
9155,-0.0002322425|N,-1.5483463151,-2.3914475268,-0.0002229348|C,0.566
3112603,-3.6166084094,-0.0003481873|C,-0.862564728,-3.5593888465,-0.00
03406989|H,2.2496528323,-2.4088231495,-0.0002393163|C,1.2359043905,-4.
8267114239,-0.0004900121|C,-1.5515531742,-4.787294057,-0.0003938053|C,
0.5314530687,-6.0481113117,-0.0006035409|C,-0.8987573218,-6.0163834395
,-0.0005041142|H,-2.6351276127,-4.7714133123,-0.0003187352|H,2.3222719
806,-4.8559557046,-0.0005621183|H,-2.6167452847,0.000020331,0.00000012
07|C,1.3368848184,7.2263094664,0.001062565|N,2.0684160494,8.1339521195
,0.0014900555|C,1.3367375089,-7.2263506806,-0.0010623045|N,2.068050989
1,-8.1341692118,-0.0014894494|O,-1.7355044406,7.0820250179,0.000608840
4|O,-1.7355115708,-7.0820360465,-0.000608676|C,-1.2751302204,8.4323557
567,-0.0009472871|H,-0.6863641417,8.6603008273,0.8925882982|H,-0.68647
97639,8.6582419612,-0.8950950791|H,-2.1837294692,9.0371189124,-0.00158
13387|C,-1.2749577007,-8.4323036626,0.0009467037|H,-0.6861533738,-8.66
01610633,-0.8925884889|H,-0.6862683094,-8.6581028629,0.89509328|H,-2.1
834701107,-9.037196774,0.0015810373||Version=IA32W-G09RevC.01|State=1-
A|HF=-1325.6785389|S2=0.|S2-1=0.|S2A=0.|RMSD=3.546e-009|RMSF=1.986e-00
5|Dipole=1.1854411,0.0001919,-0.0000007|Quadrupole=11.1094302,-21.5246
285,10.4151983,-0.0039674,-0.000001,-0.0413756|PG=C01 [X(C22H14N6O2)]|
|@
```

Table 52. Computational output parameters for triplet **TAP 51g** (X = C≡N, Y = OMe).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C22H14N6O2(3)|GAUSSIAN|0
1-Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0
,3|C,1.2321247381,0.6687653756,0.0001388303|C,0.0000007396,1.347997076
3,-0.0000000823|C,-1.2321187413,0.6687571931,-0.0001389648|C,-1.207485
0008,-0.7641153815,-0.0001390597|C,0.0000101215,-1.4635321535,-0.00000
0017|C,1.207500558,-0.7641073068,0.0001389924|N,2.4304762954,-1.410893
5619,0.0002811488|N,2.3864222112,1.4000586588,0.0002672262|C,3.5583547
806,0.720413308,0.000407581|C,3.6286128176,-0.7158573443,0.0004193983|
H,2.4530643377,-2.4217677617,0.0002968912|H,0.0000137524,-2.552020082,
0.0000000072|C,4.7715174472,1.4361054949,0.000471871|C,4.8577067529,-1
.3482198311,0.0005921066|C,6.0168518225,0.8118061999,0.0006069453|C,6.
0691181879,-0.612873206,0.0007365545|H,4.7288228002,2.5190115533,0.000
3834718|H,4.9163632739,-2.4328781807,0.0006785018|N,-2.4304563794,-1.4
109098689,-0.0002811931|N,-2.3864210562,1.4000428823,-0.0002673914|C,-
3.6285975082,-0.7158815225,-0.0004194781|C,-3.558349079,0.7203895835,-
0.0004077142|H,-2.4530376674,-2.4217842194,-0.0002968877|C,-4.85768746
03,-1.3482517819,-0.0005921519|C,-4.7715167238,1.4360733122,-0.0004720
429|C,-6.0691042392,-0.6129132214,-0.0007365959|C,-6.0168471981,0.8117
657606,-0.0006071019|H,-4.7288298333,2.5189796553,-0.000383686|H,-4.91
63368868,-2.4329105122,-0.0006784821|H,-0.0000028624,2.4319741908,-0.0
000001068|C,7.2624056799,-1.3954289231,0.0013049107|N,8.1839698462,-2.
1094896263,0.0018376206|C,-7.2623864901,-1.3954772424,-0.0013048425|N,
-8.1839366503,-2.1095559821,-0.0018382232|O,7.0637413514,1.6732878717,
0.0007288584|O,-7.0637434137,1.6732388326,-0.0007290453|C,8.422897849,
1.2400729955,-0.001139643|H,8.6626832101,0.6559082058,0.8924564185|H,8
.6601928133,0.6559490131,-0.8954424192|H,9.0095871135,2.1604720999,-0.
0019311683|C,-8.4228953139,1.2400109177,0.0011396507|H,-8.6626748552,0
.6558436545,-0.8924563992|H,-8.6601843028,0.6558847177,0.8954426017|H,
-9.0095938379,2.1604041563,0.0019311096||Version=IA32W-G09RevC.01|Stat
e=3-A|HF=-1325.6573637|S2=2.051713|S2-1=0.|S2A=2.001728|RMSD=5.631e-00
9|RMSF=2.423e-005|Dipole=-0.0000014,-0.6813149,0.0000005|Quadrupole=-2
0.2759796,11.3057661,8.9702135,-0.0001811,-0.04982,-0.0000019|PG=C01 [
X(C22H14N6O2)]||@
```

Table 53. Computational output parameters for singlet **TAP 51h** (Y = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H14N6|GAUSSIAN|18-Nov
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization||0,1|C,
-1.2364123327,-1.0844439117,0.0000235925|C,-0.00001024,-1.7491391891,0
.0000348324|C,1.2363942727,-1.0844485104,0.0000225906|C,1.2054652971,0
.3811804042,-0.0000031575|C,-0.0000049532,1.0833551773,-0.0000156921|C
,-1.2054777903,0.3811848221,-0.0000029342|N,-2.399998112,1.0160250387,
-0.0000140477|N,-2.3968183686,-1.7634519648,0.0000360243|C,-3.56952239
01,-1.0740031598,0.0000240164|C,-3.621836186,0.3512821648,-0.000002027
5|H,-2.408528946,2.0295202452,-0.0000339024|C,-4.7971193219,-1.7694609
842,0.0000368789|C,-4.8413322699,1.0303585258,-0.0000141732|C,-6.02069
84364,-1.0975759995,0.0000249795|C,-6.033127789,0.3211733699,-0.000001
3239|H,-4.754360583,-2.8547265221,0.000056903|H,-4.8567502325,2.119072
4859,-0.000034028|N,2.3999881532,1.0160162377,-0.0000137599|N,2.396798
0476,-1.7634610623,0.0000332347|C,3.6218239657,0.3512687971,-0.0000028
288|C,3.5695048128,-1.0740165462,0.0000207326|H,2.4085228026,2.0295114
875,-0.0000329863|C,4.8413227851,1.0303406021,-0.0000125891|C,4.797099
3228,-1.7694791099,0.0000342667|C,6.0331157803,0.3211508008,-0.0000014
657|C,6.0206811111,-1.0975986867,0.0000209427|H,4.7543363646,-2.854744
5643,0.0000534536|H,4.8567448523,2.1190545622,-0.0000297614|H,-0.00001
21945,-2.832639318,0.0000537789|N,7.2121694929,-1.7919531934,0.0000125
575|N,-7.2121893963,-1.7919260489,0.0000411925|H,7.2236264583,-2.79794
79578,0.0001308034|H,8.0959697394,-1.3120994907,0.0001535788|H,-8.0959
8785,-1.3120691104,0.0000089745|H,-7.2236501418,-2.7979207372,0.000037
205|H,-6.9809557092,0.8527694284,-0.0000106113|H,6.9809457585,0.852743
3173,-0.0000142912|H,-0.0000028808,2.1727226703,-0.0000349582||Version
=IA32W-G09RevC.01|State=1-A|HF=-1022.858732|S2=0.|S2-1=0.|S2A=0.|RMSD=
4.823e-009|RMSF=3.931e-005|Dipole=0.0000031,2.2308308,0.0000943|Quadru
pole=28.4948237,-4.1274825,-24.3673413,-0.0000626,0.002974,-0.0007566|
PG=C01 [X(C18H14N6)]||@
```

Table 54. Computational output parameters for triplet **TAP 51h** (Y = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H14N6(3)|GAUSSIAN|19-
Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||Optimization||0,3
|C,1.2346144246,-0.5253298124,0.0000049997|C,-0.0000000229,-1.20072089
28,0.0000129042|C,-1.2346144829,-0.5253298342,0.0000292419|C,-1.208397
5657,0.9063566398,0.0000368634|C,-0.0000000486,1.6048210581,0.00003058
```

```
46|C,1.2083974729,0.9063566681,0.0000154244|N,2.4331578096,1.555171474
,0.000009328|N,2.3909035763,-1.2570973596,-0.0000120961|C,3.5659609085
,-0.5743891349,-0.0000184024|C,3.6321830564,0.859138618,-0.0000066862|
H,2.4550518262,2.5654426222,0.0000178543|C,4.7811294925,-1.29493165,-0
.0000351031|C,4.8700251747,1.5013451597,-0.0000112553|C,6.018966663,-0
.6522525203,-0.0000414641|C,6.0508186212,0.7640408102,-0.0000277565|H,
4.7119300289,-2.3788939676,-0.0000447688|H,4.914279054,2.588781365,-0.
0000014653|N,-2.4331579117,1.5551714261,0.0000493526|N,-2.3909036283,-
1.257097411,0.0000379197|C,-3.6321831414,0.8591385467,0.0000567748|C,-
3.5659609629,-0.5743892065,0.0000537464|H,-2.4550519399,2.5654425719,0
.0000548321|C,-4.8700252769,1.5013450637,0.0000628608|C,-4.7811295423,
-1.2949317459,0.0000568786|C,-6.0508187029,0.76404069,0.0000677434|C,-
6.0189667151,-0.6522526447,0.0000716729|H,-4.7119300426,-2.378894061,0
.0000590039|H,-4.9142791694,2.5887812674,0.0000620075|H,-0.000000013,-
2.2848841895,0.0000064651|N,-7.1982837195,-1.369113656,0.0001712066|N,
7.1982836493,-1.3691135185,-0.0000753038|H,-7.1912497681,-2.3750207957
,-0.0004446517|H,-8.090593456,-0.9054787159,-0.0005106715|H,8.09059365
08,-0.905478623,0.0000454166|H,7.1912498818,-2.375020833,0.0000283862|
H,7.0072465722,1.2807902181,-0.000033357|H,-7.0072466696,1.2807900667,
0.0000861819|H,-0.0000000694,2.6940893069,0.0000373322||Version=IA32W-
G09RevC.01|State=3-A|HF=-1022.8376895|S2=2.046537|S2-1=0.|S2A=2.001389
|RMSD=7.529e-009|RMSF=3.698e-005|Dipole=0.000001,1.6987382,-0.0006975|
Quadrupole=29.4630406,-4.35466,-25.1083806,-0.0000062,0.0149485,0.0024
867|PG=C01 [X(C18H14N6)]||@
```

Table 55. Computational output parameters for singlet **TAP 51i** (X = CF_3).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H10F6N4|USER|09-Feb-2013|0|
|# opt ub3lyp/6-31g(d) geom=connectivity||X:CF3||0,1|C,-0.11022791,0.0
004918146,0.0606156235|C,-0.1032577717,0.0000078723,1.4626360904|C,1.0
741698054,-0.0004783485,2.2238023948|C,2.3451719441,0.0007648105,1.494
4794073|C,2.3843265023,0.0000024941,0.1006227539|C,1.1889286009,-0.000
7568417,-0.617286177|N,1.1744632837,-0.0026324921,-1.9704127196|N,-1.2
622852064,0.0023303834,-0.6336639246|C,-1.2157749019,0.0003882929,-1.9
880540579|C,0.005266459,-0.003999668,-2.7231291685|H,3.3391696699,0.00
00004821,-0.4221772519|C,-2.4166621002,0.0062871226,-2.7438926575|C,0.
0335612641,-0.0061808439,-4.1177801904|C,-2.3930124226,0.005875673,-4.
1240692485|C,-1.1664389699,-0.0009491404,-4.8204458219|H,-3.3512719727
,0.0147595146,-2.1931158412|H,0.9810190605,-0.0064915495,-4.6493023491
```

```
|N,3.4773692917,0.0026386253,2.2356202682|N,1.0384562526,-0.0023139225
,3.5684156511|C,3.4816545764,0.0040094487,3.6261542541|C,2.2045668748,
-0.0003733492,4.2588660256|C,4.6718715848,0.0061902394,4.3536402567|C,
2.194410391,-0.0062678529,5.6777808686|C,4.6173954136,0.000963278,5.74
31622518|C,3.3699302539,-0.0058567696,6.4013825634|H,1.2268971897,-0.0
147359771,6.1684630298|H,5.6300843197,0.0064979279,3.8417610653|H,-1.0
53412806,0.0000099717,1.9828692163|H,-3.3224441005,0.0176324014,-4.684
4271882|H,3.3413220168,-0.0176092344,7.4862909097|C,-1.1708290155,-0.0
546993797,-6.3193341222|C,5.8778216852,0.0547103664,6.554341406|F,-2.
0880040622,0.7880162129,-6.8471113693|F,0.0321155043,0.272990076,-6.84
63336414|F,6.1013756502,1.2917891374,7.0608576356|F,5.8283801724,-0.78
8035356,7.6113483458|F,-1.4770889128,-1.291788819,-6.7805435966|F,6.96
98652629,-0.2729419777,5.8247737437|H,4.3708943547,0.0041553917,1.7562
717369|H,2.0596659984,-0.0041529445,-2.4649611957||Version=IA32W-G09Re
vC.01|State=1-A|HF=-1586.2339293|S2=0.|S2-1=0.|S2A=0.|RMSD=4.994e-009|
RMSF=2.069e-006|Dipole=1.6723461,-0.0000023,-0.9156446|Quadrupole=6.90
56018,7.448815,-14.3544168,-0.5229401,-16.6239173,-0.95505|PG=C01 [X(C
20H10F6N4)]||@
```

Table 56. Computational output parameters for triplet **TAP 51i** (X = CF_3).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H10F6N4(3)|USER|10-Feb-2013
|0||# opt ub3lyp/6-31g(d) geom=connectivity||X:CF3||0,3|C,1.2325336241
,1.1606522728,0.0069951845|C,-0.0000000515,1.8399089247,-0.0000005486|
C,-1.2325336123,1.1606520637,-0.0069951143|C,-1.2071983415,-0.27073987
69,-0.0075453587|C,0.0000001781,-0.9700296437,0.0000019902|C,1.2071985
899,-0.2707396666,0.0075480211|N,2.4329935072,-0.9201161396,0.01592845
07|N,2.3877403025,1.8905328742,0.0134020058|C,3.5606678848,1.204368490
4,0.0212069666|C,3.6300515846,-0.2276378368,0.0229036604|H,0.000000267
5,-2.058642405,0.0000029561|C,4.78289227,1.9199779289,0.0329888953|C,4
.8600177423,-0.8834652314,0.0363007696|C,6.0020560583,1.2650445659,0.0
452025881|C,6.0418200616,-0.1390946618,0.0473256081|H,4.721947177,3.00
32043926,0.0362019587|H,4.9001454899,-1.9688461091,0.0462655277|N,-2.4
329931617,-0.9201165645,-0.0159247832|N,-2.3877404123,1.8905324656,-0.
0134033956|C,-3.630051336,-0.2276384382,-0.0229018631|C,-3.5606678633,
1.204367849,-0.0212076027|C,-4.8600174078,-0.883466152,-0.0362986011|C
,-4.782892398,1.9199770897,-0.032991309|C,-6.0418197651,-0.1390958361,
-0.0473254987|C,-6.0020559815,1.2650434896,-0.0452047155|H,-4.72194747
39,3.0032035576,-0.0362061655|H,-4.9001449054,-1.9688470341,-0.0462614
```

```
569|H,-0.0000001387,2.9239128668,-0.0000015465|H,6.9283543951,1.828673
252,0.0616974539|H,-6.9283544342,1.8286719842,-0.0617012812|C,7.364726
0866,-0.8500083713,-0.0038600795|C,-7.3647263627,-0.8500085366,0.00385
95141|F,8.3332818893,-0.155985445,0.6327296444|F,7.3021613706,-2.07654
87099,0.5647937957|F,-7.7882899213,-1.0341373223,1.277735138|F,-8.3332
775406,-0.1559917484,-0.6327441528|F,7.78828102,-1.0341516315,-1.27773
64973|F,-7.3021588875,-2.076554981,-0.5647806943|H,-2.4545457644,-1.93
09185776,-0.0169582691|H,2.454546264,-1.9309181481,0.0169638043||Versi
on=IA32W-G09RevC.01|State=3-A|HF=-1586.214083|S2=2.049049|S2-1=0.|S2A=
2.001566|RMSD=4.901e-009|RMSF=2.626e-006|Dipole=0.0000003,-1.3750552,0
.0000022|Quadrupole=-21.6889197,16.0311668,5.6577529,0.0000159,1.07587
73,-0.0000156|PG=C01 [X(C20H10F6N4)]||@
```

Table 57. Computational output parameters for singlet **TAP 51j** (X = C≡N).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C20H10N6|GAUSSIAN|29-Nov
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|C,
0.0219363919,-1.4386879195,0.|C,1.2196320913,-0.7109305985,0.|C,1.2626
475131,0.6898761743,0.|C,-0.0172984658,1.4027374911,0.|C,-1.2316249804
,0.7178738648,0.|C,-1.2291207184,-0.6762645261,0.|N,-2.3803203105,-1.3
878021866,0.|N,0.0229187218,-2.7842399603,0.|C,-1.1577201022,-3.444163
5329,0.|C,-2.4203810815,-2.7774862452,0.|H,-3.2611809897,-0.8853439606
,0.|H,-2.1719606983,1.2659821966,0.|C,-1.1804283244,-4.8637220636,0.|C
,-3.6256405894,-3.4728636946,0.|C,-2.3692668111,-5.5617407536,0.|C,-3.
6088343997,-4.8732592634,0.|H,-0.224263186,-5.3760141938,0.|H,-2.36923
73101,-6.6466302553,0.|H,-4.5727144797,-2.9397957609,0.|N,0.0345127638
,2.7550931007,0.|N,2.4339451403,1.3521228803,0.|C,1.2239833034,3.47480
12511,0.|C,2.4263364843,2.7046590767,0.|H,-0.8367916576,3.2739460316,0
.|C,1.2350904808,4.866232251,0.|C,3.6503545684,3.4239905396,0.|C,2.461
9059643,5.5417390854,0.|C,3.6718514027,4.8024360168,0.|H,4.6158653463,
5.3370581518,0.|H,4.5673231576,2.8444535636,0.|H,0.304522274,5.4276169
779,0.|H,2.1555147585,-1.2564473957,0.|C,-4.8394383915,-5.5989788116,0
.|N,-5.8437636043,-6.1888594993,0.|C,2.4869101401,6.9701802349,0.|N,2.
505405878,8.134777523,0.||Version=IA32W-G09RevC.01|State=1-A'|HF=-1096
.6470012|S2=0.|S2-1=0.|S2A=0.|RMSD=6.853e-009|RMSF=1.043e-004|Dipole=-
0.9263789,0.5399463,0.|Quadrupole=8.8555359,-30.5491825,21.6936466,-34
.7899122,0.,0.|PG=CS [SG(C20H10N6)]||@
```

Table 58. Computational output parameters for triplet **TAP 51j** (X = C≡N).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C20H10N6(3)|GAUSSIAN|30-
Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
|C,-0.9198631281,1.2310413748,0.|C,-1.5999897463,0.0000026584,0.|C,-0.
9198657754,-1.2310375267,0.|C,0.5110630368,-1.2065105868,0.|C,1.211458
9303,-0.0000003579,0.|C,0.5110656267,1.2065113784,0.|N,1.1595865449,2.
4316544108,0.|N,-1.6485001988,2.3886025338,0.|C,-0.9666317858,3.557767
4142,0.|C,0.4683818898,3.6293927594,0.|H,2.170624003,2.4526770381,0.|H
,2.2998642189,-0.0000015214,0.|C,-1.6864671976,4.7809533643,0.|C,1.122
9340266,4.8566515752,0.|C,-1.0382266777,5.9998586206,0.|C,0.3747405407
,6.046948027,0.|H,-2.7693754666,4.7165954119,0.|H,-1.6016003335,6.9267
155237,0.|H,2.2083839537,4.9015563901,0.|N,1.1595813131,-2.4316550138,
0.|N,-1.6485053207,-2.3885971146,0.|C,0.4683740771,-3.6293918825,0.|C,
-0.9666394192,-3.5577634716,0.|H,2.1706187251,-2.4526798205,0.|C,1.122
9235234,-4.8566521472,0.|C,-1.686477452,-4.7809478931,0.|C,0.374727467
7,-6.0469470145,0.|C,-1.0382396223,-5.9998545725,0.|H,-1.6016152651,-6
.9267102685,0.|H,-2.7693855783,-4.7165876268,0.|H,2.2083733548,-4.9015
592861,0.|H,-2.683973543,0.0000038239,0.|C,1.0508435865,7.3058072482,0
.|N,1.6032866816,8.3311549517,0.|C,1.0508274974,-7.3058078654,0.|N,1.6
032725122,-8.3311545348,0.||Version=IA32W-G09RevC.01|State=3-A'|HF=-10
96.6269631|S2=2.052103|S2-1=0.|S2A=2.001775|RMSD=5.483e-009|RMSF=1.385
e-005|Dipole=0.6369102,-0.0000017,0.|Quadrupole=29.0449398,-48.8672075
,19.8222677,-0.0000517,0.,0.|PG=CS [SG(C20H10N6)]||@
```

Table 59. Computational output parameters for singlet **TAP 51k** (Y = F).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10F2N4|GAUSSIAN|21-N
ov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|
C,0.0330770451,-1.4479205167,0.|C,1.2304026763,-0.717204303,0.|C,1.276
1789275,0.6847373655,0.|C,-0.0045156197,1.3965567733,0.|C,-1.218603686
6,0.7102943446,0.|C,-1.2174374059,-0.6843265005,0.|N,-2.3688382056,-1.
3947200877,0.|N,0.0330340324,-2.7927166702,0.|C,-1.1521428829,-3.45354
11225,0.|C,-2.4127351448,-2.7851238509,0.|H,-3.2482664785,-0.890553585
3,0.|H,-2.1593398288,1.2586405371,0.|C,-1.1728111299,-4.8699995112,0.|
C,-3.621891499,-3.4848076153,0.|C,-2.3799481964,-5.5353776306,0.|C,-3.
615999328,-4.8743150556,0.|H,-0.2337771517,-5.4107573267,0.|H,-4.53458
45716,-5.4496279093,0.|H,-4.5649614905,-2.9420484546,0.|N,0.0462099881
,2.7485225084,0.|N,2.4463165659,1.3474974599,0.|C,1.2344223902,3.47191
```

```
73885,0.|C,2.4372643137,2.7044256745,0.|H,-0.8258733002,3.2652900148,0
.|C,1.2473668109,4.8688604167,0.|C,3.6595956859,3.4204466119,0.|C,2.45
93360002,5.5484890874,0.|H,2.5072560972,6.6313037474,0.|C,3.6436846954
,4.7987262635,0.|H,4.5928915996,2.8698446234,0.|H,0.3103428533,5.42199
16875,0.|H,2.1663328489,-1.2627457838,0.|F,-2.3858102352,-6.8855443695
,0.|F,4.8156295944,5.4691962092,0.||Version=IA32W-G09RevC.01|State=1-A
'|HF=-1110.6219756|S2=0.|S2-1=0.|S2A=0.|RMSD=1.944e-009|RMSF=4.367e-00
5|Dipole=-3.0101265,1.7545737,0.|Quadrupole=6.4319562,-4.3286947,-2.10
32616,-9.4999658,0.,0.|PG=CS [SG(C18H10F2N4)]||@
```

Table 60. Computational output parameters for triplet **TAP 51k** (Y = F).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10F2N4(3)|GAUSSIAN|2
3-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0
,3|C,0.5519474704,-1.2332714509,0.|C,1.2301645441,0.0000000082,0.|C,0.
5519478585,1.2332716892,0.|C,-0.8793138643,1.2077235875,0.|C,-1.578227
3955,0.0000004443,0.|C,-0.8793142312,-1.2077229212,0.|N,-1.5287341769,
-2.4331079811,0.|N,1.2828888891,-2.3884164366,0.|C,0.5972685646,-3.562
161049,0.|C,-0.8358037686,-3.6323238893,0.|H,-2.5391999065,-2.45406389
09,0.|H,-2.6670746737,0.0000006001,0.|C,1.3191984337,-4.780318652,0.|C
,-1.4900009553,-4.8656993627,0.|C,0.6402829074,-5.9812438237,0.|C,-0.7
557773816,-6.051636431,0.|H,2.4024201272,-4.746857876,0.|H,-1.24472619
87,-7.0194895433,0.|H,-2.5769739457,-4.9011172807,0.|N,-1.5287334227,2
.4331088528,0.|N,1.2828896231,2.3884164277,0.|C,-0.8358026381,3.632324
5477,0.|C,0.5972696647,3.5621612731,0.|H,-2.5391991457,2.454065088,0.|
C,-1.4899994456,4.8657002246,0.|C,1.3191999167,4.7803186379,0.|C,-0.75
57755008,6.0516370645,0.|H,-1.2447240263,7.0194903241,0.|C,0.640284762
5,5.9812440262,0.|H,2.4024215993,4.7468575264,0.|H,-2.5769724248,4.901
1184698,0.|H,2.314199611,-0.0000001601,0.|F,1.3404899537,-7.1364687301
,0.|F,1.3404921761,7.1364687098,0.||Version=IA32W-G09RevC.01|State=3-A
'|HF=-1110.6019621|S2=2.04751|S2-1=0.|S2A=2.001465|RMSD=6.621e-009|RMS
F=3.119e-005|Dipole=-2.9436099,0.0000005,0.|Quadrupole=11.1774311,-8.1
291918,-3.0482393,-0.000003,0.,0.|PG=CS [SG(C18H10F2N4)]||@
```

Table 61. Computational output parameters for singlet **TAP 51l** (Y = OMe).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C20H16N4O2|GAUSSIAN|05-D
ec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|
```

```
C,1.2356998023,0.8298632831,0.0000159016|C,0.0000019223,1.4949811879,-
0.0000000653|C,-1.2356867427,0.8298462295,-0.0000160534|C,-1.204789040
9,-0.6363694072,-0.0000154438|C,0.0000215315,-1.3391220234,-0.00000010
66|C,1.2048223737,-0.6363527713,0.0000152501|N,2.3978424105,-1.2733673
157,0.0000305172|N,2.3964530144,1.5070371096,0.0000307332|C,3.56760186
33,0.8161938585,0.0000495877|C,3.6212296682,-0.6104179204,0.0000489715
|H,2.4051301355,-2.2869857802,0.0000319659|H,0.0000290588,-2.428256052
7,-0.0000001227|C,4.7973851876,1.5062053976,0.000051686|C,4.8355122664
,-1.2930512327,0.000066468|C,6.0091320303,0.8230515083,0.0000730599|C,
6.0360388488,-0.587770962,0.0000847926|H,4.7857119615,2.5901630807,0.0
000389701|H,4.8471537641,-2.3815250646,0.0000741656|N,-2.3978002401,-1
.2734004328,-0.0000307298|N,-2.3964493287,1.5070040617,-0.0000308693|C
,-3.6211965841,-0.6104678439,-0.0000491715|C,-3.5675885897,0.816144639
7,-0.0000497484|H,-2.405073953,-2.2870189952,-0.0000322071|C,-4.835469
6691,-1.2931178411,-0.0000666908|C,-4.7973814699,1.5061392214,-0.00005
18258|C,-6.0360060447,-0.5878541836,-0.0000850044|C,-6.0091192161,0.82
29691374,-0.0000732296|H,-4.7857229271,2.5900970648,-0.0000390759|H,-4
.8470959386,-2.3815918706,-0.0000744184|H,-0.0000055468,2.5783474685,-
0.000000053|O,7.1313203822,1.6041003232,0.0001498872|O,-7.1313172681,1
.6040047997,-0.0001500703|C,8.3983338404,0.969709952,-0.0004614917|H,8
.5431782328,0.3491587378,0.8942866008|H,8.5423817841,0.3493221144,-0.8
954476923|H,9.1355572592,1.774889092,-0.0007019414|C,-8.3983259524,0.9
696042177,0.0004614924|H,-8.5431659149,0.3490520691,-0.8942866001|H,-8
.542369221,0.3492154801,0.8954477549|H,-9.1355557839,1.7747775022,0.00
07020415|H,-6.9717496699,-1.1329013131,-0.0001331492|H,6.9717906036,-1
.1328045762,0.0001329126||Version=IA32W-G09RevC.01|State=1-A|HF=-1141.
1981739|S2=0.|S2-1=0.|S2A=0.|RMSD=7.930e-009|RMSF=3.049e-005|Dipole=0.
0000313,-3.5714779,0.|Quadrupole=22.6501808,-5.3697162,-17.2804645,0.0
001477,-0.0083981,0.0000004|PG=C01 [X(C20H16N4O2)]||@
```

Table 62. Computational output parameters for triplet **TAP 51l** (Y = OMe).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C20H16N4O2(3)|GAUSSIAN|0
6-Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0
,3|C,-1.2345029911,0.459333678,0.0000183228|C,0.0000001059,1.136394710
6,-0.0000000086|C,1.2345032817,0.4593338525,-0.0000183309|C,1.20862638
12,-0.9730024729,-0.0000178237|C,0.0000002916,-1.6709207681,-0.0000000
086|C,-1.208625896,-0.9730026389,0.0000178208|N,-2.4331002949,-1.62175
67003,0.0000360756|N,-2.3878844591,1.1912227594,0.0000350424|C,-3.5653
```

```
003812,0.5062845666,0.0000499942|C,-3.6329895263,-0.9272456237,0.00005
12086|H,-2.4544650871,-2.6320965865,0.00003465|H,0.0000003668,-2.75999
85516,-0.0000000086|C,-4.7782490933,1.2249245346,0.0000705013|C,-4.867
3387371,-1.569542762,0.0000676865|C,-6.0082893526,0.57267242,0.0000846
167|C,-6.0561875397,-0.8329341832,0.0000816131|H,-4.7371473566,2.30829
17336,0.0000739261|H,-4.9106885947,-2.6567218654,0.000066858|N,2.43310
0871,-1.621756364,-0.0000360762|N,2.3878846422,1.1912230896,-0.0000350
486|C,3.6329900055,-0.927245123,-0.0000512006|C,3.565300662,0.50628505
82,-0.0000499889|H,2.4544658019,-2.6320962485,-0.0000346414|C,4.867339
3071,-1.5695420992,-0.0000676673|C,4.7782492735,1.2249251901,-0.000070
4932|C,6.0561880079,-0.8329333606,-0.0000815813|C,6.0082896057,0.57267
32134,-0.0000845934|H,4.7371474051,2.3082923841,-0.0000739263|H,4.9106
893203,-2.6567211962,-0.000066834|H,0.0000000196,2.2204924672,-0.00000
00086|O,-7.1130459613,1.379994114,0.0000817731|O,7.1130461579,1.379994
935,-0.0000817122|C,-8.3917598022,0.7704422849,0.0002964056|H,-8.54831
2445,0.1524362172,-0.8945000548|H,-8.5480272597,0.1524754133,0.8951686
467|H,-9.113694347,1.5893385292,0.000389402|C,8.3917598799,0.770442889
8,-0.0002966542|H,8.5483126073,0.1524367611,0.8944997545|H,8.548027011
4,0.1524760107,-0.8951689472|H,9.1136945541,1.5893390181,-0.0003897843
|H,7.0017794507,-1.3616131499,-0.0000835871|H,-7.0017788755,-1.3616141
37,0.0000836444||Version=IA32W-G09RevC.01|State=3-A|HF=-1141.1783669|S
2=2.047784|S2-1=0.|S2A=2.001482|RMSD=3.986e-009|RMSF=1.331e-005|Dipole
=0.,-2.9565285,0.|Quadrupole=23.9404242,-5.9245338,-18.0158904,-0.0000
006,-0.0033631,-0.0000004|PG=C01 [X(C20H16N4O2)]||@
```

Table 63. Computational output parameters for singlet **TAP 51m** (Z = NH_2).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C18H13N5\GAUSSIAN\26-Mar-2013\0\\
# opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt\\0,1\C,0.0190641255
,0.0062903602,0.0068291677\C,0.0101572652,0.0025489478,1.4106641257\C,
1.1820279563,-0.0032775834,2.1822406831\C,2.4530429714,-0.0054381254,1
.4646124625\C,2.5220442052,-0.0018818701,0.0618440439\C,1.324041401,0.
0038977858,-0.6608376744\N,1.3247802619,0.0075372581,-2.0142603803\N,-
1.1235188357,0.0118439145,-0.7021344052\C,-1.0633371976,0.0152955339,-
2.0604615428\C,0.1639191518,0.0133146988,-2.7830467661\H,2.220676063,0
.0059519512,-2.4875248187\C,-2.2541049657,0.0211664535,-2.8286853934\C
,0.2057840882,0.0169339209,-4.1794100916\C,-2.2134535703,0.0247571975,
```

```
-4.2130883149\C,-0.9845165971,0.022669654,-4.8980513056\H,-3.194300421
3,0.0227154414,-2.2864413577\H,-3.1416948401,0.0292422067,-4.777951250
5\H,-0.9609028824,0.0255118964,-5.9835014166\H,1.1661339316,0.01524376
05,-4.6926945338\N,3.5862178306,-0.0110427265,2.1908777229\N,1.1510943
602,-0.0067775529,3.5275255267\C,3.5996641578,-0.0148052059,3.57721176
46\C,2.3233464672,-0.0123922091,4.2149289561\H,4.4504018832,-0.0123973
7,1.6531264516\C,4.7939408467,-0.0206133266,4.3057126755\C,2.317685582
8,-0.0161731292,5.6328637667\C,4.7451365506,-0.0241726971,5.6936760752
\H,5.6672459009,-0.0286867156,6.2669271044\C,3.4999450224,-0.021916278
5,6.3520116879\H,3.468716594,-0.0247243086,7.4381732835\H,1.350588069,
-0.0143720149,6.125497466\H,5.7468077606,-0.0222824436,3.779994609\H,-
0.9463972997,0.0042527227,1.9191587544\N,3.8277462903,-0.0044870128,-0
.5377388648\H,4.0223115459,-0.8328456645,-1.096926097\H,4.0276998322,0
.8256205769,-1.0924131517\\Version=IA32L-G03RevD.02\State=1-A\HF=-967.
5076418\S2=0.\S2-1=0.\S2A=0.\RMSD=8.509e-09\RMSF=4.728e-07\Thermal=0.\
Dipole=2.6061416,-0.0038652,-1.6715101\PG=C01 [X(C18H13N5)]\\@
```

Table 64. Computational output parameters for triplet **TAP 51m** (Z = NH_2).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C18H13N5(3)\GAUSSIAN\31-Mar-2013\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt\\0,3\C,0.0621683466,0.
0000000592,-0.0315560348\C,0.0511528018,0.0000001277,1.3771691936\C,1.
2366784555,0.0000009871,2.1350557841\C,2.478319635,0.0000015072,1.4275
695304\C,2.5317121546,0.000001716,0.0266827106\C,1.3298681257,0.000001
3604,-0.6953025588\N,1.3167991582,0.0000021197,-2.0824625924\N,-1.1304
018775,-0.0000009273,-0.6998082008\C,-1.0873561601,-0.0000006119,-2.06
1949216\C,0.1364127075,0.0000012447,-2.8064894423\H,2.1988539466,0.000
006369,-2.5746506844\C,-2.2988555366,-0.0000018199,-2.7938970999\C,0.1
243813182,0.0000021426,-4.2024684354\C,-2.3031327972,-0.0000010391,-4.
1811208206\C,-1.0912733231,0.0000010192,-4.8876860009\H,-3.2207394336,
-0.0000032538,-2.2209215909\H,-3.2454783885,-0.0000019655,-4.721151217
8\H,-1.0918796116,0.0000017142,-5.9738690994\H,1.0654421359,0.00000364
65,-4.74914526\N,3.6407648114,0.0000014734,2.1719537848\N,1.1610338407
,0.000000736,3.4996653923\C,3.6215797694,0.000000597,3.5522575999\C,2.
3365767365,0.0000006494,4.1902197049\H,4.5088658096,-0.0000011137,1.64
89408347\C,4.7947256685,-0.0000000825,4.3112423964\C,2.3068984548,0.00
00002678,5.6054294856\C,4.721989156,-0.0000005539,5.7040598397\H,5.639
0799958,-0.0000010784,6.2862810241\C,3.4764980553,-0.000003102,6.3508
116588\H,3.4290434339,-0.000000626,7.4359449231\H,1.329693107,0.000000
```

```
3181,6.0780381841\H,5.7590743733,-0.000000181,3.807852036\H,-0.9028525
988,-0.0000006447,1.8919681733\N,3.8341762798,0.0000016946,-0.58718765
3\H,4.0048085814,-0.8264903583,-1.1574592625\H,4.0048138498,0.82650013
69,-1.1574485185\\Version=IA32L-G03RevD.02\State=3-A\HF=-967.4880213\S
2=2.047448\S2-1=0.\S2A=2.001465\RMSD=8.739e-09\RMSF=2.662e-05\Thermal=
0.\Dipole=1.9661463,0.0000052,-1.578621\PG=C01 [X(C18H13N5)]\\@
```

Table 65. Computational output parameters for singlet **TAP 51n** (Y = Br).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C18H10Br2N4|USER|10-Feb-2013|0
||# opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene si
nglet opt Y:Br||0,1|C,1.2339501166,-0.7588086231,0.0000306134|C,-0.000
0025267,-1.4255767212,0.0000381862|C,-1.2339512147,-0.7588064663,0.000
03636|C,-1.2039190979,0.7059041258,0.0000270382|C,0.0000005971,1.40944
52149,0.0000188962|C,1.2039178672,0.7059030297,0.0000200581|N,2.397599
1081,1.3444289827,0.0000095236|N,2.3966228371,-1.4347917825,0.00003252
61|C,3.562472648,-0.7410908181,0.0000242221|C,3.6197555747,0.682633514
,0.0000117751|H,2.4042907599,2.3582126715,0.0000034021|H,0.0000007633,
2.4982428538,0.0000114204|C,4.7979705262,-1.4370230304,0.0000255235|C,
4.8340833561,1.3730972005,0.0000016083|C,5.988566401,-0.7369592576,0.0
000166431|C,6.0305837254,0.6674690511,0.000004057|H,4.7719533999,-2.52
00083831,0.0000329612|H,6.9809916689,1.1874092466,-0.0000056714|H,4.84
2999034,2.4612963079,-0.000008973|N,-2.3975979761,1.3444320682,0.00002
72611|N,-2.3966285594,-1.4347883089,0.0000427125|C,-3.6197558729,0.682
6396723,0.0000348347|C,-3.562473854,-0.7410854801,0.000041209|H,-2.404
2869093,2.3582159276,0.0000220329|C,-4.8340823082,1.3731068165,0.00003
45395|C,-4.7979762442,-1.4370143675,0.0000500984|C,-6.0305837335,0.667
4823071,0.0000401687|H,-6.9809915509,1.1874225339,0.0000375535|C,-5.98
85685426,-0.7369476012,0.0000514975|H,-4.7719608231,-2.5199998469,0.00
00536425|H,-4.8429933996,2.4613060265,0.0000284178|H,-0.000002725,-2.5
088530904,0.0000456386|Br,-7.6431659352,-1.6976107129,0.000053954|Br,7
.6431591095,-1.6976293008,0.0000204891||Version=IA32W-G09RevC.01|State
=1-A|HF=-6054.3652466|S2=0.|S2-1=0.|S2A=0.|RMSD=6.454e-009|RMSF=2.341e
-005|Dipole=0.0000149,3.6064227,-0.0000251|Quadrupole=-15.3623657,18.0
677607,-2.7053949,0.000017,0.0000093,-0.000131|PG=C01 [X(C18H10Br2N4)]
||@
```

Table 66. Computational output parameters for triplet **TAP 51n** (Y = Br).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C18H10Br2N4(3)|USER|10-Feb-201
3|0||# opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene
 triplet opt Y:Br||0,3|C,-1.2332278695,-0.152175984,0.00000207|C,-0.00
00003015,-0.8309793842,-0.0000061353|C,1.2332273503,-0.1521762056,-0.0
000050686|C,1.2073656764,1.2793163068,0.0000047657|C,0.0000000023,1.97
82739989,0.0000130342|C,-1.2073658172,1.2793165737,0.0000117973|N,-2.4
337328595,1.9294766077,0.0000199603|N,-2.3878741052,-0.8821860627,0.00
00003707|C,-3.5615073061,-0.1936979299,0.0000084492|C,-3.6306846512,1.
2373170454,0.0000185159|H,-2.4545195704,2.9400820203,0.0000261079|H,0.
0000001089,3.0670568763,0.0000204684|C,-4.779391154,-0.9161453824,0.00
00069688|C,-4.8654233576,1.8891136188,0.000026533|C,-5.9897432807,-0.2
45793854,0.0000150432|C,-6.049817215,1.1535611427,0.0000248627|H,-4.72
58449833,-1.9983000238,-0.0000006116|H,-7.0086439235,1.6590349845,0.00
00311387|H,-4.9043886235,2.9761016648,0.0000341377|N,2.433732862,1.929
4760935,0.0000056707|N,2.3878735162,-0.8821866045,-0.0000133185|C,3.63
0684493,1.2373162579,-0.0000023718|C,3.5615067871,-0.1936987213,-0.000
0118988|H,2.454519771,2.9400815007,0.0000121503|C,4.8654233486,1.88911
25525,-0.0000013887|C,4.7793905403,-0.9161464342,-0.0000201088|C,6.049
8170412,1.1535598287,-0.0000095845|H,7.0086438728,1.6590334326,-0.0000
087618|C,5.9897427794,-0.2457951798,-0.0000188583|H,4.7258440945,-1.99
83010631,-0.0000272629|H,4.9043888315,2.9761005918,0.0000058334|H,-0.0
000003851,-1.9149836837,-0.0000135313|Br,7.6224605082,-1.2416266096,-0
.0000298828|Br,-7.6224611847,-1.2416249748,0.0000129056||Version=IA32W
-G09RevC.01|State=3-A|HF=-6054.3462766|S2=2.048487|S2-1=0.|S2A=2.00153
|RMSD=5.490e-009|RMSF=2.571e-005|Dipole=0.0000002,3.0752434,0.0000203|
Quadrupole=-13.4727071,16.9190396,-3.4463325,0.0000032,0.0000285,0.000
134|PG=C01 [X(C18H10Br2N4)]||@
```

Table 67. Computational output parameters for singlet **TAP 51o** (Y = Me).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C20H16N4|GAUSSIAN|25-Nov
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|C,
0.027328467,-1.4461757861,0.0000002912|C,1.2245605419,-0.713783225,0.0
000004911|C,1.2718408881,0.6889034431,0.0000001878|C,-0.009320265,1.39
98470901,-0.0000004194|C,-1.2232223291,0.7130022415,-0.0000006457|C,-1
.2226538419,-0.6817444172,-0.0000002792|N,-2.3754536862,-1.3905576817,
-0.000004024|N,0.0250062552,-2.7909128433,0.0000006334|C,-1.163198619
```

```
2,-3.4512151559,0.0000004381|C,-2.4202556661,-2.7807876387,-0.00000007
11|H,-3.2543919867,-0.8854539358,-0.0000007104|H,-2.1641051478,1.26143
23365,-0.0000010775|C,-1.1929952658,-4.8659265238,0.0000010499|C,-3.62
56202038,-3.4839218554,0.0000001434|C,-2.3849550348,-5.5811031772,0.00
00010077|C,-3.6060872082,-4.8737650787,0.0000007971|H,-0.2335264322,-5
.3757593192,0.0000016968|H,-4.5442168936,-5.4218521682,0.0000011902|H,
-4.5708361381,-2.9435818699,0.0000001715|N,0.0393407456,2.752251519,-0
.0000007304|N,2.4408035844,1.3536179766,0.0000004758|C,1.2269557554,3.
4763485515,-0.0000004483|C,2.4298047556,2.7129236967,0.0000001904|H,-0
.8333160971,3.2681316138,-0.0000011558|C,1.2447705165,4.8716930653,-0.
000000715|C,3.64611685,3.436027629,0.0000005512|C,2.4637534225,5.53961
88313,-0.0000003432|H,2.4783516688,6.6260229703,-0.0000005259|C,3.6810
156126,4.825642041,0.0000002873|H,4.562574212,2.8524047541,0.000001075
6|H,0.3087930026,5.4278820909,-0.0000011728|H,2.1605385678,-1.25935218
87,0.0000009516|C,5.0028312297,5.5608761331,0.0000005107|H,5.602751323
1,5.3042704549,0.8818687537|H,5.6027497768,5.3042737663,-0.881869769|H
,4.8576510349,6.6460410488,0.0000026302|C,-2.373313113,-7.0935958083,-
0.000000649|H,-1.8544126509,-7.4891533442,-0.8818843667|H,-1.854364359
1,-7.4891549689,0.8818536845|H,-3.3891034719,-7.5020437073,0.000026272
7||Version=IA32W-G09RevC.01|State=1-A|HF=-990.7918974|S2=0.|S2-1=0.|S2
A=0.|RMSD=2.705e-009|RMSF=3.873e-005|Dipole=-2.3893117,1.3927032,-0.00
00023|Quadrupole=4.6157945,6.7063035,-11.3220981,1.84557,0.0000093,0.0
000107|PG=C01 [X(C20H16N4)]||@
```

Table 68. Computational output parameters for triplet **TAP 51o** (Y = Me).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C20H16N4(3)|GAUSSIAN|26-
 Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
 |C,-1.2345062895,0.5145654258,-0.0000000986|C,-0.0000001104,1.19177263
 ,-0.0000003539|C,1.2345062737,0.5145657837,0.000000081|C,1.2083192598,
 -0.9174616951,0.0000009057|C,0.0000002748,-1.6153989056,0.0000011719|C
 ,-1.2083189099,-0.9174620264,0.0000006344|N,-2.433947202,-1.567513829,
 0.0000006569|N,-2.3888761647,1.2449227122,-0.0000006258|C,-3.565481471
 5,0.5566130277,-0.0000004277|C,-3.6323697063,-0.8743284242,0.000000171
 3|H,-2.4550293621,-2.5779654514,0.0000011982|H,0.0000004243,-2.7044488
 414,0.0000017432|C,-4.784470396,1.2717684949,-0.0000012171|C,-4.867642
 6888,-1.5203390707,-0.0000002772|C,-6.022384534,0.6338762982,-0.000001
 3055|C,-6.0459696455,-0.7722438345,-0.0000011654|H,-4.7122576848,2.355
 987202,-0.0000019908|H,-7.0010191032,-1.2914111391,-0.0000018399|H,-4.
```

```
9093941904,-2.6077677598,-0.0000004306|N,2.4339477305,-1.5675131567,0.
0000014052|N,2.3888759231,1.2449233633,-0.0000003582|C,3.6323700496,-0
.8743274211,0.0000008588|C,3.5654814409,0.5566139991,-0.0000000215|H,2
.4550301754,-2.577964773,0.0000017532|C,4.867643207,-1.5203377385,0.00
00011217|C,4.7844701543,1.2717698088,-0.0000006336|C,6.0459699587,-0.7
722421762,0.0000004943|H,7.0010195561,-1.2914092238,0.0000006723|C,6.0
223844684,0.6338779477,-0.0000003843|H,4.7122571459,2.3559884952,-0.00
00013552|H,4.909395003,-2.607766416,0.0000017732|H,-0.0000002813,2.275
87727,-0.0000009665|C,7.3053795867,1.4336793423,-0.0000008846|H,7.3735
450805,2.0826422726,-0.8818588897|H,7.3735473645,2.0826397381,0.881858
8318|H,8.1832358688,0.7795730052,-0.0000029139|C,-7.3053798706,1.43367
73404,0.0000007213|H,-7.3735607967,2.0826142271,0.8818768657|H,-7.3735
325654,2.0826637394,-0.881840855|H,-8.1832359704,0.7795707589,-0.00003
10652||Version=IA32W-G09RevC.01|State=3-A|HF=-990.7735118|S2=2.048024|
S2-1=0.|S2A=2.001502|RMSD=6.025e-009|RMSF=2.539e-005|Dipole=0.0000003,
-2.1813189,0.0000023|Quadrupole=9.0509243,3.0888228,-12.1397472,0.0000
009,-0.0000156,-0.0000042|PG=C01 [X(C20H16N4)]||@
```

Table 69. Computational output parameters for singlet **TAP 51p** (Parent, X = Y = H).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C18H12N4\GAUSSIAN\30-Mar-2005\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\linear tetraazapentacene sing
let opt\\0,1\C,-1.2528558666,0.0129572165,-0.733033554\C,-1.260464853,
0.059809258,0.6694929408\C,-0.0927583804,0.0509127021,1.4477219502\C,1
.184938623,-0.0108523184,0.7343987626\C,1.2396907557,-0.0587493703,-0.
6584541693\C,0.0536396632,-0.0478188963,-1.3922571923\N,0.057480505,-0
.0928432951,-2.7450057771\N,-2.394377934,0.0232665779,-1.4440136966\C,
-2.3299635568,-0.0237125654,-2.8002851627\C,-1.0999667208,-0.084068620
5,-3.5166205581\H,0.9493831438,-0.135322958,-3.2250393998\H,2.20060400
76,-0.104295169,-1.1688178197\C,-3.5183818178,-0.0140687879,-3.5729462
099\C,-1.0541618489,-0.1318033436,-4.9128488099\C,-3.4730062358,-0.061
3237118,-4.9556852368\C,-2.2414234158,-0.1204935844,-5.6348807339\H,-4
.4596147951,0.0316683754,-3.0345122067\H,-4.3986047331,-0.0526601541,-
5.5247268829\H,-2.2146399048,-0.1575421036,-6.7196083267\H,-0.09295764
85,-0.1774093012,-5.4221744177\N,2.3092477233,-0.0193098487,1.48791111
36\N,-0.1414988707,0.0970223816,2.7909380473\C,2.3018903444,0.02709672
89,2.8782226512\C,1.0196057237,0.0858694878,3.4962587399\H,3.206370292
6,-0.0616605872,1.0176903558\C,3.485771681,0.0165384187,3.6213028547\C
,0.9958102193,0.1336615777,4.9128396729\C,3.4206114635,0.0644519862,5.
```

```
0085569873\H,4.3354358466,0.056469174,5.5931578382\C,2.1682442052,0.12
3085627,5.6487187061\H,2.1225391645,0.1603502718,6.7336794412\H,0.0226
484688,0.1784115552,5.3912500725\H,4.445959627,-0.029050689,3.11005876
02\H,-2.2164033341,0.1051400494,1.1772249426\\Version=x86-Linux-G03Rev
B.05\State=1-A\HF=-912.156554\S2=0.\S2-1=0.\S2A=0.\RMSD=2.297e-09\RMSF
=6.758e-06\Dipole=2.5714359,-0.1221197,-1.3658341\PG=C01 [X(C18H12N4)]
\\@
```

Table 70. Computational output parameters for triplet **TAP 51p** (Parent, X = Y = H).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C18H12N4(3)\GAUSSIAN\05-Apr-2005\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\linear tetraazapentacene t
riplet opt\\0,3\C,-1.1969543973,0.0113921502,-0.7615956203\C,-1.215456
9905,0.0592382884,0.6453716938\C,-0.0380900278,0.04887439,1.4173696551
\C,1.212931819,-0.0130293139,0.7235926192\C,1.2617920333,-0.0613861362
,-0.6700217602\C,0.078524378,-0.0497285871,-1.4093937742\N,0.076745655
5,-0.096305781,-2.7965378171\N,-2.3830000069,0.0252086296,-1.439269207
2\C,-2.3271307872,-0.0222357704,-2.8000143777\C,-1.0964804958,-0.08475
47194,-3.5307076193\H,0.9588292177,-0.1399972703,-3.2880391591\H,2.222
7473795,-0.1081290102,-1.1802546964\C,-3.5314479206,-0.010044021,-3.54
36684737\C,-1.096380157,-0.1316286186,-4.9265137993\C,-3.5231368838,-0
.0567625037,-4.9297917731\C,-2.3048574377,-0.117705859,-5.6231416149\H
,-4.4578149873,0.0379488682,-2.9800059713\H,-4.4598182251,-0.046194886
2,-5.4794502046\H,-2.2954412882,-0.1542622364,-6.7086807956\H,-0.15101
46416,-0.1788024706,-5.4634295673\N,2.3625083196,-0.0223573481,1.50125
97612\N,-0.1395880821,0.0977927382,2.7788262015\C,2.3149718148,0.02534
1021,2.8836848755\C,1.020342749,0.0859988663,3.4939950015\H,3.26374800
96,-0.0657155776,1.0458055271\C,3.47276811,0.0155150828,3.6645701411\C
,0.9633223518,0.1352987727,4.9074716008\C,3.3743894522,0.0651261036,5.
0551798758\H,4.2800346637,0.0571411089,5.6548226527\C,2.1175995382,0.1
251403718,5.6761512352\H,2.049387583,0.1637903463,6.7594045956\H,-0.02
25616136,0.1809897191,5.3592933393\H,4.4470490275,-0.0308906357,3.1820
122185\H,-2.1720492195,0.1058572672,1.1533421798\\Version=x86-Linux-G0
3RevB.05\State=3-A\HF=-912.1383063\S2=2.04819\S2-1=0.\S2A=2.001513\RMS
D=3.043e-09\RMSF=1.402e-05\Dipole=2.0638404,-0.1004567,-1.0958547\PG=C
01 [X(C18H12N4)]\\@
```

Table 71. Computational output parameters for singlet **TAP 51q** (Z = C≡N).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C19H11N5|USER|09-Feb-2013|0||#
 opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|C,-1.0313583
169,-1.2379081739,0.|C,-1.6948492414,0.0000000817,0.|C,-1.0313582248,1
.2379082756,0.|C,0.4265142829,1.2208852328,0.|C,1.1400641936,0.0000001
239,0.|C,0.426514131,-1.220885109,0.|N,1.0663110611,-2.4037843035,0.|N
,-1.7078813544,-2.4010989301,0.|C,-1.0176656227,-3.5695688887,0.|C,0.4
056351873,-3.6281425298,0.|H,2.0828965717,-2.4039726209,0.|C,-1.707726
4195,-4.808565093,0.|C,1.1041935122,-4.8393458189,0.|C,-1.0172341515,-
6.0070129915,0.|C,0.3917891597,-6.0308365235,0.|H,-2.7923240783,-4.773
9499925,0.|H,-1.5671721548,-6.9439641165,0.|H,0.9227823529,-6.97757955
07,0.|H,2.1923925437,-4.838484191,0.|N,1.0663114747,2.403784399,0.|N,-
1.7078812877,2.4010993736,0.|C,0.4056357772,3.6281429234,0.|C,-1.01766
52466,3.5695695088,0.|H,2.0828970615,2.4039725074,0.|C,1.1041942811,4.
839346295,0.|C,-1.7077260079,4.8085659632,0.|C,0.3917899797,6.03083723
41,0.|H,0.9227833366,6.9775802371,0.|C,-1.0172334495,6.0070138981,0.|H
,-1.5671713463,6.9439651453,0.|H,-2.7923237745,4.7739509437,0.|H,2.192
3933695,4.838484529,0.|H,-2.7780259821,0.0000001964,0.|C,2.5596491189,
0.0000006102,0.|N,3.7272942634,-0.0000026448,0.||Version=IA32W-G09RevC
.01|State=1-A'|HF=-1004.4051539|S2=0.|S2-1=0.|S2A=0.|RMSD=5.942e-009|R
MSF=2.969e-005|Dipole=1.13725,0.0000006,0.|Quadrupole=-11.3731187,18.5
672272,-7.1941085,0.0000134,0.,0.|PG=CS [SG(C19H11N5)]||@
```

Table 72. Computational output parameters for triplet **TAP 51q** (Z = C≡N).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C19H11N5(3)|GAUSSIAN|17-
Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
|C,0.9541708682,-1.237807526,0.|C,1.6278209379,0.0000014747,0.|C,0.954
1702086,1.2378102014,0.|C,-0.4735807463,1.2234339817,0.|C,-1.179569504
4,0.0000011717,0.|C,-0.4735801168,-1.2234317591,0.|N,-1.1237728094,-2.
438357182,0.|N,1.6866602667,-2.3893131271,0.|C,1.0011279041,-3.5675770
534,0.|C,-0.4282445518,-3.6386824332,0.|H,-2.13655086,-2.4542046431,0.
|C,1.7191625743,-4.7870487985,0.|C,-1.0854318367,-4.8695545282,0.|C,1.
0605046261,-6.007140209,0.|C,-0.3422929434,-6.0499735997,0.|H,2.802571
4551,-4.7228935409,0.|H,1.6303917994,-6.9315503522,0.|H,-0.8590049894,
-7.0051454406,0.|H,-2.1726899588,-4.9008089338,0.|N,-1.1237743589,2.43
83588286,0.|N,1.6866587428,2.3893162697,0.|C,-0.4282468243,3.638684438
```

```
4,0.|C,1.0011256874,3.5675798791,0.|H,-2.1365524652,2.4542052689,0.|C,
-1.0854348542,4.8695561324,0.|C,1.7191596872,4.7870520118,0.|C,-0.3422
966077,6.0499755946,0.|H,-0.8590092128,7.0051471282,0.|C,1.0605010033,
6.0071430251,0.|H,1.6303876355,6.9315535001,0.|H,2.8025686099,4.722897
3762,0.|H,-2.1726929948,4.9008098968,0.|H,2.7119195506,0.00000171,0.|C
,-2.6018927597,0.0000026429,0.|N,-3.768839163,-0.0000094054,0.||Versio
n=IA32W-G09RevC.01|State=3-A'|HF=-1004.3872358|S2=2.049781|S2-1=0.|S2A
=2.001607|RMSD=8.074e-009|RMSF=2.182e-005|Dipole=-0.53852,0.0000042,0.
|Quadrupole=-11.3753205,19.5575987,-8.1822782,-0.0000539,0.,0.|PG=CS [
SG(C19H11N5)]||@
```

Table 73. Computational output parameters for singlet **TAP 51r** (Y = CF_3).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H10F6N4|USER|07-Feb-2013|0|
|# opt ub3lyp/6-31g(d) geom=connectivity||tolyl Y:CF3||0,1|C,1.2337300
479,1.9359276832,-0.005130224|C,-0.0000001043,2.603057888,-0.000000230
8|C,-1.23373019,1.9359276246,0.0051301421|C,-1.2035100779,0.4717096623
,0.0065152337|C,-0.0000000448,-0.2322161484,0.0000005786|C,1.203509972
3,0.4717097301,-0.0065144697|N,2.3970342443,-0.1681358797,-0.014397453
5|N,2.3974051085,2.6104712319,-0.0085251065|C,3.5624536645,1.915216458
1,-0.0140538946|C,3.6189162466,0.4925152596,-0.0186393497|H,-0.0000000
29,-1.3209299757,0.0000008964|C,4.7999119047,2.6060254814,-0.016011068
4|C,4.8325726002,-0.2025327038,-0.0290111879|C,5.9984500582,1.91437551
55,-0.0248921324|C,6.0245964852,0.504435906,-0.032785835|H,4.770648397
1,3.6891490924,-0.0134452125|H,4.8362030067,-1.2906034707,-0.036958568
8|N,-2.3970343231,-0.1681359846,0.0143985864|N,-2.3974052864,2.6104712
25,0.0085246308|C,-3.6189163566,0.4925151295,0.0186400863|C,-3.5624538
179,1.915216325,0.0140538082|C,-4.8325726903,-0.2025328535,0.029012311
2|C,-4.7999120589,2.6060253418,0.0160105742|C,-6.0245965942,0.50443574
86,0.0327865391|C,-5.9984502087,1.9143753463,0.0248920255|H,-4.7706485
345,3.6891489566,0.0134440967|H,-4.8362030831,-1.290603619,0.036960322
1|H,-0.0000001608,3.6863035867,-0.0000005446|H,6.9727155937,-0.0217964
457,-0.0476121893|H,-6.9727156869,-0.0217966319,0.0476131878|C,7.30980
2767,2.6507857836,0.0169217849|C,-7.3098029339,2.6507855649,-0.0169223
216|F,8.1866372174,2.1497749573,-0.8860135655|F,7.9027366133,2.5374456
4,1.2298030384|F,-7.1736020253,3.9673125746,0.2385956653|F,-7.90273677
4,2.5374447512,-1.2298035178|F,7.1736018151,3.9673126435,-0.238596927|
F,-8.1866374066,2.1497752263,0.88601328|H,2.4029959576,-1.1820429803,-
0.0164827311|H,-2.4029960215,-1.1820430911,0.0164844529||Version=IA32W
```

```
-G09RevC.01|State=1-A|HF=-1586.2315551|S2=0.|S2-1=0.|S2A=0.|RMSD=1.781
e-009|RMSF=1.464e-006|Dipole=0.0000012,-3.8363199,0.0000012|Quadrupole
=-25.8905291,22.666732,3.2237971,-0.0000004,-0.8397381,-0.000006|PG=C0
1 [X(C20H10F6N4)]||@
```

Table 74. Computational output parameters for triplet **TAP 51r** (Y = CF_3).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H10F6N4(3)|USER|08-Feb-2013
|0||# opt ub3lyp/6-31g(d) geom=connectivity||Y:CF3||0,3|C,1.23341481,1
.8516930654,-0.0065719653|C,-0.0000000954,2.5311071774,-0.0000001792|C
,-1.233414981,1.8516930198,0.0065720155|C,-1.206881132,0.4199386158,0.
0052817497|C,-0.0000000403,-0.2790823888,0.0000006773|C,1.2068810182,0
.4199386605,-0.0052808296|N,2.4339059327,-0.2308536583,-0.0098292403|N
,2.3874935838,2.5800394399,-0.0143021652|C,3.5627474414,1.8896400356,-
0.0194579642|C,3.6293783678,0.4589648678,-0.0174656088|H,-0.000000024,
-1.3678263636,0.0000010048|C,4.780720395,2.6053267747,-0.0309685139|C,
4.8632807871,-0.1974126051,-0.0270180635|C,6.001192402,1.9424508646,-0
.040203974|C,6.0436630801,0.5390008817,-0.0379324851|H,4.724613188,3.6
878830793,-0.0390450745|H,4.8970140236,-1.284435271,-0.0308135735|N,-2
.433906019,-0.2308537453,0.0098305261|N,-2.3874937739,2.5800393569,0.0
143017446|C,-3.6293784826,0.4589647368,0.0174664549|C,-3.5627476123,1.
8896399086,0.0194579369|C,-4.8632808728,-0.1974127773,0.0270192723|C,-
4.7807205845,2.6053266041,0.0309680026|C,-6.0436631999,0.5390006735,0.
0379331753|C,-6.0011925754,1.9424506513,0.0402038071|H,-4.7246134274,3
.6878829172,0.0390439014|H,-4.8970140726,-1.284435441,0.030815449|H,-0
.000000124,3.6150937107,-0.0000005133|H,6.9997725564,0.0274351166,-0.0
541962094|H,-6.999772655,0.0274348806,0.0541971612|C,7.2863865578,2.72
04622437,0.0064176332|C,-7.2863867139,2.7204620258,-0.0064184041|F,8.2
797635292,2.0821532857,-0.6563519498|F,7.7223357716,2.8994124619,1.276
9210572|F,-7.1573850279,3.9484436306,0.5393856785|F,-7.7223352822,2.89
94123112,-1.2769220342|F,7.157384629,3.9484438505,-0.5393863641|F,-8.2
797640296,2.082153082,0.656350669|H,2.4541316837,-1.2416475214,-0.0109
724773|H,-2.4541317356,-1.2416476083,0.0109743665||Version=IA32W-G09Re
vC.01|State=3-A|HF=-1586.2137442|S2=2.048272|S2-1=0.|S2A=2.001511|RMSD
=6.262e-009|RMSF=1.244e-005|Dipole=0.,-3.3705176,0.0000011|Quadrupole=
-23.862748,21.3478245,2.5149235,0.0000002,-1.0179927,-0.0000058|PG=C01
 [X(C20H10F6N4)]||@
```

Table 75. Computational output parameters for singlet **TAP 51s** (X = Br).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10Br2N4|GAUSSIAN|19-
Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1
|C,0.035883994,-1.4493410705,0.|C,1.2334004123,-0.7189506913,0.|C,1.27
87967707,0.6829962664,0.|C,-0.0009215719,1.3940106435,0.|C,-1.21504344
78,0.7082159968,0.|C,-1.2134507608,-0.6862033476,0.|N,-2.3679372954,-1
.3945689776,0.|N,0.0330564012,-2.794849374,0.|C,-1.1533099882,-3.45201
56511,0.|C,-2.4119507657,-2.7837765396,0.|H,-3.2466247772,-0.888911030
6,0.|H,-2.1556735361,1.2564971176,0.|C,-1.1860680865,-4.869345489,0.|C
,-3.6257336466,-3.4753179053,0.|C,-2.381433284,-5.5657590128,0.|C,-3.5
976816976,-4.8627919328,0.|H,-0.2343796149,-5.3905983378,0.|H,-2.38813
29181,-6.6500509311,0.|H,-4.5712951907,-2.9408398585,0.|N,0.046517783,
2.7476621908,0.|N,2.4481811237,1.3485315717,0.|C,1.233631565,3.4705701
81,0.|C,2.4353587071,2.7046918735,0.|H,-0.8264989287,3.263048879,0.|C,
1.2372088914,4.8675261383,0.|C,3.6524901747,3.4316635955,0.|C,2.458328
9834,5.52687289,0.|C,3.6693834597,4.8149941383,0.|H,4.6095670019,5.355
1692363,0.|H,4.5750511328,2.8604397175,0.|H,0.3061605886,5.426902504,0
.|H,2.1693222074,-1.2644856975,0.|Br,-5.2435395366,-5.8303130198,0.|Br
,2.4891195599,7.4357988766,0.||Version=IA32W-G09RevC.01|State=1-A'|HF=
-6054.3654864|S2=0.|S2-1=0.|S2A=0.|RMSD=1.990e-009|RMSF=2.182e-005|Dip
ole=-1.9157573,1.116674,0.|Quadrupole=4.7385409,-5.6427092,0.9041683,-
9.164932,0.,0.|PG=CS [SG(C18H10Br2N4)]||@
```

Table 76. Computational output parameters for triplet **TAP 51s** (X = Br).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10Br2N4(3)|GAUSSIAN|
20-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||
0,3|C,-1.19797069,1.2331994774,0.|C,-1.8764487833,0.00000017,0.|C,-1.1
979706437,-1.2331991317,0.|C,0.2334336517,-1.2072654762,0.|C,0.9323472
906,0.0000002329,0.|C,0.2334335887,1.2072659233,0.|N,0.8850225527,2.43
36447695,0.|N,-1.9267424818,2.388655585,0.|C,-1.2381797418,3.562034762
6,0.|C,0.1935730625,3.6303724075,0.|H,1.8956663267,2.4535781338,0.|H,2
.0211301076,0.0000002534,0.|C,-1.9501481449,4.784943253,0.|C,0.8542000
263,4.8595828215,0.|C,-1.2985966459,6.0089512102,0.|C,0.1009264868,6.0
3235128,0.|H,-3.0338139092,4.7277289957,0.|H,-1.8579440796,6.937311757
7,0.|H,1.9388751077,4.9047542441,0.|N,0.8850226749,-2.4336442877,0.|N,
-1.9267423503,-2.3886552439,0.|C,0.1935732489,-3.6303719639,0.|C,-1.23
```

```
81795445,-3.5620344132,0.|H,1.8956664498,-2.453577613,0.|C,0.854200289
8,-4.8595823464,0.|C,-1.9501478877,-4.7849429225,0.|C,0.100926809,-6.0
323508326,0.|C,-1.2985963209,-6.0089508511,0.|H,-1.8579436991,-6.93731
14314,0.|H,-3.0338136552,-4.7277287266,0.|H,1.9388753731,-4.904753704,
0.|H,-2.9604739513,0.00000016,0.|Br,1.0097020308,7.7099962979,0.|Br,1.
0097024514,-7.7099958115,0.||Version=IA32W-G09RevC.01|State=3-A'|HF=-6
054.3480463|S2=2.048331|S2-1=0.|S2A=2.001522|RMSD=5.282e-009|RMSF=2.32
0e-005|Dipole=1.7107864,0.0000001,0.|Quadrupole=10.2794239,-9.335411,-
0.944013,0.0000008,0.,0.|PG=CS [SG(C18H10Br2N4)]||@
```

Table 77. Computational output parameters for singlet **TAP 51t** (Y = C≡N).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H10N6|USER|06-Feb-2013|0||#
opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene Y:CN
singlet opt||0,1|C,1.2330070593,-0.771297883,0.0000396943|C,-0.0000037
682,-1.4388896327,0.0000545256|C,-1.2330096708,-0.7712952161,0.0000520
693|C,-1.2029654091,0.6932496196,0.0000344755|C,0.0000003263,1.3976699
935,0.0000165057|C,1.2029627362,0.6932482627,0.0000166555|N,2.39682360
14,1.3332975123,-0.0000058493|N,2.3963181984,-1.4455090989,0.000046406
3|C,3.56109995,-0.7505974699,0.0000283057|C,3.6179738013,0.6737846801,
0.000002715|H,2.4027669797,2.3473725748,-0.0000198238|H,0.0000005146,2
.4862952235,0.0000007356|C,4.7956369504,-1.4412084559,0.0000326653|C,4
.8302760685,1.3712531791,-0.0000136002|C,6.0029206856,-0.7460794206,0.
0000138779|C,6.0248854572,0.6698269289,-0.000009105|H,4.7703872357,-2.
524903033,0.0000501536|H,6.9733019132,1.1946870383,-0.0000220516|H,4.8
318996024,2.4591636098,-0.0000323157|N,-2.3968230901,1.3333014333,0.00
00369607|N,-2.3963265064,-1.4455045833,0.0000643361|C,-3.6179753263,0.
673792343,0.0000527343|C,-3.5611024441,-0.7505905844,0.0000662559|H,-2
.4027630451,2.3473766634,0.0000282573|C,-4.8302756474,1.3712652662,0.0
000552523|C,-4.7956447694,-1.4411972576,0.0000818273|C,-6.0248864421,0
.6698435014,0.000065058|H,-6.9733026415,1.1947038301,0.0000617804|C,-6
.0029242001,-0.7460647959,0.0000806915|H,-4.7703975428,-2.5248919617,0
.0000885431|H,-4.8318935956,2.4591757522,0.0000432169|H,-0.0000038882,
-2.5221031435,0.0000694803|C,-7.243625987,-1.4659429466,0.0000879529|N
,-8.2570373961,-2.0373804084,0.0000940666|C,7.2436189847,-1.4659634049
,0.0000106836|N,8.2570270644,-2.037406836,0.000004833||Version=IA32W-G
09RevC.01|State=1-A|HF=-1096.6423964|S2=0.|S2-1=0.|S2A=0.|RMSD=6.134e-
009|RMSF=8.400e-005|Dipole=0.0000102,4.6812594,-0.0000488|Quadrupole=-
```

```
49.0278118,30.5864591,18.4413527,0.0001324,0.0003208,-0.0001999|PG=C01
 [X(C20H10N6)]||@
```

Table 78. Computational output parameters for triplet **TAP 51t** (Y = C≡N).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H10N6(3)|USER|06-Feb-2013|0
||# opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene Y:
CN singlet opt||0,3|C,1.2331258192,-0.439320434,-0.0000019645|C,-0.000
0000467,-1.1196747867,0.0000139637|C,-1.2331258275,-0.4393203848,0.000
0128913|C,-1.206339893,0.9928101303,-0.0000052138|C,-0.0000000296,1.69
24846252,-0.0000212439|C,1.2063398273,0.9928101245,-0.0000197873|N,2.4
345291535,1.6429067843,-0.0000356228|N,2.3860387646,-1.1669625357,0.00
0000372|C,3.5623509611,-0.4767339307,-0.0000150077|C,3.6282931515,0.95
48633403,-0.0000334505|H,2.4547830335,2.6539567203,-0.0000468975|H,-0.
0000000069,2.7811046396,-0.0000348421|C,4.7766484763,-1.1933642768,-0.
0000128807|C,4.8625943404,1.6137033291,-0.0000487102|C,6.0058888948,-0
.528485089,-0.0000282219|C,6.0435920433,0.8822352519,-0.0000462114|H,4
.7239287214,-2.2762538828,0.0000010501|H,7.0004584822,1.3930083038,-0.
0000581245|H,4.8948044807,2.7005859235,-0.0000625644|N,-2.4345292192,1
.6429068084,-0.0000059445|N,-2.3860388664,-1.1669625369,0.000028901|C,
-3.6282932188,0.9548633598,0.000009713|C,-3.5623509838,-0.4767339276,0
.0000272318|H,-2.4547830832,2.6539567456,-0.0000179937|C,-4.8625944079
,1.6137033477,0.0000088141|C,-4.7766485644,-1.1933642558,0.000043379|C
,-6.0435921178,0.882235288,0.0000249093|H,-7.0004585664,1.3930083183,0
.0000241838|C,-6.0058889534,-0.5284850726,0.0000423278|H,-4.7239287762
,-2.2762538612,0.0000566136|H,-4.8948045322,2.7005859429,-0.0000045279
|H,-0.0000000687,-2.2036090167,0.0000275497|C,-7.2306630828,-1.2713682
344,0.0000589306|N,-8.2315694722,-1.8650488593,0.0000723524|C,7.230662
9498,-1.2713683612,-0.000025861|N,8.2315696074,-1.8650485376,-0.000024
1179||Version=IA32W-G09RevC.01|State=3-A|HF=-1096.6252017|S2=2.048739|
S2-1=0.|S2A=2.001538|RMSD=6.193e-009|RMSF=2.140e-005|Dipole=0.,4.23211
08,-0.0000522|Quadrupole=-47.851212,29.7405432,18.1106687,-0.0000025,0
.0003881,-0.000138|PG=C01 [X(C20H10N6)]||@
```

Table 79. Computational output parameters for singlet **TAP 51u** (X = Me).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H16N4|USER|05-Feb-2013|0||#
opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene X:Me
singlet opt||0,1|C,1.2355908516,-0.7742504372,0.0000709901|C,-0.000002
8376,-1.4400594086,0.0000908968|C,-1.2355919954,-0.774247118,0.0000887
594|C,-1.2047473985,0.6895102609,0.0000648634|C,0.0000015291,1.3924180
964,0.00004658|C,1.2047473842,0.689508082,0.0000496945|N,2.3976384575,
1.3305363179,0.0000325848|N,2.3998096152,-1.4481789492,0.0000693805|C,
3.5662799399,-0.7516775149,0.0000575406|C,3.6226880302,0.6717004509,0.
0000444654|H,2.4019637127,2.3442419075,0.000018087|H,0.0000022834,2.48
14770109,0.0000290646|C,4.8096574094,-1.4282267286,0.0000272525|C,4.83
16296266,1.3697421262,0.0000103555|C,6.0053876224,-0.7304853574,-0.000
0053815|C,6.0447243156,0.6802762463,0.0000043787|H,4.786546834,-2.5133
373091,0.0000007848|H,6.9431607129,-1.2810058738,-0.000039657|H,4.8215
942937,2.4596319782,-0.0000145477|N,-2.3976356251,1.33054147,0.0000616
59|N,-2.3998158235,-1.4481733208,0.0001059084|C,-3.6226869706,0.671709
6464,0.0000803194|C,-3.5662809327,-0.7516690183,0.0001018941|H,-2.4019
57366,2.3442472016,0.0000451115|C,-4.8316266775,1.3697557098,0.0000713
946|C,-4.8096631203,-1.4282138052,0.0001108585|C,-6.0447226844,0.68029
45464,0.0000901811|C,-6.0053894515,-0.7304688131,0.00010383|H,-6.94316
50304,-1.2809851542,0.000111109|H,-4.7865553943,-2.5133245181,0.000119
4485|H,-4.8215859,2.4596455756,0.0000524015|H,-0.0000035626,-2.5234452
049,0.0001069078|C,-7.3577769013,1.4271924728,0.0001394241|H,-7.457825
2232,2.0723663785,0.8828306222|H,-7.4573810603,2.073260969,-0.88194240
61|H,-8.2061640629,0.7356273137,-0.0004138625|C,7.3577793358,1.4271730
942,0.0001944161|H,7.4566862951,2.0746310399,-0.8809388727|H,7.4585256
3,2.0709548028,0.8838297861|H,8.2061652587,0.7356099036,-0.0020874029|
|Version=IA32W-G09RevC.01|State=1-A|HF=-990.7919439|S2=0.|S2-1=0.|S2A=
0.|RMSD=2.398e-009|RMSF=4.402e-005|Dipole=0.0000074,3.0302689,0.000085
5|Quadrupole=9.3891319,0.8225508,-10.2116828,-0.0000387,0.0008816,0.00
0185|PG=C01 [X(C20H16N4)]||@
```

Table 80. Computational output parameters for triplet **TAP 51u** (X = Me).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C20H16N4(3)|USER|05-Feb-2013|0
||# opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene X:
Me singlet opt||0,3|C,-1.2342478664,0.8354664257,-0.0000078499|C,0.000
0000376,1.5127361346,0.0000198166|C,1.2342479094,0.8354664051,0.000012
```

```
9204|C,1.2082624371,-0.5963591825,-0.0000250139|C,0.0000000548,-1.2942
683673,-0.0000527823|C,-1.2082623301,-0.5963591926,-0.0000436699|N,-2.
4342047193,-1.2476035318,-0.0000685459|N,-2.3895437827,1.5643260191,-0
.0000014341|C,-3.5640314542,0.8742122424,-0.0000202769|C,-3.6337894536
,-0.5571739854,-0.0000512655|H,-2.4536878473,-2.2581026918,-0.00009573
68|H,0.0000000456,-2.3833638409,-0.0000811421|C,-4.7889432581,1.579208
4764,-0.0000442995|C,-4.8632970097,-1.2133923652,-0.0000940233|C,-6.00
59741806,0.9135939138,-0.0000856535|C,-6.0650771309,-0.491464559,-0.00
00858123|H,-4.7361165961,2.6634088379,-0.000060098|H,-6.9311943866,1.4
840255256,-0.0001212737|H,-4.8864279385,-2.3025453466,-0.000137783|N,2
.4342048388,-1.2476035207,-0.0000320653|N,2.3895438674,1.5643260453,0.
0000416295|C,3.6337895773,-0.5571739662,-0.0000014185|C,3.5640315057,0
.8742122984,0.0000353259|H,2.4536879584,-2.2581026811,-0.000059752|C,4
.86329712,-1.2133923077,-0.0000131991|C,4.7889433022,1.5792085534,0.00
00571549|C,6.0650772551,-0.4914644451,0.0000163298|C,6.005974242,0.913
5939998,0.0000456187|H,6.9311944388,1.4840256177,0.0000585729|H,4.7361
166064,2.6634089129,0.0000754808|H,4.8864280417,-2.302545295,-0.000046
7157|H,0.0000000461,2.5968476377,0.0000472743|C,7.3880957603,-1.218165
6706,0.0000716024|H,7.4926039673,-1.8628658483,0.8823216756|H,7.492167
9801,-1.8638096562,-0.8815333512|H,8.2276293285,-0.5164260474,-0.00049
72862|C,-7.3880956226,-1.2181657768,0.0001436526|H,-7.4914751669,-1.86
53057971,-0.8804359121|H,-7.4932973231,-1.8613671482,0.8834140682|H,-8
.2276282528,-0.5164288221,-0.0022337619||Version=IA32W-G09RevC.01|Stat
e=3-A|HF=-990.7750717|S2=2.048158|S2-1=0.|S2A=2.00151|RMSD=5.689e-009|
RMSF=2.437e-005|Dipole=-0.0000005,-2.4663894,0.0001079|Quadrupole=11.1
121164,0.5126388,-11.6247552,-0.0000032,-0.0012023,-0.0001151|PG=C01 [
X(C20H16N4)]||@
```

Table 81. Computational output parameters for singlet **TAP 51v** (Y = NO_2).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10N6O4|GAUSSIAN|26-N
ov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|
C,0.0449024332,-1.4531154839,-0.0000167087|C,1.2428008999,-0.724419434
2,0.0000001053|C,1.2865379016,0.6770252187,0.0000168291|C,0.0064878347
,1.3881074119,0.0000160094|C,-1.2081244209,0.7041955135,-0.0000000887|
C,-1.2046549001,-0.6897205301,-0.0000160933|N,-2.3597915295,-1.3982824
372,-0.0000317737|N,0.040849715,-2.7978901845,-0.0000328703|C,-1.14604
50307,-3.4535368255,-0.0000485614|C,-2.4060309424,-2.7842146539,-0.000
0484227|H,-3.2384779812,-0.8919304774,-0.0000315421|H,-2.1485850727,1.
```

```
2523793227,-0.0000001664|C,-1.1722217405,-4.8685223786,-0.0000662547|C
,-3.6215044915,-3.4783834706,-0.0000641919|C,-2.3855572757,-5.53123839
48,-0.000085361|C,-3.6214970453,-4.8638249256,-0.0000813792|H,-0.23751
95951,-5.4138484422,-0.0000675291|H,-4.5396101263,-5.4357946987,-0.000
0948296|H,-4.5609894342,-2.93009044,-0.0000634226|N,0.0537773006,2.742
4210717,0.0000315947|N,2.4546821539,1.3432645952,0.0000330825|C,1.2369
441202,3.4656511016,0.0000483234|C,2.4402767047,2.6991350076,0.0000486
72|H,-0.8198411688,3.2574677862,0.0000312137|C,1.241974634,4.865372016
4,0.0000639728|C,3.6586111976,3.4192256093,0.000066473|C,2.4475048629,
5.5481203582,0.0000812463|H,2.4927452417,6.6288770498,0.0000945793|C,3
.6373266112,4.8015872787,0.0000854537|H,4.5937471348,2.8746440833,0.00
00679367|H,0.3019003717,5.4126535459,0.0000630563|H,2.1786148432,-1.26
98953516,0.000000178|N,-2.3888621134,-7.003302388,-0.0001086688|O,-3.4
831000392,-7.5694129321,0.0002730725|O,-1.3033555348,-7.5805597366,0.0
002850723|N,4.9165969208,5.5299071802,0.0001088616|O,4.8699420706,6.76
10291914,-0.0002732424|O,5.9538358901,4.8698420733,-0.0002846266||Vers
ion=IA32W-G09RevC.01|State=1-A|HF=-1321.1585503|S2=0.|S2-1=0.|S2A=0.|R
MSD=2.144e-009|RMSF=5.688e-005|Dipole=-4.0307562,2.3494823,-0.0000002|
Quadrupole=9.9141783,-29.048379,19.1342007,-34.3976941,0.0054575,0.009
3616|PG=C01 [X(C18H10N6O4)]||@
```

Table 82. Computational output parameters for triplet **TAP 51v** (Y = NO_2).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10N6O4(3)|GAUSSIAN|2
7-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0
,3|C,-1.2331080816,0.3094936497,0.0000032734|C,-0.000000028,0.99062635
69,0.0000093768|C,1.2331080522,0.3094936559,0.0000108981|C,1.205760785
4,-1.1232849303,0.0000060476|C,-0.0000000022,-1.8234628821,-0.00000008
63|C,-1.2057607975,-1.1232849354,-0.0000015036|N,-2.4343463098,-1.7727
308057,-0.0000074614|N,-2.3851226425,1.0355522478,0.0000022183|C,-3.56
26010497,0.3457070131,-0.0000036586|C,-3.6267653954,-1.0875862608,-0.0
000082776|H,-2.454270793,-2.784036572,-0.000010814|H,0.000000003,-2.91
2043652,-0.0000037503|C,-4.7767600103,1.0610895843,-0.0000037369|C,-4.
8603760684,-1.7512059487,-0.0000137725|C,-5.9839458922,0.3751693518,-0
.0000083787|C,-6.0430423325,-1.0235041087,-0.0000137875|H,-4.750516643
7,2.1430555842,0.0000001031|H,-7.0079444943,-1.5142476518,-0.000016918
1|H,-4.8895089819,-2.8379730785,-0.0000174423|N,2.4343463043,-1.772730
7957,0.0000076182|N,2.3851226012,1.0355522652,0.0000168569|C,3.6267653
829,-1.0875862408,0.0000130987|C,3.562601011,0.3457070354,0.0000181216
```

```
|H,2.4542707994,-2.7840365621,0.0000043979|C,4.8603760653,-1.751205935
3,0.000014108|C,4.7767599554,1.0610896175,0.0000231044|C,6.0430423178,
-1.0235040891,0.0000190318|H,7.0079445123,-1.5142475983,0.0000189074|C
,5.9839458012,0.3751693431,0.0000238921|H,4.7505166127,2.1430556236,0.
0000266452|H,4.8895089947,-2.8379730642,0.0000104631|H,-0.0000000171,2
.0745350728,0.000013026|N,-7.2371281594,1.1328194736,-0.0000069976|O,-
8.2922700209,0.4937009544,0.000006352|O,-7.1645968315,2.3620467547,0.0
000063459|N,7.2371280419,1.1328193754,0.0000283696|O,8.2922696934,0.49
37005044,-0.0000886503|O,7.1645966102,2.3620466477,-0.0000760002||Vers
ion=IA32W-G09RevC.01|State=3-A|HF=-1321.1427824|S2=2.047523|S2-1=0.|S2
A=2.001446|RMSD=7.589e-009|RMSF=3.156e-005|Dipole=0.0000008,-4.2904486
,0.0000834|Quadrupole=-49.8061346,30.061699,19.7444356,0.0000056,0.001
7919,0.0002731|PG=C01 [X(C18H10N6O4)]||@
```

Table 83. Computational output parameters for singlet **TAP 51w** (X = F).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10F2N4|GAUSSIAN|29-N
ov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|
C,0.0384389258,-1.4519288899,0.|C,1.2361657859,-0.7205640434,0.|C,1.28
23089361,0.6820465051,0.|C,0.0030498165,1.3918361438,0.|C,-1.211099481
2,0.7059199075,0.|C,-1.2096021197,-0.6885836863,0.|N,-2.3660908296,-1.
3953817885,0.|N,0.0330096034,-2.7972185331,0.|C,-1.1557834364,-3.45396
84231,0.|C,-2.4135134563,-2.7838361647,0.|H,-3.2431711562,-0.887316283
6,0.|H,-2.1518776601,1.2542906569,0.|C,-1.1876448506,-4.8717036519,0.|
C,-3.6296342533,-3.4738271316,0.|C,-2.3835693424,-5.5686843962,0.|C,-3
.5895663415,-4.8573974462,0.|H,-0.2348876131,-5.3905956465,0.|H,-2.410
059083,-6.6532746059,0.|H,-4.5843733049,-2.9555495423,0.|N,0.048139549
3,2.7464571784,0.|N,2.4502211504,1.3497367894,0.|C,1.2329181628,3.4719
596725,0.|C,2.4358416691,2.7078035241,0.|H,-0.8261792618,3.2592602476,
0.|C,1.2339954216,4.8701865614,0.|C,3.6537676393,3.4341940931,0.|C,2.4
576402637,5.5171524192,0.|C,3.6708799642,4.8182913329,0.|H,4.601570487
3,5.3758330181,0.|H,4.5748000236,2.8608756611,0.|H,0.3125223258,5.4455
344502,0.|H,2.1721177244,-1.2661184529,0.|F,-4.7533457654,-5.542187206
8,0.|F,2.4799877262,6.8672708218,0.||Version=IA32W-G09RevC.01|State=1-
A'|HF=-1110.6202765|S2=0.|S2-1=0.|S2A=0.|RMSD=9.361e-009|RMSF=4.484e-0
05|Dipole=-2.0656451,1.204044,0.|Quadrupole=5.1890276,-3.7131268,-1.47
59008,-7.8592174,0.,0.|PG=CS [SG(C18H10F2N4)]||@
```

Table 84. Computational output parameters for triplet **TAP 51w** (X = F).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H10F2N4(3)|GAUSSIAN|3
0-Nov-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0
,3|C,0.8235405323,-1.2339847223,0.|C,1.5015917652,-0.0000000474,0.|C,0
.823540563,1.2339846756,0.|C,-0.6080361927,1.2073794716,0.|C,-1.306561
3848,-0.0000000125,0.|C,-0.6080362031,-1.2073795287,0.|N,-1.2608866355
,-2.4345205458,0.|N,1.5512928559,-2.3886698161,0.|C,0.8610423428,-3.56
44905006,0.|C,-0.5712555429,-3.6310713542,0.|H,-2.2713816636,-2.453044
6378,0.|H,-2.3955169826,-0.000000017,0.|C,1.5747513144,-4.7859506383,0
.|C,-1.2322558228,-4.8603528464,0.|C,0.9247936981,-6.0119839974,0.|C,-
0.4702791971,-6.0234426645,0.|H,2.6580051527,-4.7247344457,0.|H,1.4681
978113,-6.9504065187,0.|H,-2.3162361548,-4.9261196678,0.|N,-1.26088660
37,2.4345204976,0.|N,1.5512928743,2.3886697342,0.|C,-0.5712554993,3.63
10713,0.|C,0.8610423727,3.5644904505,0.|H,-2.2713816317,2.4530446088,0
.|C,-1.232255777,4.8603528,0.|C,1.5747513632,4.7859505661,0.|C,-0.4702
79142,6.0234426082,0.|C,0.9247937542,6.0119839297,0.|H,1.4681978674,6.
9504064518,0.|H,2.6580052004,4.7247343598,0.|H,-2.3162361098,4.9261196
159,0.|H,2.5856370418,-0.0000000609,0.|F,-1.1143835189,-7.2078276593,0
.|F,-1.1143834473,7.2078276117,0.||Version=IA32W-G09RevC.01|State=3-A'
|HF=-1110.604775|S2=2.047078|S2-1=0.|S2A=2.001432|RMSD=5.327e-009|RMSF
=2.314e-005|Dipole=-1.8509323,0.,0.|Quadrupole=9.8095785,-7.1577366,-2
.6518419,0.,0.,0.|PG=CS [SG(C18H10F2N4)]||@
```

Table 85. Computational output parameters for singlet **TAP 51x** (asymmetric X = NH_2, Y = NO_2).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C18H12N6O2\GAUSSIAN\16-Jun-2005\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\linear tetraazapentacene Y:
NO2 X:NH2 asymmetrical singlet opt\\0,1\C,-1.4265961696,0.0139088664,-
1.3250662203\C,-1.4263597257,0.0370871483,0.081726501\C,-0.2556453023,
0.0185992387,0.8483104706\C,1.0132672953,-0.0277552761,0.1217068034\C,
1.0604430302,-0.0506747035,-1.2701422147\C,-0.1320865894,-0.0298293155
,-1.9960745072\N,-0.1368991095,-0.0491734012,-3.3521403762\N,-2.571851
8401,0.0307300587,-2.0290323176\C,-2.5167756678,0.0078798436,-3.382930
2296\C,-1.2948201798,-0.0314208564,-4.1139638061\H,0.7533662446,-0.082
6365486,-3.8362284219\H,2.018209633,-0.0844910655,-1.7872845584\C,-3.7
093042739,0.0246151645,-4.1516875123\C,-1.2547527569,-0.0466751262,-5.
```

```
5107553681\C,-3.6780427483,0.0046475102,-5.5288918012\C,-2.4477125737,
-0.0299857032,-6.2367393237\H,-4.6497408473,0.054790015,-3.6111611182\
H,-0.2973301322,-0.080207668,-6.0283236962\N,2.1499098073,-0.047263368
6,0.8651293266\N,-0.2925330814,0.0422763443,2.1967806012\C,2.155267425
1,-0.024451252,2.2544742171\C,0.8751701787,0.0216858544,2.8850522212\H
,3.0419083716,-0.0801165444,0.3852019312\C,3.3486779595,-0.0454956754,
2.9819868479\C,0.8668513204,0.0459594582,4.2996323485\C,3.314593175,-0
.0210908397,4.3690821425\C,2.0622311089,0.0245483479,4.9991007577\H,-0
.0816830337,0.0811250053,4.8191046298\H,4.3021699856,-0.0809241902,2.4
589198794\H,-2.3794485802,0.0701253046,0.5956617078\N,2.0230746119,0.0
507411701,6.4684642142\O,0.9219863461,0.0907826625,7.0168261728\O,3.09
92947885,0.0309630648,7.0706851088\N,-2.4479605752,-0.1071640677,-7.62
78499229\H,-3.2776579436,0.2552851612,-8.0803272805\H,-1.6021719186,0.
2081264064,-8.0857897402\H,-4.607950109,0.0108337182,-6.0925326897\H,4
.2174675287,-0.0362186671,4.9642804674\\Version=x86-Linux-G03RevB.05\S
tate=1-A\HF=-1172.0119571\S2=0.\S2-1=0.\S2A=0.\RMSD=3.100e-09\RMSF=1.9
90e-05\Dipole=1.5584352,0.2928985,-5.6592477\PG=C01 [X(C18H12N6O2)]\\@
```

Table 86. Computational output parameters for triplet **TAP 51x** (asymmetric X = NH_2, Y = NO_2).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H12N6O2(3)|GAUSSIAN|0
1-Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||linear tetraaza
pentacene Y:NO2 X:NH2 asymmetrical triplet opt||0,3|C,-1.7807008442,-0
.7247452802,0.0010492919|C,-0.4915698715,-1.2830382658,0.0020771032|C,
0.675532541,-0.4903456963,0.0009547501|C,0.514198447,0.9315932347,-0.0
015615564|C,-0.7530588815,1.5149361921,-0.0018118698|C,-1.8890175489,0
.7062455918,-0.0002188882|N,-3.1705154589,1.2397003951,0.0008035792|N,
-2.864480584,-1.5547125497,0.0007236159|C,-4.0954365971,-0.9771927169,
-0.0013219779|C,-4.3015023388,0.4416060699,-0.0000417949|H,-3.28250907
37,2.2441455066,-0.0064287398|H,-0.855073504,2.5991932797,-0.003354707
9|C,-5.2525807114,-1.7919499717,-0.0031857909|C,-5.5807014731,0.986458
5668,0.0038193911|C,-6.5257795446,-1.2538712194,-0.0021240423|C,-6.709
6581134,0.1469368402,0.0022299417|H,-5.0994215243,-2.866402512,-0.0031
65006|H,-5.7104094125,2.067409876,-0.0008048344|N,1.6780076226,1.69526
33836,-0.0035028625|N,1.8907380439,-1.1040493204,0.0020653873|C,2.9277
92938,1.1275402264,-0.0027185132|C,2.998687532,-0.3060109327,0.0003712
072|H,1.600978239,2.7037350084,-0.0062725122|C,4.0948630771,1.90494818
37,-0.004713048|C,4.2752039687,-0.9013030259,0.0015766572|C,5.34085858
```

```
2,1.2934850293,-0.00350472|C,5.4146891643,-0.1046674072,-0.0002858846|
H,4.3516104115,-1.9807665985,0.0038908135|H,4.0198862641,2.9897219828,
-0.0071932456|H,-0.3883476485,-2.3621052169,0.003176882|N,6.7306753951
,-0.7386764533,0.0011556004|O,6.7773338978,-1.9706501296,0.0040538132|
O,7.7240824227,-0.0044221808,-0.0006043305|N,-7.9864261186,0.687614019
2,-0.0509009432|H,-8.7373192561,0.083646133,0.256845625|H,-8.088728875
4,1.6369076761,0.2833367429|H,-7.3956768819,-1.9056587004,-0.008804711
3|H,6.2548637156,1.8734209823,-0.0049734221||Version=IA32W-G09RevC.01|
State=3-A|HF=-1171.997432|S2=2.044356|S2-1=0.|S2A=2.001255|RMSD=7.622e
-009|RMSF=1.608e-005|Dipole=-4.2155393,3.2907257,0.3881058|Quadrupole=
-6.2549014,10.0067523,-3.7518509,4.810899,-6.5639918,0.7330982|PG=C01
[X(C18H12N6O2)]||@
```

Table 87. Computational output parameters for singlet **TAP 51y** (X = OMe).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C20H16N4O2\GAUSSIAN\20-May-2005\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\linear tetraazapentacene X:
MeO singlet opt\\0,1\C,-1.4355923078,0.0463181336,-0.6221253511\C,-1.4
260415107,-0.0034491902,0.7810668418\C,-0.2486117487,-0.0504060487,1.5
445936842\C,1.0185714613,-0.0461548636,0.8145814775\C,1.0566152201,0.0
025261228,-0.5787247743\C,-0.1381081131,0.0482419909,-1.296824328\N,-0
.1440383156,0.0963589526,-2.6516541778\N,-2.5847226185,0.0905516909,-1
.3213153193\C,-2.5306614737,0.1377586114,-2.6782422925\C,-1.3075384985
,0.1429785252,-3.4110218802\H,0.7442381785,0.0985033197,-3.1396724177\
H,2.0118169607,0.0048267262,-1.1019050881\C,-3.717573996,0.1850099203,
-3.4454201314\C,-1.2686659788,0.1916368407,-4.8024328092\C,-3.69418701
81,0.2336990792,-4.8312215618\C,-2.4643791559,0.2373066152,-5.52069378
47\H,-4.6589977914,0.1818186149,-2.9055105858\H,-4.6308362207,0.268895
2479,-5.3756547763\H,-0.3259330734,0.1948314264,-5.3435972389\N,2.1571
92634,-0.0915412326,1.5490179837\N,-0.2780465278,-0.0974822543,2.88930
14247\C,2.1707378361,-0.1409288301,2.9382348039\C,0.8946415942,-0.1417
347429,3.574318624\H,3.0467277918,-0.0894123593,1.0632977635\C,3.36430
75533,-0.1866052847,3.6546158611\C,0.902165507,-0.1918103665,4.9874668
375\C,3.325866037,-0.235254405,5.0488460702\C,2.0826715303,-0.23759477
78,5.7138791421\H,2.0372099106,-0.27513925,6.7962301742\H,-0.059717576
2,-0.1931982337,5.4900309849\H,4.3279539472,-0.1851997058,3.1516266789
\H,-2.376280902,-0.0057382483,1.3015283496\O,-2.3356239498,0.283226864
5,-6.8813213323\O,4.5418801419,-0.2779393972,5.6729128658\C,-3.5157087
225,0.3307341604,-7.6664541731\H,-3.1819558253,0.3617492622,-8.7054103
```

```
997\H,-4.1401568886,-0.5595295291,-7.5137091845\H,-4.1100990396,1.2284
960884,-7.450660295\C,4.5681965039,-0.3279781879,7.0899807907\H,5.6234
906203,-0.3555386336,7.3681438535\H,4.0998830409,0.5597015752,7.535565
3531\H,4.0696828081,-1.2283359494,7.4729769004\\Version=x86-Linux-G03R
evB.05\State=1-A\HF=-1141.1990443\S2=0.\S2-1=0.\S2A=0.\RMSD=7.324e-09\
RMSF=8.015e-06\Dipole=1.9870703,0.0048986,-1.0883406\PG=C01 [X(C20H16N
4O2)]\\@
```

Table 88. Computational output parameters for triplet **TAP 51y** (X = OMe).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C20H16N4O2(3)|GAUSSIAN|0
7-Dec-2012|0||# opt ub3lyp/6-31g(d) guess=mix geom=connectivity||linea
r tetraazapentacene X:MeO triplet||0,3|C,1.2347183409,0.8700916374,-0.
0000005602|C,0.0000008101,1.5468313209,0.0000014649|C,-1.2347168799,0.
8700918879,0.0000038742|C,-1.2082004354,-0.5619917293,0.0000045381|C,0
.0000005621,-1.2595058298,0.0000022405|C,1.2082016655,-0.5619919295,-0
.0000004516|N,2.4341604373,-1.216058371,-0.0000027946|N,2.3905717485,1
.5968226612,-0.0000026685|C,3.5648023997,0.9046620765,-0.0000045503|C,
3.6337433365,-0.5289253954,-0.0000045788|H,2.451487999,-2.2264694883,0
.0000014375|H,0.0000004562,-2.3486854806,0.0000025862|C,4.7893174488,1
.6057989871,-0.0000064592|C,4.8570423443,-1.1877609275,-0.0000066159|C
,6.0170118699,0.9538020379,-0.0000083126|C,6.0512003216,-0.4509942712,
-0.0000085732|H,4.7368725397,2.6899241777,-0.0000064677|H,6.9317034783
,1.5344439495,-0.0000087085|H,4.9133823989,-2.2728954954,-0.000007164|
N,-2.4341593429,-1.2160579671,0.0000075899|N,-2.3905701742,1.596823130
3,0.000005382|C,-3.6337421423,-0.528924744,0.0000080462|C,-3.564800997
2,0.9046627576,0.00000721|H,-2.4514870749,-2.2264690929,0.0000035406|C
,-4.8570412866,-1.1877600176,0.0000106822|C,-4.7893159636,1.6057999413
,0.0000081184|C,-6.0511989523,-0.4509929106,0.0000116384|C,-6.01701045
9,0.9538032253,0.0000096743|H,-6.9317022489,1.5344450414,0.000007634|H
,-4.7368708954,2.6899251299,0.0000070335|H,-4.9133816356,-2.2728945755
,0.0000127752|H,0.0000009184,2.6309519006,0.000001105|O,7.1913670966,-
1.1979337732,-0.0000093212|O,-7.1913662195,-1.1979312022,0.0000104571|
C,8.4406902236,-0.5234175528,-0.0000249425|H,9.2017352819,-1.305799519
5,-0.000034069|H,8.5613602453,0.1006912675,-0.8948303981|H,8.561382798
,0.1006915626,0.8947773837|C,-8.4406874647,-0.5234117636,0.0000536164|
H,-9.2017344858,-1.3057918047,0.0000789632|H,-8.5613358835,0.100697337
4,0.8948617098|H,-8.5613981797,0.1006978117,-0.8947460657||Version=IA3
2W-G09RevC.01|State=3-A|HF=-1141.185473|S2=2.04554|S2-1=0.|S2A=2.00133
```

```
|RMSD=5.004e-009|RMSF=3.055e-005|Dipole=0.0000008,-1.7080946,0.0000129
|Quadrupole=28.136336,-9.7056974,-18.4306385,-0.0000207,-0.0004598,-0.
0000251|PG=C01 [X(C20H16N4O2)]||@
```

Table 89. Computational output parameters for singlet **TAP 51z** (X = NH_2).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C18H14N6\GAUSSIAN\17-Mar-2013\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt\\0,1\C,-0.0085967071,-0.0
202931853,-0.0018762189\C,0.0062390471,-0.0273748413,1.4026029366\C,1.
1870409664,-0.0109941538,2.1629666912\C,2.4493755459,0.0127520532,1.42
97220732\C,2.4819036121,0.0197617019,0.0350956271\C,1.2842074142,0.003
6639359,-0.679969098\N,1.2731118485,0.0090350498,-2.0372716464\N,-1.16
08852074,-0.0341106968,-0.6996243882\C,-1.1100719703,-0.0253934018,-2.
056760501\C,0.1075135233,-0.0049648467,-2.7940616241\H,2.160438629,0.0
297255129,-2.5262438785\H,3.4352920792,0.0381662774,-0.491528816\C,-2.
301626015,-0.0385289225,-2.8240845102\C,0.1430910979,-0.003613374,-4.1
902483466\C,-2.2753145539,-0.0329863119,-4.2051266884\C,-1.0511255962,
-0.0169258288,-4.9154483459\H,-3.2418689889,-0.0547754434,-2.282163281
6\H,-3.2085860845,-0.0366011668,-4.7639443744\H,1.1001622824,0.0166710
634,-4.7101672623\N,3.5922381412,0.027319271,2.1618780423\N,1.16407025
66,-0.0158875982,3.509963773\C,3.6120796665,0.022332201,3.5514878986\C
,2.3397675301,0.0015862369,4.1894941817\H,4.4785717733,0.0479964385,1.
6711007948\C,4.8128888982,0.0324592062,4.2648852201\C,2.3546751094,-0.
0020947797,5.6068472057\C,4.7906973876,0.0282889008,5.6617968586\C,3.5
374670251,0.0123314274,6.3199009457\H,3.5136260951,0.0161258832,7.4074
210364\H,1.3952411119,-0.0184093044,6.1140206331\H,5.7624746383,0.0519
6873,3.7314140594\H,-0.9420779561,-0.0441777235,1.9264040842\N,-1.0481
167922,0.0498145671,-6.3151640062\N,5.9764942159,0.1039533384,6.404515
8984\H,5.9034970704,-0.273075777,7.3419997696\H,6.7945268798,-0.262975
0874,5.9326622419\H,-1.8790641917,-0.3328679649,-6.7504581086\H,-0.211
7828315,-0.3174584818,-6.7535014796\\Version=IA32L-G03RevD.02\State=1-
A\HF=-1022.8603283\S2=0.\S2-1=0.\S2A=0.\RMSD=8.925e-09\RMSF=2.396e-05\
Thermal=0.\Dipole=2.9134765,-0.8606159,-1.6037185\PG=C01 [X(C18H14N6)]
\\@
```

Table 90. Computational output parameters for triplet **TAP 51z** (X = NH_2).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C18H14N6(3)\GAUSSIAN\19-Mar-2013\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt\\0,3\C,0.068827032,-0.
0028162124,-0.03495921\C,0.0592519786,-0.0018362233,1.3726282468\C,1.2
399181388,-0.0028348046,2.1390630583\C,2.487503088,-0.0057836592,1.436
7708531\C,2.5288565063,-0.0073203774,0.0423143487\C,1.3416715694,-0.00
576533,-0.6903593285\N,1.3363775216,-0.0079882491,-2.0814217207\N,-1.1
186548668,-0.0000481714,-0.7103688571\C,-1.0641642985,0.0007299763,-2.
0710280259\C,0.1631310753,-0.0042961526,-2.811958258\H,2.2187380282,-0
.0017605526,-2.5737833273\H,3.4880132412,-0.0094072762,-0.4743592051\C
,-2.2626475943,0.0050063744,-2.8219810828\C,0.1670140437,-0.0093334613
,-4.2042583223\C,-2.2614803172,0.0025408672,-4.2060371272\C,-1.0433897
921,-0.0054441069,-4.9183302973\H,-3.1937950223,0.0077354126,-2.264098
4577\H,-3.2004075034,0.0110435779,-4.7542079084\H,1.1133694455,-0.0071
891651,-4.743066849\N,3.6461890409,-0.0080203925,2.2065298754\N,1.1505
835877,-0.0000860153,3.5022612799\C,3.6107203667,-0.0043577732,3.58817
10517\C,2.3167738961,0.00067058,4.2053707203\H,4.5427923809,-0.0018254
938,1.7406082697\C,4.775488745,-0.009424336,4.3509477752\C,2.284468523
7,0.0049226745,5.619318409\C,4.7058273298,-0.0055582858,5.7545591252\C
,3.4408591169,0.0024317852,6.3798275665\H,3.3820240667,0.0109192716,7.
4654674536\H,1.3063110856,0.0076538813,6.0899313744\H,5.7460863265,-0.
0072862825,3.8571425523\H,-0.8952543954,0.0010768624,1.8867970524\N,-1
.0392462576,0.0485952242,-6.3107573955\N,5.8708451696,0.0484532636,6.5
171898005\H,5.777812829,-0.2821876345,7.4693601889\H,6.7026758113,-0.3
175034773,6.071252523\H,-1.8855478009,-0.2820093773,-6.7569428245\H,-0
.2092244013,-0.317385493,-6.7600331942\\Version=IA32L-G03RevD.02\State
=3-A\HF=-1022.8480105\S2=2.044239\S2-1=0.\S2A=2.001252\RMSD=6.635e-09\
RMSF=1.379e-05\Thermal=0.\Dipole=2.5125651,-0.8488154,-1.3534632\PG=C0
1 [X(C18H14N6)]\\@
```

Table 91. Computational output parameters for singlet **TAP 51aa** (X = OMe, Y = C≡N).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C22H14N6O2|USER|04-Feb-2013|0|
|# opt ub3lyp/6-31g(d) geom=connectivity||X:MeO Y:CN opt||0,1|C,1.2025
955397,-0.6901397062,0.031835203|C,0.0000003885,-1.3944818176,-0.00000
25505|C,-1.2025956572,-0.690140577,-0.0318388342|C,-1.2331341742,0.772
9248673,-0.0349627529|C,-0.0000011584,1.4403591735,0.0000013702|C,1.23
```

```
31325476,0.7729258737,0.0349634036|N,2.3974304782,1.4458843971,0.07069
72395|N,2.3958739161,-1.3338796854,0.0614062795|C,3.6165813572,-0.6763
419062,0.0937459826|C,3.5602637787,0.7476622986,0.0997401603|H,-0.0000
022791,2.523584582,0.0000030819|C,4.8253825552,-1.3763564991,0.1118918
383|C,4.7967583462,1.4299982955,0.1483864556|C,6.027542859,-0.68228970
61,0.1529587956|C,6.0083399621,0.7409738221,0.1808198648|H,4.849238029
9,-2.4628103679,0.105801374|H,4.7763372791,2.5137099568,0.1715088044|N
,-2.3974328435,1.4458822135,-0.0706945911|N,-2.3958732151,-1.333881610
8,-0.0614121619|C,-3.5602653773,0.7476595995,-0.0997405994|C,-3.616581
4984,-0.676344753,-0.0937503728|C,-4.7967608705,1.4299959136,-0.148383
6894|C,-4.825382268,-1.3763613656,-0.1119024945|C,-6.0083404687,0.7409
693265,-0.1808178082|C,-6.0275410398,-0.6822931789,-0.1529714384|H,-4.
8492363183,-2.4628153224,-0.1058200749|H,-4.776340421,2.5137077839,-0.
171496212|H,0.0000008916,-2.4831419256,-0.0000040807|O,7.1920202538,-1
.3935455658,0.238626298|O,-7.1920278245,-1.3935347609,-0.2386446687|C,
8.0378050101,-1.3773657305,-0.9211949649|H,8.3994119388,-0.369092199,-
1.1449679138|H,8.8865166219,-2.018672674,-0.6773211209|H,7.5059503863,
-1.7834096232,-1.7910073828|C,-8.0377670152,-1.3774012126,0.9212100222
|H,-7.5058772622,-1.7834706416,1.7909890916|H,-8.3993672091,-0.3691345
284,1.1450287645|H,-8.8864856346,-2.0187035258,0.6773479956|C,7.235615
1678,1.4726425686,0.2752655388|N,8.2306089321,2.071857354,0.346331979|
C,-7.2356245073,1.4726290716,-0.2752241014|N,-8.2306250745,2.071827096
4,-0.3463350156|H,2.3996504665,-2.3478012032,0.0619145754|H,-2.3996485
896,-2.347803107,-0.0619222892||Version=IA32W-G09RevC.01|State=1-A|HF=
-1325.6755872|S2=0.|S2-1=0.|S2A=0.|RMSD=8.448e-009|RMSF=9.253e-006|Dip
ole=0.0000277,-4.4443797,0.0000211|Quadrupole=-37.031477,20.7024826,16
.3289944,-0.0000104,-19.464507,0.0000143|PG=C01 [X(C22H14N6O2)]||@
```

Table 92. Computational output parameters for triplet **TAP 51aa** (X = OMe, Y = C≡N).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C22H14N6O2(3)|GAUSSIAN|0
8-Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||X:MeO Y:CN opt|
|0,3|C,1.205407719,-0.8324174475,-0.0541190909|C,-0.0002198572,-1.5310
464826,-0.0042395142|C,-1.2057469675,-0.8323924156,0.0476783553|C,-1.2
326829115,0.6009367938,0.0507643955|C,-0.0000194727,1.2799328504,-0.00
01506956|C,1.2325460043,0.6009113646,-0.0530374308|N,2.3851681809,1.32
54967957,-0.1003923059|N,2.4313603263,-1.4861465178,-0.1069262924|C,3.
6247499714,-0.8025633812,-0.1562129291|C,3.5578525159,0.6313904957,-0.
1509543422|H,0.000058065,2.3639134735,0.0014166874|C,4.8476804803,-1.4
```

```
56318761,-0.2096329024|C,4.774846628,1.3256595991,-0.2007000843|C,6.05
68165705,-0.744323289,-0.2595615702|C,6.0237443746,0.677808651,-0.2545
090849|H,4.9042014176,-2.5408200641,-0.2147937941|H,4.7348657296,2.409
1392318,-0.1963077885|N,-2.3852020167,1.3255451102,0.100214542|N,-2.43
17918173,-1.4860962515,0.09861724|C,-3.5579834881,0.6314630015,0.14886
15997|C,-3.6250793477,-0.8024902147,0.1499966708|C,-4.7748942364,1.325
7680417,0.2002538662|C,-4.8480622843,-1.4562376264,0.2024981181|C,-6.0
238593701,0.6779227698,0.2523401622|C,-6.0570684198,-0.7442091944,0.25
47516421|H,-4.9046817455,-2.5407412371,0.2057045496|H,-4.7348039371,2.
4092501151,0.1979041728|H,-0.0002981675,-2.6198948299,-0.0058216524|O,
7.1427850543,-1.5462432358,-0.3070819422|O,-7.1432097695,-1.5460198809
,0.3003219943|C,8.479865983,-1.0443223798,-0.3794718366|H,8.7333681857
,-0.4503201429,0.5026431458|H,9.1091372252,-1.93515246,-0.415856347|H,
8.6350790912,-0.4468308091,-1.2818867841|C,-8.4788874434,-1.0443277702
,0.3965577691|H,-8.6186845166,-0.4494593146,1.3032945001|H,-8.74734823
39,-0.4477729729,-0.4793053556|H,-9.1074987893,-1.9352602218,0.4410462
69|C,7.176349651,1.5227306141,-0.2976058802|N,8.0697334961,2.269606887
9,-0.3299721127|C,-7.1766247715,1.5227505555,0.2927896787|N,-8.0702429
328,2.2694652648,0.322273874|H,2.448300895,-2.4971771877,-0.1091302182
|H,-2.4488810647,-2.4971265279,0.097799722||Version=IA32W-G09RevC.01|S
tate=3-A|HF=-1325.6631452|S2=2.046509|S2-1=0.|S2A=2.001365|RMSD=6.633e
-009|RMSF=6.051e-007|Dipole=0.0010295,-4.1471807,0.0104442|Quadrupole=
-14.405748,7.4755259,6.9302221,-0.0025226,0.2018036,0.0053484|PG=C01 [
X(C22H14N6O2)]||@
```

Table 93. Computational output parameters for singlet **TAP 51ab** (E = NH_2).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H13N5|GAUSSIAN|04-Dec
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,1|C,
0.0202564312,-1.4356617493,0.|C,1.2396491958,-0.7225835835,0.|C,1.2591
994115,0.6898687142,0.|C,-0.0111376467,1.3915584275,0.|C,-1.234720246,
0.7196970446,0.|C,-1.2163399801,-0.6760906205,0.|N,-2.363551775,-1.398
1697824,0.|N,0.0413915548,-2.7881132782,0.|C,-1.1373255478,-3.45745448
65,0.|C,-2.399413771,-2.7907711765,0.|H,-3.2458611951,-0.9001340914,0.
|H,-2.1742205493,1.2673179533,0.|C,-1.1655941727,-4.875787167,0.|C,-3.
60741314,-3.4923819555,0.|C,-2.364049277,-5.5683480319,0.|C,-3.5935011
285,-4.8829983629,0.|H,-0.2106632656,-5.391967534,0.|H,-2.3564426773,-
6.6550083015,0.|H,-4.5291889223,-5.4335068693,0.|H,-4.5493545973,-2.94
61862858,0.|N,0.0518182404,2.7456385546,0.|N,2.4464323525,1.3379771258
```

```
,0.|C,1.2459003068,3.463127366,0.|C,2.4479717205,2.6934822123,0.|H,-0.
8163508903,3.2679331575,0.|C,1.2610884828,4.860014492,0.|C,3.668186419
2,3.417042828,0.|C,2.4779726817,5.5332138533,0.|H,2.4958797107,6.61868
65176,0.|C,3.6802033078,4.8011640998,0.|H,4.6294971403,5.3300586254,0.
|H,4.5879320835,2.8404989246,0.|H,0.3216275952,5.4104654593,0.|N,2.420
3471789,-1.4107985504,0.|H,3.2827821827,-0.8923066806,0.|H,2.394202065
5,-2.4167532383,0.||Version=IA32W-G09RevC.01|State=1-A'|HF=-967.510949
6|S2=0.|S2-1=0.|S2A=0.|RMSD=6.738e-009|RMSF=1.840e-004|Dipole=-1.89594
36,1.1051402,0.|Quadrupole=7.5798693,3.6091996,-11.1890689,-3.5054555,
0.,0.|PG=CS [SG(C18H13N5)]||@
```

Table 94. Computational output parameters for triplet **TAP 51ab** (E = NH_2).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H13N5(3)|GAUSSIAN|05-
Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
|C,0.5390094767,-1.2470056754,0.|C,1.2435119873,-0.0000003191,0.|C,0.5
390101634,1.2470053785,0.|C,-0.8852319034,1.2064821068,0.|C,-1.5896151
56,0.0000003468,0.|C,-0.8852325047,-1.206481805,0.|N,-1.5292101106,-2.
4345870343,0.|N,1.2719499053,-2.3877181487,0.|C,0.5906785575,-3.575035
6731,0.|C,-0.8369777911,-3.6382262268,0.|H,-2.539359736,-2.4561983927,
0.|H,-2.6776798881,0.0000005884,0.|C,1.3012363952,-4.7942674019,0.|C,-
1.4969184933,-4.86813067,0.|C,0.63873586,-6.0159988465,0.|C,-0.7611582
336,-6.0548060821,0.|H,2.3854860409,-4.737328677,0.|H,1.2077391236,-6.
9413103296,0.|H,-1.2826687472,-7.0076127497,0.|H,-2.5849093146,-4.8942
872342,0.|N,-1.5292088269,2.4345876834,0.|N,1.271951169,2.3877173397,0
.|C,-0.8369758541,3.6382265095,0.|C,0.5906804269,3.5750353063,0.|H,-2.
5393584393,2.4561996791,0.|C,-1.4969159499,4.8681312991,0.|C,1.3012389
09,4.794266598,0.|C,-0.7611550784,6.0548063144,0.|H,-1.2826650748,7.00
76132622,0.|C,0.6387390158,6.0159984013,0.|H,1.207742701,6.941309613,0
.|H,2.3854885334,4.7373272758,0.|H,-2.5849067604,4.8942884023,0.|N,2.5
896767604,-0.0000005618,0.|H,3.0710830936,0.887434059,0.|H,3.071082743
4,-0.8874353523,0.||Version=IA32W-G09RevC.01|State=3-A'|HF=-967.508423
9|S2=2.037433|S2-1=0.|S2A=2.000901|RMSD=5.465e-009|RMSF=1.662e-004|Dip
ole=-1.3858817,0.0000007,0.|Quadrupole=10.7855239,0.6640872,-11.449611
2,-0.0000018,0.,0.|PG=CS [SG(C18H13N5)]||@
```

Table 95. Computational output parameters for singlet **TAP 51ac** (X = NH_2, E = NH_2).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C18H15N7|USER|04-Feb-2013|0||#
opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene E:NH2
+ X:NH2 singlet||0,1|C,1.230425,0.740343,-0.033598|C,0.000072,1.43105
9,-0.062747|C,-1.230443,0.740478,-0.039666|C,-1.19778,-0.707633,-0.043
954|C,-0.000002,-1.42444,-0.052584|C,1.197812,-0.707739,-0.041222|N,2.
39924,-1.34329,-0.030074|N,2.392649,1.43456,0.004956|C,3.559946,0.7453
99,0.021321|C,3.621227,-0.67898,-0.002639|H,2.406047,-2.356102,-0.0321
82|H,-0.00006,-2.512341,-0.0587|C,4.806098,1.42077,0.059617|C,4.829384
,-1.378556,0.00158|C,6.004587,0.733658,0.068939|C,6.03981,-0.680511,0.
037301|H,4.784403,2.505892,0.077253|H,6.942584,1.283536,0.104056|H,4.8
26026,-2.467848,-0.013995|N,-2.399216,-1.343171,-0.032681|N,-2.392856,
1.43478,-0.009684|C,-3.621322,-0.678863,-0.01156|C,-3.560215,0.745683,
0.002788|H,-2.406062,-2.355968,-0.038566|C,-4.829276,-1.378628,0.00417
7|C,-4.806563,1.421149,0.03171|C,-6.039879,-0.680451,0.031388|C,-6.005
018,0.733996,0.044188|H,-6.943339,1.284245,0.058697|H,-4.785136,2.5063
55,0.04344|H,-4.825994,-2.467902,-0.012712|N,0.00046,2.817642,-0.13919
8|H,-0.857045,3.232828,0.205104|H,0.855654,3.232349,0.211368|N,7.26491
4,-1.359318,0.107763|H,7.254124,-2.2882,-0.297071|H,8.052259,-0.826854
,-0.243374|N,-7.266867,-1.357459,-0.01865|H,-7.242797,-2.299307,0.3543
23|H,-8.042124,-0.837293,0.375109||Version=IA32W-G09RevC.01|State=1-A|
HF=-1078.2155212|S2=0.|S2-1=0.|S2A=0.|RMSD=7.172e-009|RMSF=1.150e-005|
Dipole=0.0118496,-2.8498012,0.3973726|Quadrupole=19.6751406,0.3261517,
-20.0012923,0.17187,-13.9460675,2.9939834|PG=C01 [X(C18H15N7)]||@
```

Table 96. Computational output parameters for triplet **TAP 51ac** (X = NH_2, E = NH_2).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C18H15N7(3)|GAUSSIAN|04-
Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||optimization||0,3
|C,-1.7881134961,-0.7280894866,0.0331128293|C,-0.4826539574,-1.3098813
882,0.0520879989|C,0.6897424123,-0.4927807456,0.0216531722|C,0.5159882
249,0.921026018,0.0024265372|C,-0.7506513743,1.5097324715,0.0023890914
|C,-1.8837909852,0.6931244407,0.0135474613|N,-3.1695765354,1.221629135
9,0.0041496837|N,-2.8583424651,-1.563515812,0.0285641417|C,-4.10168294
39,-0.9926756664,0.0124805836|C,-4.3014881473,0.4231662033,0.002564465
6|H,-3.2818871571,2.2252734592,-0.0207148722|H,-0.853598638,2.59308663
,-0.0118940663|C,-5.2566113034,-1.801593495,0.0073532144|C,-5.58191486
```

```
82,0.9713800467,-0.0065813497|C,-6.5330514964,-1.2591323705,-0.0036927
494|C,-6.7130718103,0.1378357593,-0.0101464497|H,-5.110246216,-2.87742
21399,0.0163783761|H,-5.7067032364,2.0531679639,-0.020731933|N,1.67917
29292,1.6821007495,-0.0183904758|N,1.897992727,-1.1118124076,0.0065660
361|C,2.94108459,1.1109851671,-0.0308707286|C,3.0114766486,-0.31713821
53,-0.0203562127|H,1.6003294141,2.6889304675,-0.043112974|C,4.09530638
71,1.8904069776,-0.0511358458|C,4.2979139873,-0.8942152523,-0.03664110
5|C,5.363063348,1.2846775637,-0.0657116818|C,5.4492870919,-0.121193627
6,-0.0588277291|H,4.3567373954,-1.9783558419,-0.0271935989|H,4.0141197
133,2.9763338747,-0.0654734461|N,-7.995114201,0.6893774621,-0.08023185
55|H,-8.7333528933,0.0867450924,0.2622204298|H,-8.080227423,1.62568432
76,0.2961985734|H,-7.4033887536,-1.9108707921,-0.0116348539|N,6.517719
1975,2.0676409139,-0.1469762402|H,7.3590733371,1.6151871209,0.18899343
03|H,6.4282506581,3.0036112908,0.2293207802|H,6.4266380257,-0.59746331
7,-0.0752427402|N,-0.3545608993,-2.6558567314,0.1131379075|H,0.5675184
517,-3.0416178332,-0.0320473836|H,-1.1888265887,-3.2084015338,-0.02405
84511||Version=IA32W-G09RevC.01|State=3-A|HF=-1078.2154394|S2=2.037072
|S2-1=0.|S2A=2.000874|RMSD=5.705e-009|RMSF=6.917e-006|Dipole=-0.182939
9,1.9506695,0.6742016|Quadrupole=19.3300076,2.495474,-21.8254817,1.629
4252,-0.5273296,3.6233146|PG=C01 [X(C18H15N7)]||@
```

Table 97. Computational output parameters for singlet **TAP 51ad** (X = NH_2, Y = NO_2).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C18H12N8O4\GAUSSIAN\06-Jun-2005\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\linear tetraazapentacene Y:
NO2 X:NH2 singlet opt\\0,1\C,-1.0576899873,-0.0028404604,-0.8263221313
\C,-1.0448847336,0.0009174011,0.577140602\C,0.1362806868,0.0036182863,
1.3352572493\C,1.3983689667,0.0008740405,0.6013526031\C,1.4339778436,-
0.001321326,-0.7920717802\C,0.2355351789,-0.0024033893,-1.5038620247\N
,0.2295517214,-0.0031669724,-2.8634718269\N,-2.2082047902,-0.006743401
1,-1.525564601\C,-2.1555444776,-0.0096216819,-2.8809179542\C,-0.930604
1801,-0.0066117582,-3.6197975712\H,1.1189673556,-0.0039845707,-3.34987
22362\H,2.3871553309,-0.0021801597,-1.3185672477\C,-3.3340862218,-0.01
10021809,-3.6453383772\C,-0.8942709616,-0.0084479668,-5.0073238753\C,-
3.3088095345,-0.0112672187,-5.0377974622\C,-2.0764506595,-0.0144474124
,-5.7706613358\H,-4.2864785784,-0.0071683992,-3.1326138637\H,0.0627169
787,-0.0163632036,-5.5256715926\N,2.5460394449,0.0006120621,1.33034798
82\N,0.1155730422,0.0085779755,2.6814268098\C,2.5685161498,0.005075754
3,2.715076413\C,1.2908668624,0.0103520469,3.3585190733\H,3.4313291969,
```

```
-0.0001793881,0.8364782202\C,3.7623468575,0.0057707749,3.4231090955\C,
1.3103962015,0.0128325406,4.7631208178\C,3.7790317841,0.0128015137,4.8
302169839\C,2.5025083666,0.0119970367,5.4831644689\H,0.3692848355,0.01
07816904,5.2962746601\H,4.7106680811,0.0118828584,2.889046748\H,-1.993
1090869,0.00177447,1.1009005996\N,-4.5962341518,0.0117293848,-5.713555
9449\O,-4.6235573984,0.0633114509,-6.9589939338\O,-5.6182066415,-0.015
259364,-5.0294435706\N,2.3890009815,-0.0095614174,6.9327453282\O,1.265
8425061,0.0195124026,7.4335879017\O,3.4285919266,-0.0619747578,7.61906
9303\N,-2.0030876867,-0.0636787047,-7.132288786\H,-2.8600079306,0.0917
958163,-7.6464772751\H,-1.1207371452,0.1483801904,-7.57278022\N,4.9706
812191,0.0606317503,5.4930826321\H,4.949492053,-0.0935719688,6.4923963
123\H,5.8131884531,-0.1523459296,4.9808883261\\Version=x86-Linux-G03Re
vB.05\State=1-A\HF=-1431.8699401\S2=0.\S2-1=0.\S2A=0.\RMSD=5.685e-09\R
MSF=4.236e-06\Dipole=5.0694554,-0.0041642,-2.7995279\PG=C01 [X(C18H12N
8O4)]\\@
```

Table 98. Computational output parameters for triplet **TAP 51ad** (X = NH_2, Y = NO_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H12N8O4(3)|GAUSSIAN|0
4-Dec-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||linear tetraaza
pentacene Y:NO2 X:NH2 singlet opt||0,3|C,-1.2332634801,-0.4409606126,0
.0030842673|C,-0.0000000764,-1.1203721765,-0.0000039498|C,1.2332618767
,-0.4409576216,-0.0030680377|C,1.2052518951,0.9935794303,-0.0029776472
|C,-0.0000034179,1.693806237,0.0000465637|C,-1.2052570297,0.9935765391
,0.0030453724|N,-2.4320584039,1.6460558629,0.0061513316|N,-2.388773545
8,-1.1579777582,0.0059412721|C,-3.5620592243,-0.4693439909,0.008872005
5|C,-3.6277584898,0.9723414307,0.0090785366|H,-2.4440450619,2.65760372
53,0.0060906676|H,-0.0000046697,2.7828408002,0.0000660649|C,-4.7792934
53,-1.1604222606,0.0118336826|C,-4.8444188838,1.6341735481,0.012136117
5|C,-6.0116694739,-0.4989402471,0.0149157445|C,-6.0723676997,0.9327320
72,0.0152011913|H,-4.76242211,-2.2420528562,0.0116737305|H,-4.86922878
47,2.7219183937,0.0123274259|N,2.4320518002,1.6460614305,-0.0060616046
|N,2.3887736034,-1.1579718784,-0.0059497597|C,3.6277535101,0.972349492
9,-0.0090134825|C,3.5620580706,-0.4693356114,-0.0088558665|H,2.4440362
758,2.6576093014,-0.0059592974|C,4.8444122138,1.6341841252,-0.01204642
79|C,4.7792940473,-1.1604111441,-0.0118453906|C,6.0723633436,0.9327458
872,-0.0151339759|C,6.011670895,-0.4989278336,-0.0149075877|H,4.762423
7961,-2.2420409857,-0.011730667|H,4.8692183829,2.7219290594,-0.0121800
729|H,0.0000012663,-2.204297059,-0.0000229848|N,-7.1995240017,-1.31278
```

```
25626,0.0175817772|O,-8.321409449,-0.7559211631,0.0203968085|O,-7.0732
279655,-2.5397905719,0.0170105014|N,7.1995319479,-1.3127665529,-0.0176
421961|O,7.073257267,-2.5397769695,-0.0170657428|O,8.3214163106,-0.755
9046625,-0.020464044|N,-7.2341698193,1.6228359584,0.0184018207|H,-8.10
08771949,1.0983831168,0.0200013601|H,-7.2274345304,2.630591577,0.01735
88297|N,7.2341612782,1.6228576609,-0.0182309588|H,8.1008729676,1.09841
34563,-0.0200647249|H,7.2274170172,2.630613413,-0.0174436528||Version=
IA32W-G09RevC.01|State=3-A|HF=-1431.8661983|S2=2.044801|S2-1=0.|S2A=2.
001234|RMSD=9.156e-009|RMSF=7.779e-006|Dipole=-0.0000283,5.6887072,-0.
000187|Quadrupole=-28.9264942,21.1766664,7.7498278,0.0001296,0.1063566
,-0.0009337|PG=C01 [X(C18H12N8O4)]||@
```

Table 99. Computational output parameters for singlet **TAP 51ae**
(X = NH_2, Y = NO_2, E = NH_2).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C18H13N9O4\GAUSSIAN\21-Jun-2005\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\linear tetraazapentacene E:
NH2 + X:NH2 + Y:NO2 singlet opt\\0,1\C,-0.9326711084,-0.0744818143,-0.
8902666365\C,-0.9530440398,-0.0932960679,0.5213072021\C,0.244567632,-0
.0417882964,1.267145545\C,1.4978534461,-0.0255916464,0.5439482126\C,1.
5583995834,-0.0377901453,-0.8499952211\C,0.3534256119,-0.0549795903,-1
.5532703718\N,0.3397907891,-0.0489143833,-2.9151905292\N,-2.0978261971
,-0.071312679,-1.579492403\C,-2.0516370548,-0.062402715,-2.9322427275\
C,-0.8223713567,-0.0547974277,-3.6692662042\H,1.2274917107,-0.03770758
06,-3.4035683044\H,2.5127749373,-0.0269011827,-1.3709320954\C,-3.22856
84165,-0.0560774427,-3.7004441878\C,-0.7856255564,-0.0503695026,-5.056
2336692\C,-3.2002526326,-0.0481467933,-5.0934094976\C,-1.9664553409,-0
.0514586071,-5.8228771119\H,-4.1832103718,-0.0543036248,-3.1921721388\
H,0.1721227963,-0.0565177611,-5.5732367812\N,2.6355877732,0.0075422585
,1.2919177104\N,0.19342839,-0.0057330714,2.6194981017\C,2.640661193,0.
0352891806,2.6770264119\C,1.3557574989,0.0331822173,3.3120066412\H,3.5
264908858,0.0198177061,0.8094289368\C,3.8267219316,0.0690939492,3.3962
706906\C,1.3648008409,0.0685854847,4.717050661\C,3.8322916611,0.106909
2881,4.8035074781\C,2.5513907919,0.1028018286,5.4464053647\H,0.4209265
83,0.0626367807,5.2450238709\H,4.7795577323,0.0789304217,2.870323658
2\
N,-2.1614902498,-0.1930081183,1.1822902567\H,-2.135656626,0.1250321642
,2.1427543145\H,-2.9592495682,0.1014395907,0.6334924336\N,-1.889158928
3,-0.095135461,-7.1846016743\H,-2.745019508,0.0622332722,-7.7001118009
\H,-1.005484815,0.1185604048,-7.621640629\N,5.0190198051,0.188002924,5
```

```
.4735375908\H,4.9910470236,0.0496417512,6.4751673617\H,5.8658746709,-0
.0349482203,4.9725693254\N,-4.4844421206,-0.0157540602,-5.7720770211\O
,-4.5093487126,0.0340511188,-7.0182692824\O,-5.5091091809,-0.033000949
7,-5.0902466083\N,2.4273879636,0.113419599,6.8940892677\O,3.4620908605
,0.0894923632,7.5902683609\O,1.2994652662,0.1407381955,7.386138439\\Ve
rsion=x86-Linux-G03RevB.05\State=1-A\HF=-1487.2265342\S2=0.\S2-1=0.\S2
A=0.\RMSD=6.336e-09\RMSF=8.016e-06\Dipole=4.6303419,0.3364945,-2.53342
76\PG=C01 [X(C18H13N9O4)]\\@
```

Table 100. Computational output parameters for triplet **TAP 51ae** (X = NH_2, Y = NO_2, E = NH_2).

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C18H13N9O4(3)|GAUSSIAN|0
3-Dec-2012|0||# opt ub3lyp/6-31g(d) guess=mix geom=connectivity||optim
ization||0,3|C,-1.2442278593,0.3380744885,-0.0047171345|C,0.0000170646
,1.0453832248,-0.0042433433|C,1.2442624578,0.338079872,-0.0017217856|C
,1.2024443182,-1.0885233142,0.0002648054|C,0.0000182381,-1.79687919,-0
.0001762929|C,-1.2024084617,-1.0885287064,-0.0026336166|N,-2.431830861
1,-1.7353228286,-0.0031920809|N,-2.3867114873,1.0589417412,-0.00709837
47|C,-3.5714408015,0.3770045898,-0.0075379203|C,-3.6305411175,-1.06194
55119,-0.0055842619|H,-2.4443595305,-2.7466206647,-0.0017042317|H,0.00
00187736,-2.8847773573,0.0013717643|C,-4.7859028584,1.063055278,-0.010
0746981|C,-4.8450578539,-1.7291718696,-0.0060640743|C,-6.0192137676,0.
3964183361,-0.0106321104|C,-6.0759259228,-1.0335704188,-0.0084332619|H
,-4.7772799557,2.1446726023,-0.0118061695|H,-4.8643598931,-2.817063640
7,-0.0042340163|N,2.4318673444,-1.7353121211,0.0026725731|N,2.38674559
85,1.058951944,-0.001356484|C,3.630576996,-1.0619301202,0.0031654205|C
,3.5714754216,0.3770204033,0.0010515589|H,2.4443964615,-2.7466099391,0
.0041753755|C,4.8450938545,-1.7291513717,0.0055814017|C,4.7859367625,1
.0630767651,0.0015367349|C,6.0759609711,-1.0335433701,0.0060889181|C,6
.0192491251,0.3964460235,0.0039687335|H,4.7773128644,2.1446942816,-0.0
000285688|H,4.8643964854,-2.8170434283,0.0071799663|N,0.0000164455,2.3
913799881,-0.0062121506|H,0.8852606869,2.8767962732,-0.0056525576|H,-0
.8852287665,2.8767923127,-0.0077800841|N,-7.2361359877,-1.7296415489,-
0.0075091691|H,-8.1047507788,-1.2092543927,-0.0133779616|H,-7.22442954
42,-2.737117367,-0.0116904632|N,7.2361680798,-1.7296060708,0.008625683
6|H,8.1047968726,-1.2092111983,0.0084717276|H,7.224478167,-2.737088962
8,0.0094372822|N,-7.2071022466,1.2060979501,-0.0141421612|O,-8.3288151
109,0.6477882224,-0.015750649|O,-7.0845919939,2.4348847173,-0.01559982
```

```
56|N,7.2071383683,1.206129441,0.0041562636|O,8.3288536365,0.6478235865
,0.0061295728|O,7.084630795,2.4349163519,0.0023346657||Version=IA32W-G
09RevC.01|State=3-A|HF=-1487.2364229|S2=2.036158|S2-1=0.|S2A=2.000805|
RMSD=7.674e-009|RMSF=2.084e-006|Dipole=0.0000536,-4.7664107,0.0017113|
Quadrupole=-38.0891465,29.8195048,8.2696416,-0.0007157,0.0054031,-0.00
02977|PG=C01 [X(C18H13N9O4)]||@
```

Table 101. Computational output parameters for singlet 3,9-di-trifluoromethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91h**
(R = Tolyl, X = CF_3).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H22F6N4\GAUSSIAN\13-Feb-2013\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\tolyl X:CF3 singlet\\0,1\C,
-0.0432645087,-0.0016303241,0.0231513348\C,-0.0314826885,-0.0000067253
,1.4233430173\C,1.1418090391,0.0016172024,2.1875825634\C,2.4162211505,
0.000831875,1.4662750175\C,2.4432906193,-0.0000234027,0.0683505504\C,1
.2509790133,-0.0008566328,-0.6619359454\N,1.2479056583,-0.0013984992,-
2.0303928064\N,-1.2053398218,-0.003714808,-0.6504010769\C,-1.169717820
3,-0.0044406105,-2.0023869394\C,0.0416299633,-0.0033357511,-2.75684782
61\H,3.3907878444,-0.0000375052,-0.4504253328\C,-2.3906238969,-0.00144
20336,-2.7265060954\C,0.0193115057,0.0007591974,-4.1552564005\C,-2.409
5235729,0.0031395777,-4.1051341469\C,-1.1996042705,0.0054202424,-4.826
4612674\H,-3.3065328053,0.0022997477,-2.1450026379\H,0.9421978376,0.00
83129208,-4.7205807023\N,3.5674683115,0.0013795231,2.206081876\N,1.083
2309354,0.0037042261,3.5294694884\C,3.5296479671,0.003339641,3.6137064
138\C,2.241447414,0.0044397853,4.2278026086\C,4.6957612338,-0.00072454
95,4.3858625057\C,2.1937771791,0.0014506069,5.6464949649\C,4.604583734
8,-0.0053718538,5.7743718355\C,3.3450672084,-0.0031079998,6.4051144842
\H,1.2104498724,-0.0023004672,6.1048646578\H,5.6692167011,-0.008267448
3,3.912898008\H,-0.9817245811,-0.0000055207,1.9436212827\H,-3.35324109
91,0.0142135033,-4.6406821467\H,3.2878565475,-0.0141745737,7.488692676
1\C,-1.230322437,-0.0475800843,-6.3244522933\C,5.8500652406,0.04765802
82,6.6072543315\F,-2.2451241074,0.6904466837,-6.8319210264\F,-0.082115
216,0.4096745262,-6.8778477845\F,6.1458117272,1.3106632111,7.006298341
\F,5.7309266666,-0.6903915384,7.7355804451\F,-1.4071419489,-1.31058161
77,-6.7886141733\F,6.9348734909,-0.4095477948,5.9380297204\C,4.8528316
748,0.0030133706,1.5449197194\C,5.4750098602,-1.2064701434,1.233113703
\C,5.4727317847,1.2143027069,1.2359223782\C,6.7223518965,-1.1969815851
```

```
,0.6105418934\H,4.9840392999,-2.1432569735,1.4790635263\C,6.7201531251
,1.2085833112,0.6132808424\H,4.9799773998,2.1496274985,1.4839054201\C,
7.3670802854,0.006818548,0.2943271985\H,7.2035518228,-2.1416336035,0.3
69871442\H,7.1995694012,2.1546750096,0.3747647128\C,2.4973749323,-0.00
30427986,-2.7571120106\C,3.0953450436,1.2064534427,-3.1131636426\C,3.0
915450959,-1.2143190321,-3.1130696642\C,4.2917970894,1.1969675234,-3.8
28647958\H,2.6237122163,2.1432371144,-2.8318947083\C,4.28811714,-1.208
5971027,-3.828611623\H,2.6171009826,-2.1496468797,-2.8316463365\C,4.90
54280364,-0.0068474899,-4.2016564911\H,4.7538616926,2.1416228782,-4.10
42764095\H,4.7472480187,-2.1546855736,-4.1041645796\C,6.1813365938,-0.
0085371796,-5.0100537074\H,6.7789007706,-0.9048172564,-4.8146901738\H,
5.9647385883,0.0104630904,-6.0861754483\H,6.7984562197,0.8681230387,-4
.7877231645\C,8.7354840977,0.0085975203,-0.3451417911\H,8.8821418867,-
0.8700897323,-0.9816741867\H,8.8912397786,0.9029702225,-0.9570502363\H
,9.5254612676,-0.0062298313,0.417112358\\Version=IA32L-G03RevD.02\Stat
e=1-A\HF=-2126.9598335\S2=0.\S2-1=0.\S2A=0.\RMSD=4.050e-09\RMSF=2.157e
-06\Thermal=0.\Dipole=3.119275,0.000163,-1.7078835\PG=C01 [X(C34H22F6N
4)]\\@
```

Table 102. Computational output parameters for triplet 3,9-di-trifluoromethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91h**
(R = Tolyl, X = CF_3).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H22F6N4(3)\GAUSSIAN\10-Feb-201
3\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\tolyl X:CF3 triplet\\0,3
\C,0.,0.,0.\C,-0.000000015,-0.0000000002,1.4061004626\C,1.1846186763,0
.,2.1635919971\C,2.4305274185,-0.0003574869,1.4594712525\C,2.455419960
1,-0.0000008443,0.06169771\C,1.2644065555,0.0003577454,-0.6703363024\N
,1.2563683172,0.0010314086,-2.0749283903\N,-1.2017512474,0.,-0.6443704
46\C,-1.1725962074,0.0011834324,-2.0004246006\C,0.041040132,0.00186197
18,-2.7662009004\H,3.4040382096,-0.0000022387,-0.4576940781\C,-2.40451
05281,0.0062277164,-2.7011759286\C,-0.017942726,0.0078780034,-4.162747
4145\C,-2.4523006955,0.0113778375,-4.082491959\C,-1.2537404407,0.01304
92637,-4.8133296419\H,-3.3085430327,0.0099682175,-2.1012459202\H,0.893
0439179,0.0171797323,-4.7471403202\N,3.6095454212,-0.0010311682,2.2229
231342\N,1.0800856565,0.,3.5231851909\C,3.5372129674,-0.0018529157,3.6
192203071\C,2.2382482962,-0.0011774476,4.2291548433\C,4.682007493,-0.0
078601048,4.4212593362\C,2.1649650314,-0.0062197091,5.6445316479\C,4.5
643663602,-0.0130266558,5.8128825738\C,3.3029591418,-0.0113599274,6.42
```

```
89364499\H,1.1725136488,-0.0099645089,6.0829732124\H,5.6651164128,-0.0
171626182,3.9685906508\H,-0.9508102121,0.0000000046,1.9266924036\H,-3.
4039038296,0.0224612281,-4.6024967528\H,3.2284086683,-0.0224401007,7.5
107844188\C,-1.2942407313,-0.0468146177,-6.3138685965\C,5.8067331111,0
.0468532449,6.6553665882\F,-2.3863588127,0.5744034626,-6.8133906095\F,
-0.2072555685,0.5305660044,-6.8764215992\F,6.168877774,1.3241101845,6.
931703963\F,5.6392227893,-0.574304857,7.844592003\F,-1.332024927,-1.32
40662163,-6.7678492143\F,6.8662421314,-0.5305776756,6.0426775077\C,4.8
92626648,0.0022241093,1.5727328529\C,5.5202177069,-1.2051106492,1.2566
623989\C,5.5167139981,1.2129220994,1.2628474611\C,6.7687385561,-1.1952
225701,0.6363690421\H,5.0285527041,-2.1428375579,1.4981797206\C,6.7652
686895,1.2097756036,0.6424367956\H,5.0223266684,2.1480108339,1.5090288
924\C,7.413712007,0.0090493525,0.3230163813\H,7.2504974098,-2.13933697
51,0.3939255647\H,7.244285325,2.1564915334,0.4047794025\C,2.4953642462
,-0.0022295954,-2.8056361693\C,3.0997558368,1.2051153185,-3.1640894515
\C,3.092633598,-1.2129165933,-3.1644907535\C,4.2949355859,1.1952313752
,-3.8817822584\H,2.6314130774,2.1428396588,-2.8799663726\C,4.287947353
,-1.2097679759,-3.8821615614\H,2.6188903262,-2.1480080391,-2.880612831
4\C,4.9063869878,-0.0090534987,-4.2563712551\H,4.7587291021,2.13934744
89,-4.1570359919\H,4.7462183842,-2.1564823947,-4.157710453\C,6.1812655
91,-0.0124480892,-5.0666961542\H,6.7806536987,-0.9068723629,-4.8679340
71\H,5.9640112656,0.0012940495,-6.1428722519\H,6.7975252259,0.86605359
16,-4.8490248422\C,8.7832010821,0.0125034419,-0.3145096484\H,8.9328049
849,-0.8673098351,-0.9489011077\H,8.9376461855,0.9056757232,-0.9286554
467\H,9.5728327305,0.0014824828,0.4483177175\\Version=IA32L-G03RevD.02
\State=3-A\HF=-2126.9412387\S2=2.049998\S2-1=0.\S2A=2.001628\RMSD=4.38
5e-09\RMSF=1.912e-06\Thermal=0.\Dipole=0.0000041,-2.755217,-0.0001216\
PG=C01 [X(C34H22F6N4)]\\@
```

Table 103. Computational output parameters for singlet 3,9-di-cyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91f** (R = Tolyl, X = C≡N).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H22N6\GAUSSIAN\10-Feb-2013\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\singlet tolyl X:CN\\0,1\C,-0.
0395629171,0.0000108613,0.0209066489\C,-0.0280345691,0.0000000654,1.42
05633695\C,1.1465555858,-0.0000107237,2.1818187873\C,2.4202413735,-0.0
000044569,1.4600532823\C,2.4463698665,-0.0000002127,0.0623698297\C,1.2
53225037,0.0000043546,-0.6660580097\N,1.2476466956,0.0000005351,-2.034
4401952\N,-1.2037002553,0.0000238642,-0.6506158475\C,-1.171979416,0.00
```

```
00294552,-1.999772862\C,0.0401671776,0.0000168455,-2.7577647152\H,3.39
33188033,-0.0000004914,-0.4574077901\C,-2.397046059,0.000047264,-2.719
7068967\C,0.0150152589,0.0000219103,-4.1528277453\C,-2.4246440271,0.00
00523013,-4.0959700367\C,-1.2122700847,0.0000398292,-4.8281981449\H,-3
.3100562408,0.0000563517,-2.1338373617\H,-3.3688483933,0.0000658483,-4
.6306122564\H,0.9350946652,0.0000124532,-4.7234239277\N,3.5716423064,-
0.0000008276,2.1994965215\N,1.0879959002,-0.0000238002,3.5244760039\C,
3.5335117605,-0.0000169571,3.606532669\C,2.243205452,-0.0000294726,4.2
221301075\C,4.6969115015,-0.0000218641,4.3768144912\C,2.1927715124,-0.
0000472551,5.6421826678\C,4.6076913917,-0.0000396311,5.7748108341\C,3.
3389978624,-0.0000522068,6.4044337203\H,3.2830536121,-0.0000657166,7.4
880546533\H,1.2082891324,-0.0000563654,6.0978415073\H,5.6723047295,-0.
0000124019,3.9069911031\H,-0.977697774,0.0000000677,1.9418307279\C,-1.
2307647953,0.0000457403,-6.2569261979\N,-1.2456365893,0.0000516982,-7.
4218075349\C,5.8030662141,-0.000045268,6.5575526242\N,6.7777996235,-0.
0000503888,7.1955685487\C,4.8581942127,0.0000291662,1.5390470242\C,5.4
798740535,-1.2107123959,1.2312905963\C,5.4798491915,1.2107936057,1.231
3651081\C,6.7299936768,-1.2028456271,0.6142304067\H,4.9875929542,-2.14
70028602,1.4766363738\C,6.7299766223,1.2029844908,0.6143030521\H,4.987
5546988,2.147062425,1.4767663432\C,7.3775013391,0.0000885606,0.3001058
432\H,7.2116148028,-2.1481409141,0.3773330749\H,7.2115836922,2.1483010
568,0.3774673114\C,2.4956154704,-0.0000297588,-2.7651819211\C,3.089050
5625,1.2107120743,-3.1243964306\C,3.0889718687,-1.2107940485,-3.124418
5649\C,4.2808530253,1.202845217,-3.8477002801\H,2.6177475448,2.1470025
438,-2.8408319513\C,4.2807805699,-1.2029849453,-3.8477284108\H,2.61761
34099,-2.1470629224,-2.8408751916\C,4.8935260857,-0.0000893554,-4.2252
876379\H,4.7393065579,2.148140541,-4.1268054069\H,4.7391727739,-2.1483
014939,-4.1268575328\C,8.7495886469,0.000099135,-0.3310404541\H,8.9051
493545,0.8873068351,-0.9532810764\H,9.5342741102,-0.0009005793,0.43671
36446\H,8.9044483926,-0.8861420368,-0.9548412941\C,6.1627012803,-0.000
0983002,-5.0439227985\H,6.7711268399,-0.8873439746,-4.8411101675\H,5.9
363356118,0.0009822291,-6.1181369606\H,6.772139515,0.8861047628,-4.839
5649227\\Version=IA32L-G03RevD.02\State=1-A\HF=-1637.3743105\S2=0.\S2-
1=0.\S2A=0.\RMSD=2.987e-09\RMSF=9.119e-06\Thermal=0.\Dipole=2.5407308,
0.000003,-1.3945968\PG=C01 [X(C34H22N6)]\\@
```

Table 104. Computational output parameters for triplet 3,9-di-cyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91f** (R = Tolyl, X = C≡N).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H22N6(3)\GAUSSIAN\09-Feb-2013\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\triplet tolyl X:CN\\0,3\C,
0.,0.0000002776,0.\C,-0.0000000793,0.0000000009,1.4051749755\C,1.18543
56168,-0.0000002839,2.1596680069\C,2.4306419501,-0.0000002884,1.455282
8606\C,2.4551278976,-0.000000016,0.0575623199\C,1.2628337505,0.0000002
648,-0.6722709025\N,1.2530902282,0.0000005422,-2.075534886\N,-1.202714
1905,0.000000543,-0.6455989317\C,-1.1767651822,0.000000806,-1.99631060
68\C,0.0378903703,0.0000008179,-2.7663027807\H,3.4031019134,-0.0000000
226,-0.4627778794\C,-2.4134852825,0.,-2.6947579276\C,-0.0219578652,0.,
-4.1598987559\C,-2.4679254001,0.,-4.0723496161\C,-1.2659293693,0.,-4.8
14681735\H,-3.3149943191,0.,-2.0912666861\H,-3.4198915045,0.,-4.592348
5435\H,0.8862578584,0.,-4.7490122211\N,3.6092336172,-0.0000005739,2.21
69694271\N,1.0842928254,-0.0000005403,3.5209503216\C,3.5394922856,-0.0
000008408,3.6130378802\C,2.2377149483,-0.0000008115,4.2243085426\C,4.6
830246563,0.,4.4118027208\C,2.1628962166,0.,5.6426557953\C,4.567477074
6,0.,5.8128218532\C,3.2958317301,0.,6.4282644268\H,3.2233664525,0.,7.5
105708215\H,1.16972397,0.,6.0791497133\H,5.667669465,0.,3.9619304322\H
,-0.9502392912,0.0000000075,1.9267585343\C,-1.30617445,0.,-6.243402893
6\N,-1.3395789022,0.0000018903,-7.4078037769\C,5.7511674892,0.,6.61390
91253\N,6.7155446963,-0.0000008148,7.2673017157\C,4.8930477251,-0.0000
005934,1.5660334929\C,5.5187027115,-1.2094160004,1.2546155774\C,5.5187
117147,1.2094089988,1.2546402947\C,6.7683686461,-1.2026420003,0.636580
0633\H,5.0257002561,-2.1460039968,1.4979116203\C,6.7683861054,1.202632
9987,0.6366035612\H,5.0257224719,2.1459990014,1.4979541814\C,7.4157742
978,-0.0000006384,0.3216419314\H,7.2493731817,-2.1479889986,0.39786308
27\H,7.2494017947,2.1479769983,0.397908977\C,2.4915630909,0.0000005442
,-2.8090750844\C,3.0902211108,1.2094149969,-3.1696790901\C,3.090203736
8,-1.2094089988,-3.1697003536\C,4.2826016471,1.2026419969,-3.892077067
7\H,2.6202597813,2.1460039981,-2.8844059138\C,4.2825912031,-1.20263399
89,-3.8921044167\H,2.6202339692,-2.1459990013,-2.8844487827\C,4.895907
7838,0.0000005552,-4.2691389049\H,4.7422592766,2.1479889959,-4.1696845
883\H,4.7422349644,-2.1479779987,-4.1697351251\C,8.7867292882,-0.00002
39991,-0.3123838189\H,8.9408390193,0.8870900022,-0.9352609687\H,9.5738
188545,-0.0010579992,0.4530392805\H,8.9400837459,-0.8861639998,-0.9368
426965\C,6.1669041668,0.0000240028,-5.085272737\H,6.7750878247,-0.8871
269936,-4.8808938301\H,5.9437958011,0.0011400027,-6.1602635104\H,6.776
0878531,0.8861260033,-4.8792901635\\Version=IA32L-G03RevD.02\State=3-A
```

```
\HF=-1637.355164\S2=2.05251\S2-1=0.\S2A=2.001803\RMSD=4.320e-09\RMSF=1
.427e-05\Thermal=0.\Dipole=0.0000036,-2.1862751,0.0000064\PG=C01 [X(C3
4H22N6)]\\@
```

Table 105. Computational output parameters for singlet 2,10-di-fluoro-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91k** (R = Tolyl, Y = F).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C32H22F2N4\GAUSSIAN\12-Feb-2013\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt ground state singlet Y:
F\\0,1\C,-0.0376515181,0.0000110675,0.0204609531\C,-0.0268512955,0.000
000103,1.4213340415\C,1.1451349037,-0.0000108236,2.1888041432\C,2.4199
723277,-0.000005209,1.4690658455\C,2.44888223,0.0000001829,0.070872576
3\C,1.2576511943,0.0000055141,-0.6617589483\N,1.2560897434,0.000004240
9,-2.0302613539\N,-1.1984639501,0.0000244732,-0.6547871494\C,-1.162271
6246,0.0000317733,-2.0083812585\C,0.0515322021,0.0000205782,-2.7615191
656\H,3.3972300228,0.0000002221,-0.4464314098\C,-2.3840357171,0.000049
4287,-2.7271425765\C,0.0284816758,0.0000272577,-4.1625781427\C,-2.3704
059104,0.0000555452,-4.1033911225\C,-1.1828773669,0.0000448491,-4.8440
743257\H,-3.3146937543,0.0000575988,-2.1720305305\H,-1.2227467088,0.00
00504463,-5.9274894081\H,0.9554199909,0.000018848,-4.7236162213\N,3.56
97437367,-0.0000040056,2.2112439477\N,1.084445213,-0.0000243236,3.5303
569054\C,3.5324640948,-0.0000204779,3.6198987924\C,2.2421206807,-0.000
0316879,4.2327213721\C,4.6979748001,-0.0000273014,4.3977699205\C,2.185
0188311,-0.0000494446,5.6490778926\C,4.6151739047,-0.0000449964,5.7852
038436\H,5.5045090894,-0.0000506872,6.4052530735\C,3.3495269525,-0.000
0556609,6.3826770128\H,1.214459084,-0.0000576081,6.1310405464\H,5.6715
032167,-0.0000189144,3.9221428\H,-0.9779478633,0.0000000651,1.94013775
16\C,4.8543260513,0.000022638,1.5514181101\C,5.4757065744,-1.209870265
8,1.2392832146\C,5.4756818404,1.2099362163,1.2393437412\C,6.7215393834
,-1.2025910379,0.6133248989\H,4.9832795094,-2.1456236957,1.4862277242\
C,6.7215211023,1.2027083979,0.6133832978\H,4.9832406726,2.1456703181,1
.4863330906\C,7.3663424718,0.000075673,0.2933879995\H,7.2005680117,-2.
1480428915,0.3709416037\H,7.2005348969,2.1481793325,0.3710493767\C,2.5
062945254,-0.0000223945,-2.7531094574\C,3.1051286822,1.2098702416,-3.1
065771616\C,3.1050649834,-1.209935917,-3.1065881676\C,4.3058803834,1.2
025910464,-3.8151804391\H,2.6309166754,2.1456236445,-2.8262403627\C,4.
3058218189,-1.2027082757,-3.8151956065\H,2.6308079527,-2.145669904,-2.
8262629598\C,4.9239551927,-0.0000755416,-4.1841168646\H,4.7690037122,2
.1480428339,-4.0867221778\H,4.7688960135,-2.1481792231,-4.0867507423\C
```

```
,6.2066488866,-0.0000870154,-4.9821419563\H,6.0003982181,0.0007417267,
-6.0605721293\H,6.8128203029,0.8860092906,-4.7671700136\H,6.8120575638
,-0.8869880771,-4.7683655409\C,8.7317206185,0.0000865985,-0.353055817\
H,8.8797389226,0.8869988337,-0.9777882777\H,9.5267909748,-0.0007659072
,0.4041853016\H,8.879128934,-0.8859985172,-0.9791129261\F,3.2811118845
,-0.0000726882,7.7323189889\F,-3.5422023045,0.000072488,-4.7765233879\
\Version=IA32L-G03RevD.02\State=1-A\HF=-1651.3468188\S2=0.\S2-1=0.\S2A
=0.\RMSD=4.973e-09\RMSF=1.047e-05\Thermal=0.\Dipole=4.3388816,-0.00000
11,-2.3667732\PG=C01 [X(C32H22F2N4)]\\@
```

Table 106. Computational output parameters for triplet 2,10-di-fluoro-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91k** (R = Tolyl, Y = F).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C32H22F2N4(3)\GAUSSIAN\12-Feb-201
3\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt ground state triplet
 Y:F\\0,3\C,0.0018803617,0.000007429,0.0000179929\C,0.0009563235,-0.00
00000267,1.4061660343\C,1.1837248306,-0.0000074443,2.1666341967\C,2.43
05628373,-0.0000046928,1.4644171813\C,2.4571746485,0.0000000645,0.0663
495869\C,1.2672934864,0.0000047596,-0.6681461877\N,1.2608814044,0.0000
057497,-2.0725543008\N,-1.1996679699,0.0000158874,-0.6452483153\C,-1.1
700850664,0.0000237168,-2.0018138282\C,0.044549811,0.000018829,-2.7677
718044\H,3.4066917261,0.0000001314,-0.4515924063\C,-2.4048530691,0.000
0363461,-2.6967645214\C,-0.0153938528,0.0000272199,-4.1665209181\C,-2.
420478514,0.000044101,-4.0743224828\C,-1.2440567429,0.000039878,-4.826
5976212\H,-3.3232201321,0.0000395785,-2.1213721194\H,-1.2987206958,0.0
000465228,-5.9097840928\H,0.8990820337,0.0000236785,-4.747446729\N,3.
6078968895,-0.0000056209,2.2301115024\N,1.0757739778,-0.0000159102,3.5
262053105\C,3.5339410537,-0.0000187287,3.6291541951\C,2.2323692588,-0.
0000236745,4.2357350802\C,4.6775367596,-0.0000271085,4.4367934627\C,2.
1482081916,-0.0000362965,5.650134388\C,4.5673592821,-0.000039772,5.827
1799826\H,5.4484929086,-0.0000463983,6.4595442852\C,3.2979792084,-0.00
00440128,6.4090393242\H,1.1672513209,-0.0000395518,6.1107840344\H,5.66
10394768,-0.0000235363,3.982411079\H,-0.9507017447,-0.0000000465,1.925
2758913\C,4.8907746676,0.0000179075,1.5829515848\C,5.5178869942,-1.208
5023266,1.2695420611\C,5.5178715117,1.2085550368,1.2696062597\C,6.7665
426069,-1.2023159508,0.6491715745\H,5.0238022352,-2.1446716661,1.51219
69927\C,6.7665337437,1.2024119547,0.6492340607\H,5.0237799367,2.144708
3964,1.5123086779\C,7.4132446302,0.0000629192,0.332425703\H,7.24633514
64,-2.1478161156,0.4076680232\H,7.2463189914,2.1479281581,0.407783006\
```

```
C,2.4995141654,-0.0000177408,-2.8008263891\C,3.1025232192,1.2085024007
,-3.1584231424\C,3.102461305,-1.2085549627,-3.1584442543\C,4.300105084
8,1.20231598,-3.8724247621\H,2.6310202603,2.1446717742,-2.8743702241\C
,4.3000480459,-1.2024119254,-3.8724503958\H,2.630914931,-2.1447082889,
-2.8744107498\C,4.9165249187,-0.0000628076,-4.2446853542\H,4.762902366
7,2.1478161149,-4.1450848944\H,4.7627975429,-2.147928157,-4.1451322156
\C,6.1954959151,-0.0000703817,-5.048940178\H,5.9848550341,0.0007571515
,-6.1266344044\H,6.8028540925,0.8859693546,-4.8367687224\H,6.802089726
3,-0.8869121723,-4.8379595345\C,8.7818454375,0.0000699897,-0.307515279
7\H,8.932855904,0.8869229003,-0.9317306705\H,9.5739201581,-0.000781140
1,0.4530187581\H,8.932251113,-0.8859585935,-0.9330540268\F,3.205037406
3,-0.0000560544,7.7573840564\F,-3.6044624351,0.0000561592,-4.726130561
\\Version=IA32L-G03RevD.02\State=3-A\HF=-1651.328498\S2=2.048787\S2-1=
0.\S2A=2.001547\RMSD=7.466e-09\RMSF=5.424e-06\Thermal=0.\Dipole=3.6102
933,-0.0000011,-1.9693406\PG=C01 [X(C32H22F2N4)]\\@
```

Table 107. Computational output parameters for singlet 2,10-di-methoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91c** (R = Tolyl, Y = OMe).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H28N4O2\GAUSSIAN\10-Feb-2013\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\singlet Y:OMe\\0,1\C,-0.052
4711559,0.000021575,0.027535498\C,-0.0405953611,0.0000195061,1.4290020
541\C,1.1305820683,0.0000199409,2.1988026709\C,2.4062905284,0.00001734
06,1.4781339684\C,2.4355496671,0.0000163235,0.0798307542\C,1.244728525
3,0.0000212411,-0.6536901848\N,1.2438067352,0.000016371,-2.0217495359\
N,-1.2124188131,0.0000139796,-0.6475877117\C,-1.1776074283,0.000007644
4,-2.0037506682\C,0.0391158129,0.0000094384,-2.7535026281\H,3.38431846
71,0.0000072669,-0.4371226739\C,-2.3923467356,-0.0000025576,-2.7222157
525\C,0.0085062083,0.0000034073,-4.1503116503\C,-2.4133987016,-0.00000
95572,-4.1106058201\C,-1.2043024961,-0.0000056664,-4.8346408451\H,-3.3
205911127,-0.0000054975,-2.1622366414\H,0.9329488801,0.0000051033,-4.7
163334654\N,3.5553355918,0.0000052335,2.2206181073\N,1.0689912601,0.00
00115195,3.5395026675\C,3.5170713044,-0.0000014364,3.6296172761\C,2.22
74132421,0.00000186,4.2455113845\C,4.6741783696,-0.0000111943,4.412634
292\C,2.17253554,-0.0000079333,5.6557497061\C,4.5916638574,-0.00001886
33,5.8027432006\C,3.3277501598,-0.0000183123,6.4261712478\H,1.19874092
73,-0.0000077881,6.1321301015\H,5.6509893757,-0.000012695,3.9427245061
\H,-0.9920026909,0.0000156318,1.9473931171\H,-1.1967540161,-0.00001036
7,-5.9177460873\H,5.5058616191,-0.000024397,6.3836187458\O,-3.65207994
```

```
96,-0.000020114,-4.6917199611\O,3.1444796058,-0.000024317,7.7820609162
\C,-3.7337882086,-0.0000338551,-6.1056955102\H,-4.7993669809,-0.000044
1862,-6.3438224769\H,-3.2677874597,0.8945479216,-6.5410426605\H,-3.267
7738602,-0.8946167299,-6.5410259434\C,4.2883075135,-0.0000740355,8.617
3218408\H,3.9106832867,-0.000096088,9.6418034235\H,4.9067434086,-0.894
6650362,8.4617447685\H,4.9067824525,0.8944996088,8.4617989372\C,4.8400
014742,-0.0000043766,1.5630327322\C,5.4624167854,-1.2095355164,1.25140
21235\C,5.4624154113,1.2095279711,1.2513596491\C,6.7087644862,-1.20254
42259,0.6263846595\H,4.9691342508,-2.1450212518,1.4975761671\C,6.70875
37789,1.2025243097,0.6263451242\H,4.9691247799,2.1450171294,1.49750502
11\C,7.3537688547,-0.000018578,0.3067367891\H,7.1877591793,-2.14806254
37,0.3837918875\H,7.1877413231,2.1480391344,0.3837179527\C,2.492855506
5,0.000018869,-2.7447032763\C,3.0921832391,1.2095560881,-3.0987228558\
C,3.0921726711,-1.2095073974,-3.0987499121\C,4.2930849106,1.20256426,-
3.8071305938\H,2.6179017573,2.1450407781,-2.8176737081\C,4.2930798363,
-1.202504269,-3.8071618875\H,2.6178885651,-2.1449976106,-2.8177240124\
C,4.911357276,0.0000290314,-4.1758409761\H,4.7566376055,2.1480834767,-
4.0780681714\H,4.7566263763,-2.1480181873,-4.0781241096\C,8.7194103184
,-0.0000013248,-0.3394682353\H,8.8666144981,0.8858254607,-0.9660492072
\H,9.5149725545,0.0012463435,0.4173794003\H,8.8675353931,-0.8870138116
,-0.9641392585\C,6.1947453559,0.0000524205,-4.973006316\H,5.9901092577
,0.0009482938,-6.0518308815\H,6.8008908719,0.8860511797,-4.7572435378\
H,6.8001108561,-0.8867887236,-4.7585451649\\Version=IA32L-G03RevD.02\S
tate=1-A\HF=-1681.9222086\S2=0.\S2-1=0.\S2A=0.\RMSD=8.594e-09\RMSF=3.8
52e-05\Thermal=0.\Dipole=4.2442859,0.0000661,-2.312597\PG=C01 [X(C34H2
8N4O2)]\\@
```

Table 108. Computational output parameters for triplet 2,10-di-Methoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91c** (R= Tolyl, Y = OMe).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H28N4O2(3)\GAUSSIAN\09-Feb-201
3\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\triplet Y:OMe\\0,3\C,0.,
0.,0.\C,0.0000000127,0.,1.4068829734\C,1.1821672559,0.,2.1696412434\C,
2.4300277849,0.,1.4669030408\C,2.4562456278,0.0000004628,0.068554247\C
,1.2670350911,0.000000145,-0.6675469726\N,1.2607190331,0.,-2.070906509
4\N,-1.2012131267,0.,-0.6436737368\C,-1.1736974409,0.,-2.003375934\C,0
.0427240396,0.,-2.7667656488\H,3.4061012845,0.,-0.4489913533\C,-2.4024
100184,0.,-2.696244701\C,-0.0263669448,0.,-4.1601606647\C,-2.454411925
```

```
2,0.,-4.0856725178\C,-1.2582766076,0.,-4.8222854587\H,-3.3176471141,0.
,-2.1150881241\H,0.8844664296,0.,-4.7475852543\N,3.605810082,0.,2.2330
582939\N,1.0717776464,0.,3.5279648386\C,3.5301729023,0.,3.6337757187\C
,2.229218095,0.,4.2420228096\C,4.6635480994,0.,4.447276731\C,2.1452566
399,0.,5.6501251498\C,4.5520190649,0.,5.8413977706\C,3.2845633489,0.,6
.4471157891\H,1.160719665,0.,6.1040950842\H,5.6509648745,0.,4.00040628
38\H,-0.9519095482,0.,1.9255476796\H,-1.2670617944,0.,-5.9058346251\H,
5.4577343345,0.,6.4362387795\O,-3.7050928213,0.,-4.6419905667\O,3.0739
514821,0.,7.7996449447\C,-3.8101390361,0.,-6.0543126015\H,-4.879345468
7,0.,-6.275351535\H,-3.3509030075,0.8946003056,-6.4970843831\H,-3.3508
703883,-0.8945847008,-6.4970849321\C,4.2037370054,-0.0000882121,8.6536
197106\H,3.8097873281,-0.0001335254,9.6718850274\H,4.8247445349,-0.894
6942767,8.5077229711\H,4.824807038,0.8944907235,8.5078304024\C,4.88903
02725,0.,1.5893637999\C,5.5177413702,-1.2081235579,1.2770868299\C,5.51
77158092,1.2081314368,1.2770285836\C,6.7674330835,-1.2022317171,0.6586
930619\H,5.0227256827,-2.1440414657,1.5187300846\C,6.7673987631,1.2022
452774,0.6586395624\H,5.0226742348,2.1440475301,1.518631943\C,7.414554
4222,0.0000017775,0.3427037448\H,7.2474983255,-2.1477748417,0.41746605
6\H,7.2474378395,2.1477921481,0.4173660223\C,2.4973118827,0.,-2.800176
5438\C,3.1005968088,1.2081324529,-3.1591237977\C,3.1005844169,-1.20812
25518,-3.1591470404\C,4.297745341,1.2022473248,-3.8739317695\H,2.62918
36548,2.1440485217,-2.8741510983\C,4.2977394736,-1.2022286801,-3.87395
96765\H,2.6291657967,-2.1440414856,-2.8741977095\C,4.914090895,0.00000
78398,-4.2464174387\H,4.7607321372,2.147794196,-4.1464996878\H,4.76071
63731,-2.147771811,-4.1465508756\C,8.7838689747,0.0000289503,-0.296075
9632\H,8.9344888583,0.8857873938,-0.9220758707\H,9.5759330646,0.001298
1241,0.464583236\H,8.9354206149,-0.8869296105,-0.9201344319\C,6.19323
05775,0.00002919,-5.0506958192\H,5.9834953323,0.0009286337,-6.12864714
33\H,6.8007363252,0.8859646063,-4.8381319985\H,6.7999428167,-0.8867533
889,-4.8394316707\\Version=IA32L-G03RevD.02\State=3-A\HF=-1681.9043626
\S2=2.049322\S2-1=0.\S2A=2.001582\RMSD=5.067e-09\RMSF=3.287e-05\Therma
l=0.\Dipole=-0.0000016,-3.9225419,-0.000044\PG=C01 [X(C34H28N4O2)]\\@
```

Table 109. Computational output parameters for singlet 2,10-di-Methyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91e** (R = Tolyl, Y = Me).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H28N4\GAUSSIAN\14-Feb-2013\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt ground state singlet\\0,1
\C,0.00489256,0.0000087319,-0.0030880568\C,0.0054788659,0.0000001563,1
```

```
.3985373347\C,1.1707225759,-0.0000085346,2.177486163\C,2.4509341685,-0
.0000113824,1.4675907152\C,2.4912062644,-0.0000001559,0.0695591308\C,1
.3062584349,0.0000112347,-0.6734164603\N,1.3179399467,0.0000228601,-2.
042471844\N,-1.1491292569,0.0000137988,-0.6896974204\C,-1.0997430572,0
.0000232204,-2.0453307687\C,0.1200957635,0.0000343623,-2.7844137272\H,
3.443928782,-0.0000002503,-0.4398079018\C,-2.3098065162,0.0000564729,-
2.7803076368\C,0.1029867891,0.0000971717,-4.1839346263\C,-2.3364414677
,0.0000882025,-4.168072773\C,-1.1103241349,0.0001396699,-4.8629168446\
H,-3.2280362753,0.0000748487,-2.1993242167\H,-1.108626825,0.0002162672
,-5.9497765809\H,1.0322392968,0.0001559007,-4.7422163787\N,3.595906646
,-0.0000231447,2.2182484234\N,1.1007535884,-0.0000133818,3.5184943033\
C,3.5476123369,-0.0000344134,3.626430219\C,2.255505598,-0.0000229053,4
.2303428545\C,4.7019292823,-0.000097217,4.4179501394\C,2.1946327457,-0
.0000558009,5.6448176581\C,4.5926885198,-0.0001393211,5.8040261184\H,5
.4974464163,-0.0002158178,6.4062553815\C,3.3338830562,-0.0000875737,6.
4377300835\H,1.2015124289,-0.0000737889,6.0857253737\H,5.6822933131,-0
.0001560897,3.9552676799\H,-0.9500177921,0.000000297,1.9093874458\C,4.
8849884584,-0.0000084707,1.5687442573\C,5.5093146448,-1.20955072,1.261
1637264\C,5.5093170832,1.2095439221,1.2612389052\C,6.7597419929,-1.202
5128868,0.6444443856\H,5.0148336966,-2.1451250329,1.5045673752\C,6.759
750233,1.2025368836,0.6445165929\H,5.0148428293,2.1451071109,1.5046985
846\C,7.4068591977,0.0000235882,0.329164311\H,7.2405277431,-2.14801119
75,0.4054290778\H,7.2405416953,2.1480463727,0.4055611599\C,2.574011892
2,0.0000077811,-2.7537178359\C,3.1765412604,1.2095497372,-3.1020680034
\C,3.1764796926,-1.209544943,-3.1021110836\C,4.3838813247,1.2025114047
,-3.7993782206\H,2.6994966656,2.1451242528,-2.8260519728\C,4.383825292
7,-1.2025383743,-3.7994243784\H,2.6993917591,-2.1451079172,-2.82613110
99\C,5.005471128,-0.0000252199,-4.1624039323\H,4.8496707114,2.14800952
49,-4.0664434552\H,4.8495676995,-2.1480480639,-4.0665269755\C,6.295911
654,-0.0000259584,-4.9480610004\H,6.1006829114,0.0008007415,-6.0286000
457\H,6.9000819693,0.886012613,-4.7269974297\H,6.8993450098,-0.8868601
387,-4.7281998509\C,8.7769083811,0.0000233513,-0.3075923286\H,8.929230
1202,0.886867998,-0.9314914534\H,9.567037557,-0.0008259928,0.454887002
3\H,8.9286224805,-0.8860047219,-0.9328062518\C,-3.6500895257,-0.000152
4269,-4.916928316\H,-4.2514988229,-0.883635693,-4.6696352092\H,-4.254
7238397,0.8796533003,-4.6645449298\H,-3.4927800186,0.003198843,-6.0003
859224\C,3.2270206825,0.0001526068,7.94605243\H,2.6873441279,0.8836301
836,8.3088280929\H,2.6813388987,-0.8796588414,8.3086836557\H,4.2153763
042,-0.0031880335,8.4169875386\\Version=IA32L-G03RevD.02\State=1-A\HF=
-1531.5156643\S2=0.\S2-1=0.\S2A=0.\RMSD=8.383e-09\RMSF=6.860e-06\Therm
al=0.\Dipole=3.5935537,-0.000002,-1.9212806\PG=C01 [X(C34H28N4)]\\@
```

Table 110. Computational output parameters for triplet 2,10-di-Methyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91e** (R = Tolyl, Y = Me).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H28N4(3)\GAUSSIAN\17-Feb-2013\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt ground state triplet\\
0,3\C,0.0485356876,-0.0000166799,-0.0247287277\C,0.0366748338,-0.00000
02927,1.382037597\C,1.2124608409,0.0000161448,2.1544749371\C,2.4657746
313,0.0000079613,1.4622122083\C,2.5037635863,-0.0000002021,0.064351377
5\C,1.320849405,-0.0000083976,-0.6814181095\N,1.3268691144,-0.00000823
18,-2.0865196436\N,-1.1464050935,-0.0000365922,-0.680101757\C,-1.10418
15785,-0.000044646,-2.0401803217\C,0.1166585791,-0.0000148174,-2.79183
58125\H,3.4578963611,-0.0000000952,-0.445256403\C,-2.3273796257,-0.000
0355915,-2.7496607773\C,0.0607118514,0.0000650195,-4.1883875898\C,-2.3
854988294,-0.0000063549,-4.1392290586\C,-1.1709388202,0.0000901643,-4.
8453299468\H,-3.2323938889,-0.0000216018,-2.1481632772\H,-1.1840856527
,0.0001951028,-5.9325846083\H,0.9766288772,0.000164666,-4.7680567735\N
,3.6369287715,0.0000080345,2.2385784496\N,1.0926537475,0.0000361804,3.
5120623353\C,3.5501389444,0.0000147814,3.6366299419\C,2.2465211805,0.0
000444639,4.2333018795\C,4.6797280175,-0.0000646049,4.4597431978\C,2.1
559700866,0.0000356947,5.6444632737\C,4.5408110491,-0.0000894365,5.848
7135775\H,5.4371381949,-0.0001938717,6.4642565761\C,3.2785469421,0.000
0068131,6.4654986287\H,1.1527805537,0.0000217402,6.062148347\H,5.67083
85899,-0.0001639353,4.0208580247\H,-0.9195483233,-0.0000002879,1.89276
18595\C,4.9248347651,0.0000198433,1.6032585822\C,5.5552542481,-1.20812
66936,1.2948977043\C,5.5552750016,1.2081750351,1.2950042861\C,6.809113
038,-1.2021974136,0.6850871327\H,5.0589063674,-2.1441201636,1.53349361
01\C,6.8091396565,1.202273156,0.6851914399\H,5.058947452,2.144158844,1
.5336800802\C,7.4584433662,0.0000484239,0.3737017688\H,7.2909493717,-2
.14773628,0.4474812707\H,7.2909962611,2.1478220277,0.4476705616\C,2.57
10930724,-0.0000199571,-2.8036248787\C,3.1779503262,1.2081265115,-3.15
61008921\C,3.1778736691,-1.2081752143,-3.1561769978\C,4.3820396372,1.2
021972263,-3.8590944699\H,2.7036322843,2.1441199952,-2.8762588122\C,4.
3819679895,-1.2022733426,-3.859174085\H,2.7035006996,-2.1441590081,-2.
8763958589\C,5.0019271341,-0.0000485157,-4.2256052809\H,4.8474648377,2
.1477360774,-4.1274266926\H,4.8473340805,-2.1478222303,-4.1275699791\C
,6.2885895386,-0.0000473978,-5.0177335363\H,6.088827727,0.0007882706,-
6.0975571434\H,6.8940313427,0.8859248429,-4.7995388089\H,6.8932798513,
-0.8868250656,-4.80075192\C,8.832302209,0.0000468759,-0.2551695926\H,8
.9882378052,0.8868351967,-0.8783842033\H,9.6186776768,-0.0008113173,0.
5113402827\H,8.987631194,-0.8859146774,-0.8797179896\C,-3.7123920646,-
```

```
0.0003517938,-4.8633297634\H,-4.3095336083,-0.8843344687,-4.6070367104
\H,-4.31334527,0.8791840706,-4.6008573354\H,-3.573772931,0.0036739079,
-5.9493525144\C,3.14248268,0.0003514727,7.970973305\H,2.5973939061,0.8
843272004,8.3247452073\H,2.590161549,-0.8791914336,8.3244780662\H,4.12
21822448,-0.0036613275,8.4596956662\\Version=IA32L-G03RevD.02\State=3-
A\HF=-1531.4991952\S2=2.049662\S2-1=0.\S2A=2.001609\RMSD=6.026e-09\RMS
F=2.874e-05\Thermal=0.\Dipole=2.8151112,-0.0000014,-1.5035671\PG=C01 [
X(C34H28N4)]\\@
```

Table 111. Computational output parameters for singlet 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91p**
(R = Tolyl, parent, X = Y = H).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C32H24N4|GAUSSIAN|26-Feb
-2012|0||# opt ub3lyp/6-31g(d) geom=connectivity||opt ground state sin
glet||0,1|C,-1.2359152393,2.6364280436,-0.0000158197|C,0.0000002145,3.
2972024737,-0.0000073804|C,1.235915639,2.6364279307,0.0000065955|C,1.2
139341652,1.1732767439,0.000007828|C,0.0000000848,0.478577955,0.000004
7711|C,-1.2139339313,1.1732768945,-0.0000046556|N,-2.4158294126,0.5170
659592,-0.0000018896|N,-2.3860387144,3.3297382054,-0.0000312113|C,-3.5
571538229,2.6466608132,-0.0000377552|C,-3.6360529096,1.22254396,-0.000
0225704|H,0.0000000357,-0.6016844824,0.0000093696|C,-4.7782316679,3.36
82476653,-0.0000592497|C,-4.8765782021,0.5693003757,-0.0000295095|C,-5
.9979862146,2.7177546784,-0.0000659413|C,-6.0510875799,1.3128612639,-0
.0000511595|H,-4.7064488627,4.4512538508,-0.0000702762|H,-6.9193091553
,3.2940721266,-0.0000825496|H,-7.0082794868,0.799848971,-0.000056781|H
,-4.9216470202,-0.5137202881,-0.0000178512|N,2.4158296347,0.5170656616
,0.0000103554|N,2.3860391751,3.3297379871,0.0000174411|C,3.6360532525,
1.2225435733,0.0000213777|C,3.5571543119,2.646660467,0.0000260555|C,4.
8765785327,0.5692998891,0.0000292841|C,4.7782322227,3.3682472479,0.000
0387708|C,6.0510880127,1.312860712,0.00004174|H,7.0082798854,0.7998483
238,0.0000478075|C,5.9979867653,2.7177541412,0.0000464913|H,6.91930975
24,3.2940715351,0.0000562513|H,4.7064494978,4.4512534594,0.0000419062|
H,4.9216472767,-0.5137207921,0.0000257954|H,0.0000002787,4.3806649056,
-0.000117799|C,2.4484074874,-0.9263673743,-0.0000041054|C,2.469983653
4,-1.6218440384,1.2096191551|C,2.4700190099,-1.6218151234,-1.209635187
1|C,2.5131078621,-3.0154117504,1.2025276077|H,2.4526244903,-1.07106442
94,2.1452454171|C,2.5131438642,-3.0153898489,-1.2025700034|H,2.4526877
```

```
32,-1.0710189433,-2.1452521303|C,2.5389269145,-3.7347929973,-0.0000319
176|H,2.5280909298,-3.5520873054,2.1480217567|H,2.5281580678,-3.552045
821,-2.1480736601|C,-2.4484073996,-0.9263670674,0.0000314456|C,-2.4699
834306,-1.6218600782,-1.2095821339|C,-2.4700192096,-1.6217984298,1.209
6721803|C,-2.5131077983,-3.0154278834,-1.2024717045|H,-2.4526239351,-1
.0710933164,-2.145215934|C,-2.5131442252,-3.0153730383,1.2026258945|H,
-2.4526881341,-1.0709894336,2.1452815668|C,-2.5389271469,-3.7347926573
,0.0000974383|H,-2.5280906939,-3.5521161996,-2.1479585925|H,-2.5281587
223,-3.5520162487,2.1481368061|C,-2.6208323174,-5.2433205263,0.0001154
223|H,-3.665252286,-5.5821806379,-0.0007297967|H,-2.1403878605,-5.6711
365773,-0.885921411|H,-2.1418332158,-5.6710336914,0.8869784493|C,2.620
8318947,-5.243320875,-0.0000287153|H,2.1418522811,-5.6710454016,-0.886
8967021|H,3.6652518036,-5.5821811042,0.0008442651|H,2.1403678584,-5.67
11254537,0.8860031287||Version=IA32W-G09RevC.01|State=1-A|HF=-1452.880
2554|S2=0.|S2-1=0.|S2A=0.|RMSD=2.834e-009|RMSF=9.139e-006|Dipole=-0.00
00014,-4.251033,0.0000231|Quadrupole=1.778568,-2.1169808,0.3384128,-0.
0000044,0.0002344,-0.0000158|PG=C01 [X(C32H24N4)]||@
```

Table 112. Computational output parameters for triplet 5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91p**
(R = Tolyl, parent, X = Y = H).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C32H24N4(3)\GAUSSIAN\11-Feb-2013\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt ground state triplet\\
0,3\C,0.0404735637,0.0000082741,-0.020501511\C,0.0286733816,0.00000010
3,1.3861364727\C,1.204964901,-0.0000081731,2.1575688517\C,2.4577286877
,-0.0000043397,1.465181558\C,2.4953348651,-0.0000000429,0.0673517543\C
,1.3120354642,0.0000042637,-0.6777287358\N,1.3177246857,0.0000031421,-
2.0836352989\N,-1.1543424238,0.0000189818,-0.6760842086\C,-1.111765592
,0.0000272431,-2.0357523076\C,0.108074802,0.0000192325,-2.7894160463\H
,3.4491899859,-0.0000000066,-0.4426207756\C,-2.3366650235,0.0000435023
,-2.746532498\C,0.0602026555,0.0000278783,-4.1888519786\C,-2.369955106
2,0.0000517031,-4.1313035844\C,-1.1675472775,0.0000440074,-4.851696402
2\H,-3.2447069616,0.0000488578,-2.1517829874\H,-3.3214216128,0.0000640
8,-4.6553446508\H,-1.1814712132,0.0000506591,-5.9380636402\H,0.9808556
098,0.0000220658,-4.7607783517\N,3.6300179379,-0.0000031656,2.24128948
32\N,1.0865374969,-0.0000186706,3.5152686867\C,3.5450957047,-0.0000191
926,3.6392048899\C,2.2408629226,-0.0000269732,4.2350206728\C,4.6822561
621,-0.0000280312,4.456259812\C,2.1516285586,-0.0000430674,5.648394055
```

```
5\C,4.5515760266,-0.0000440265,5.8453801585\H,5.4472483596,-0.00005082
29,6.4603262717\C,3.2846928312,-0.0000513985,6.4451779366\H,3.19203354
9,-0.0000636429,7.5274541567\H,1.1527188362,-0.0000482119,6.073184012\
H,5.6691906744,-0.000022456,4.0083067987\H,-0.9273194476,0.0000002091,
1.8972518986\C,4.9167224358,0.0000283662,1.602812408\C,5.546042041,-1.
2081914786,1.2926092042\C,5.5460246206,1.2082736047,1.2927034268\C,6.7
982082181,-1.2021879605,0.6793472557\H,5.0504938733,-2.1442422261,1.53
26585622\C,6.7981980579,1.202330345,0.6794408292\H,5.0504680559,2.1443
016998,1.5328235165\C,7.4466622585,0.0000904857,0.3661796828\H,7.27942
31929,-2.1477182085,0.4405439339\H,7.2794046764,2.1478831831,0.4407143
976\C,2.5633063402,-0.000028817,-2.7990287592\C,3.1707894755,1.2081907
105,-3.1500756738\C,3.1707021197,-1.2082743819,-3.1501109346\C,4.37622
01367,1.2021866943,-3.8507521627\H,2.6959411551,2.1442416711,-2.871309
9044\C,4.3761372317,-1.2023316102,-3.8507929288\H,2.6957906755,-2.1443
022692,-2.871375409\C,4.9967962409,-0.0000919055,-4.2160618851\H,4.842
0711956,2.1477167468,-4.1182928371\H,4.841920219,-2.1478846472,-4.1183
671922\C,6.2849620533,-0.0001086651,-5.0056927252\H,6.0871529149,0.000
7546164,-6.0858561665\H,6.8899735182,0.885857294,-4.7863435044\H,6.889
1778621,-0.8869203187,-4.787594629\C,8.8187525738,0.0001062186,-0.2664
783538\H,8.9729757487,0.8869293926,-0.890047236\H,9.6071362788,-0.0007
818547,0.4979381619\H,8.9723587036,-0.8858481868,-0.8914413374\\Versio
n=IA32L-G03RevD.02\State=3-A\HF=-1452.8638892\S2=2.049827\S2-1=0.\S2A=
2.001619\RMSD=3.567e-09\RMSF=2.987e-05\Thermal=0.\Dipole=2.9812111,-0.
0000015,-1.5938854\PG=C01 [X(C32H24N4)]\\@
```

Table 113. Computational output parameters for singlet 2,10-di-trifluoromethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91i** (R = Tolyl, Y = CF_3).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H22F6N4\GAUSSIAN\12-Feb-2013\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\tolyl Y:CF3        \\0,1\C,
-0.0463985418,0.0006887268,0.0249288306\C,-0.0344922715,0.0000004849,1
.425616129\C,1.138845764,-0.0006866014,2.1906942494\C,2.4121205965,0.0
014982056,1.4694197387\C,2.4397346712,0.0000028869,0.0715621084\C,1.24
747628,-0.0014936131,-0.6587038795\N,1.2467669761,-0.0048096958,-2.028
55656\N,-1.2068629839,0.0033919041,-0.6512885022\C,-1.1673187935,0.002
8799322,-2.004697114\C,0.0434686145,-0.0029694897,-2.7570860822\H,3.38
73088161,0.0000037628,-0.4470106188\C,-2.3879651536,0.0078115934,-2.72
```

```
62603436\C,0.0195095985,-0.008652466,-4.1597669719\C,-2.3994216233,0.0
037522964,-4.108136282\C,-1.1921717216,-0.0059416081,-4.8334153483\H,-
3.3052076986,0.0116595349,-2.149473956\H,0.9462953174,-0.01776216,-4.7
209552836\N,3.5655233688,0.0048148728,2.208445394\N,1.0828468968,-0.00
33913242,3.5326375178\C,3.5304955543,0.0029729737,3.6146656016\C,2.244
0982525,-0.0028786446,4.2288946\C,4.6990156043,0.0086563914,4.39097005
71\C,2.1938513863,-0.0078119111,5.645971265\C,4.6132441837,0.005943908
5,5.7746669254\C,3.3515876444,-0.0037521004,6.4005301591\H,1.213596092
5,-0.0116614895,6.1076161204\H,5.6712774187,0.0177677471,3.9128790348\
H,-0.984832624,-0.0000004967,1.9457026939\H,-1.2088163348,-0.017018479
4,-5.9179550416\H,5.5177464807,0.0170211448,6.3733145499\C,-3.69500862
66,0.0513348263,-4.8691183406\C,3.2941448263,-0.0513363289,7.901975976
5\F,-3.7118430032,-0.8554850588,-5.8762042233\F,-3.8893604921,1.263253
7556,-5.4444220014\F,2.0585002603,0.1936871095,8.3833589165\F,3.673939
9032,-1.2632554582,8.3757925721\F,-4.7665449168,-0.1936902185,-4.08786
53625\F,4.1333070644,0.8554836704,8.4590324416\C,2.4981120158,-0.00901
28744,-2.7516181194\C,3.0972195458,1.1991684874,-3.1101011745\C,3.0952
336703,-1.2212903001,-3.0994523592\C,4.2975005506,1.1875939213,-3.8193
645703\H,2.6238852225,2.1367353964,-2.8343027086\C,4.2954885509,-1.217
8957863,-3.8088731528\H,2.6203952331,-2.1556421731,-2.8154374518\C,4.9
142423974,-0.0172876499,-4.183570536\H,4.7608647953,2.1314506643,-4.09
57178464\H,4.7572944782,-2.1648888689,-4.0769748191\C,4.8490819396,0.0
090202532,1.5442467792\C,5.4739750876,-1.1991605433,1.2328771235\C,5.4
639335946,1.2212982465,1.2288140725\C,6.7183850296,-1.1875841955,0.604
250268\H,4.9865248174,-2.1367280897,1.4828795773\C,6.7084628532,1.2179
055185,0.6002937723\H,4.9687513229,2.1556494836,1.4756575566\C,7.35760
28723,0.0172987766,0.2811171711\H,7.2009289984,-2.1314403089,0.3629409
044\H,7.1832158025,2.1648992311,0.3558525372\C,6.1959042871,-0.0217887
886,-4.9830265585\H,6.8003737251,-0.9087159685,-4.7669915823\H,5.98774
00899,-0.0245958898,-6.0610261484\H,6.8033019782,0.8644053355,-4.77222
98624\C,8.7218485901,0.021799647,-0.3674356574\H,8.8657713745,0.908778
5561,-0.992934002\H,9.517602953,0.0244987339,0.3889974416\H,8.87168296
74,-0.8643430485,-0.9927425539\\Version=IA32L-G03RevD.02\State=1-A\HF=
-2126.9570439\S2=0.\S2-1=0.\S2A=0.\RMSD=3.489e-09\RMSF=1.677e-06\Therm
al=0.\Dipole=4.8002309,-0.0000006,-2.6269914\PG=C01 [X(C34H22F6N4)]\\@
```

Table 114. Computational output parameters for triplet 2,10-di-trifluoromethyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91i**
(R = Tolyl, Y = CF_3).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H22F6N4(3)\GAUSSIAN\10-Feb-201
3\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\tolyl Y:CF3 triplet\\0,3
\C,0.,0.,0.\C,0.0000000469,0.0000000259,1.4067397257\C,1.1848538427,0.
,2.1650520809\C,2.4306435219,0.0012429878,1.4602598964\C,2.4557970703,
0.0000020739,0.0627717134\C,1.2651762296,-0.0012388684,-0.6693676455\N
,1.2574244331,-0.0037604077,-2.0762699506\N,-1.1999996976,0.0012427149
,-0.6441392713\C,-1.1681871501,0.000509434,-2.0039240328\C,0.044859207
5,-0.003928106,-2.7671765994\H,3.4045810487,0.0000038737,-0.4564630988
\C,-2.3995612008,0.0023282151,-2.6997478808\C,-0.0166892347,-0.0112602
147,-4.1681067285\C,-2.4417717954,-0.0040965463,-4.0849019232\C,-1.245
3496529,-0.0120239503,-4.819482335\H,-3.304617272,0.0036990977,-2.1036
555705\H,0.8973866388,-0.0199331537,-4.7495087853\N,3.6114557186,0.003
7655172,2.2251891332\N,1.0805247926,-0.0012438157,3.5230027875\C,3.539
7447443,0.0039311315,3.6189331847\C,2.2429787484,-0.0005095268,4.22920
9156\C,4.6865277872,0.0112651522,4.4259552327\C,2.1652699643,-0.002329
4168,5.6414473177\C,4.5728430479,0.0120277547,5.8119472657\C,3.3091885
363,0.0040972786,6.4236757321\H,1.1753225814,-0.0037028948,6.082419969
5\H,5.6689623548,0.019940696,3.9694653285\H,-0.9509059433,-0.000000767
1,1.9271358421\H,-1.27622815,-0.0255360673,-5.9041459596\H,5.469776350
3,0.0255416067,6.4226496286\C,-3.7506824548,0.0446642826,-4.8195618606
\C,3.2223931561,-0.0446647282,7.9221545559\F,-3.7604568036,-0.80650637
89,-5.8740124329\F,-3.9979447039,1.2784224276,-5.3243154092\F,1.993587
8698,0.276320976 5,8.3781446201\F,3.5142457643,-1.2784228366,8.40250543
19\F,-4.7971442913,-0.2763243433,-4.0303814202\F,4.1052546459,0.806506
6704,8.4987964572\C,2.4977294689,-0.0053386319,-2.8044590883\C,3.09871
45175,1.2028840975,-3.1656433568\C,3.1016800928,-1.2148995378,-3.15611
0055\C,4.2964440538,1.1951426365,-3.8793064416\H,2.6259348141,2.139738
6286,-2.8859779564\C,4.2993872736,-1.2098014967,-3.8698743826\H,2.6312
181227,-2.1507082419,-2.869123301\C,4.9143211179,-0.0080363072,-4.2467
973244\H,4.7577434945,2.14010885,-4.1560023268\H,4.7630254179,-2.15576
20485,-4.1391523139\C,4.8933828306,0.0053468703,1.5730528373\C,5.52156
2464,-1.2028758064,1.2615567908\C,5.5151303351,1.2149078046,1.25392744
7\C,6.768301872,-1.195133278,0.6374502511\H,5.0311535392,-2.1397311381
,1.5090058912\C,6.7619448184,1.2098108227,0.6298955785\H,5.0198055728,
2.1507156805,1.4954838809\C,7.4108997605,0.0080477226,0.3151327019\H,7
.250020716,-2.1400986828,0.3980632872\H,7.2386772633,2.1557731592,0.38
```

```
4545352\C,6.1929866817,-0.0095569093,-5.0513247707\H,6.8007010425,-0.8
948264248,-4.8372722379\H,5.9813932987,-0.0132147915,-6.1287605375\H,6
.7991203922,0.8781731083,-4.8430344209\C,8.7778015183,0.0095665538,-0.
3281609993\H,8.9251510242,0.8948992703,-0.955307839\H,9.5712325585,0.0
130949284,0.4308556966\H,8.9290577335,-0.8781003833,-0.9510694167\\Ver
sion=IA32L-G03RevD.02\State=3-A\HF=-2126.9406449\S2=2.049525\S2-1=0.\S
2A=2.001593\RMSD=4.696e-09\RMSF=1.630e-06\Thermal=0.\Dipole=0.0000019,
-4.6937539,0.0000057\PG=C01 [X(C34H22F6N4)]\\@
```

Table 115. Computational output parameters for singlet 2,10-di-cyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91g** (R = Tolyl, Y = C≡N).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C34H22N6\GAUSSIAN\11-Feb-2013\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt singlet tolyl Y:CN tight\
\0,1\C,-0.0415602619,0.0000117396,0.0228294954\C,-0.0295482565,-0.0000
005068,1.4232080945\C,1.1444914499,-0.0000128555,2.1866445441\C,2.4176
18246,-0.0000056843,1.464509532\C,2.444892208,-0.0000005006,0.06689331
07\C,1.2520478796,0.0000045482,-0.6619396403\N,1.2509354488,0.00000048
27,-2.0322020365\N,-1.2019226386,0.0000261483,-0.6528443207\C,-1.16305
92473,0.0000319012,-2.0059032234\C,0.0490073736,0.0000177032,-2.759655
8644\H,3.3921443514,-0.0000002738,-0.4523238739\C,-2.3824588198,0.0000
516203,-2.7245758356\C,0.0263646432,0.0000221838,-4.1626118866\C,-2.39
63151061,0.0000563288,-4.1153399818\C,-1.1819318169,0.0000416388,-4.84
04468068\H,-3.3019221611,0.0000623121,-2.1502810323\H,0.9538982739,0.0
000111539,-4.7223896946\N,3.5721336468,-0.0000011629,2.2025572832\N,1.
0898780555,-0.0000267418,3.5282828961\C,3.5388106282,-0.0000179568,3.6
070891642\C,2.2513955299,-0.0000320928,4.2233771614\C,4.70930446,-0.00
00220954,4.3808736777\C,2.2012715519,-0.0000512402,5.6379135568\C,4.63
07275711,-0.0000410642,5.7640823399\C,3.3662143214,-0.0000555562,6.397
7328096\H,1.2225382135,-0.000061802,6.104077068\H,5.68014144,-0.000011
1565,3.9000978165\H,-0.9795089963,-0.0000003515,1.9439100086\C,-3.6428
036089,0.0000763394,-4.8247976201\N,-4.6471204285,0.0000925474,-5.4122
902037\C,3.2937501944,-0.0000749595,7.830147783\N,3.2487431546,-0.0000
906679,8.9928060349\H,-1.2009159986,0.0000458147,-5.9245174777\H,5.534
3731684,-0.000044976,6.3632436444\C,2.5030576587,-0.0000328981,-2.7558
433209\C,3.1005189582,1.2105184907,-3.1088536761\C,3.1004412161,-1.210
6108572,-3.1088642094\C,4.3002988939,1.2027894295,-3.8190115896\H,2.62
6888014,2.1466717903,-2.8287041016\C,4.3002270161,-1.2029467725,-3.819
0274073\H,2.6267550371,-2.1467396945,-2.8287264984\C,4.9176610804,-0.0
```

```
000996604,-4.1890584969\H,4.7626508282,2.1481836577,-4.0915497405\H,4.
7625185118,-2.1483652133,-4.0915796673\C,4.8557124948,0.0000323846,1.5
363050304\C,5.4746899509,-1.2105192083,1.2225479994\C,5.4746574711,1.2
106101626,1.2226208718\C,6.7187455924,-1.2027901508,0.5931665328\H,4.9
837451193,-2.146672458,1.4711105341\C,6.7187211957,1.202946056,0.59323
71344\H,4.9836936293,2.146739032,1.4712374252\C,7.3627906714,0.0000992
168,0.271799399\H,7.1972060353,-2.1481844274,0.3500164634\H,7.19716168
65,2.1483644532,0.3501469371\C,6.1983603521,-0.0001149429,-4.989850105
4\H,5.9884853825,0.0008650244,-6.0674822595\H,6.8048784567,0.886032678
6,-4.7766421308\H,6.8039727325,-0.8872132613,-4.7780535855\C,8.7267788
22,0.0001131697,-0.3770412198\H,9.522310241,-0.000933196,0.3795750546\
H,8.8732887955,-0.8860031737,-1.0030704152\H,8.8740410528,0.8872426702
,-1.0014466994\\Version=IA32L-G03RevD.02\State=1-A\HF=-1637.3687879\S2
=0.\S2-1=0.\S2A=0.\RMSD=1.536e-09\RMSF=4.144e-05\Thermal=0.\Dipole=5.6
846771,-0.0000039,-3.1159412\PG=C01 [X(C34H22N6)]\\@
```

Table 116. Computational output parameters for triplet 2,10-di-cyano-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91g** (R = Tolyl, Y = C≡N).

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C34H22N6(3)\GAUSSIAN\26-Nov-2008\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt NEW\\0,3\C,0.,0.,0.\C,
0.0000000189,0.,1.4070353945\C,1.1861148052,0.,2.1639238413\C,2.431678
0282,0.,1.4578491393\C,2.456391636,-0.0000778749,0.0606097011\C,1.2652
39614,0.0000292202,-0.670175407\N,1.2561976623,0.0000423028,-2.0774478
393\N,-1.1989423177,0.,-0.6429942021\C,-1.1682761113,0.,-2.0038422501\
C,0.0464688514,0.00015061,-2.7672957736\H,3.4047682375,-0.0002836312,-
0.4592254171\C,-2.3977804631,0.,-2.6959169751\C,-0.0138133395,0.000358
5753,-4.1692481975\C,-2.4432184113,0.0001003001,-4.0907729087\C,-1.238
9471235,0.0003696317,-4.8240666971\H,-3.3049596796,-0.0000715773,-2.10
22267879\H,0.9009429702,0.0004398714,-4.7493645493\N,3.6131287333,0.,2
.2224874113\N,1.0832029016,0.,3.520505341\C,3.5439120798,0.,3.61336677
43\C,2.2468786432,0.,4.2266969542\C,4.6933138547,0.0001915974,4.418337
3216\C,2.1689016619,0.,5.6354433724\C,4.5862796143,0.0000923506,5.8033
590608\C,3.3203068509,0.000100232,6.4240838313\H,1.1804270164,-0.00007
40968,6.0808219066\H,5.6744201096,0.0003459533,3.959270561\H,-0.950517
0599,0.,1.9280437743\C,-3.6995284571,0.0000988821,-4.7785787213\N,-4.7
149083399,0.0000907843,-5.3474204327\C,3.2243112043,0.0000988149,7.853
1321293\N,3.1576335899,0.0000895345,9.015083632\H,-1.2714605663,0.0005
315014,-5.9084339064\H,5.4829001848,0.000242771,6.4140830836\C,2.49784
```

```
33365,0.0001631074,-2.8056115324\C,3.1005823569,1.2097930587,-3.159524
9826\C,3.0991332489,-1.2087709352,-3.1623572027\C,4.2989085446,1.20343
40958,-3.871707642\H,2.6291259969,2.1461002347,-2.8757723697\C,4.29782
24056,-1.20177379,-3.8748994258\H,2.6269310339,-2.1454126628,-2.880984
6023\C,4.9152517226,0.00072367,-4.2446505071\H,4.7619764685,2.14901801
57,-4.1431480609\H,4.7598646833,-2.1470508146,-4.1488347281\C,4.894881
7461,0.0001216354,1.5674968163\C,5.5190610089,-1.2088125272,1.25250953
1\C,5.5174649946,1.2097515006,1.2497872571\C,6.7645385526,-1.201815633
9,0.6253270969\H,5.0278500666,-2.1454551558,1.4992026282\C,6.762443626
3,1.2033922873,0.6227163803\H,5.0246577584,2.1460578095,1.4945881387\C
,7.4083745991,0.0006806688,0.3037524001\H,7.2440052515,-2.1470927489,0
.3831801788\H,7.240368668,2.1489751456,0.3783792828\C,6.1952265293,0.0
024039627,-5.0468885101\H,5.9861306331,0.0672385203,-6.1227828135\H,6.
829582271,0.856826773,-4.7885809528\H,6.7728923032,-0.9128199295,-4.88
25381228\C,8.7731911355,0.0023623092,-0.3437041443\H,8.9454002297,-0.9
128729955,-0.9190569206\H,9.5676770298,0.0672227937,0.4113179768\H,8.8
966704882,0.856769875,-1.0174288022\\Version=AM64L-G03RevD.02\State=3-
A\HF=-1637.3528705\S2=2.049804\S2-1=0.\S2A=2.001608\RMSD=8.755e-09\RMS
F=3.128e-06\Thermal=0.\Dipole=-0.0000008,5.7576729,-0.0053491\PG=C01 [
X(C34H22N6)]\\@
```

Table 117. Computational output parameters for singlet 3,9-di-methyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91d** (R = Tolyl, X = Me).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H28N4\GAUSSIAN\10-Feb-2013\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\linear tetraazapentacene toly
l X:CH3 singlet\\0,1\C,-0.0468302898,-0.0000247128,0.0242109973\C,-0.0
35479689,-0.0000449203,1.4258591692\C,1.1362683593,-0.0000483254,2.195
1140544\C,2.4096240616,-0.0000269023,1.4760929443\C,2.4384351224,-0.00
00199022,0.0776252227\C,1.2475915518,-0.0000188033,-0.656155212\N,1.24
96665987,-0.0000118411,-2.0266026645\N,-1.2063770652,-0.0000107574,-0.
6547883031\C,-1.1635251963,0.0000132623,-2.0094599955\C,0.0463886309,0
.0000129479,-2.7602184527\H,3.3869936489,-0.0000093654,-0.4393201567\C
,-2.3766641916,0.0000382908,-2.7448290364\C,0.0274664923,0.0000388847,
-4.1627705881\C,-2.3823354764,0.0000637072,-4.1248717944\C,-1.17731296
4,0.0000655891,-4.8617328576\H,-3.2980441003,0.0000366854,-2.170942163
\H,-3.3306332534,0.0000829021,-4.6581311195\H,0.9611997849,0.000038804
4,-4.7145915271\N,3.5624289438,-0.000011589,2.2171539958\N,1.078384316
,-0.0000641923,3.5375886437\C,3.5267399091,-0.0000458013,3.6259820242\
```

```
C,2.2400334387,-0.0000668919,4.2358315438\C,4.6951436006,0.0000159498,
4.4020896053\C,2.2004728751,-0.0000118914,5.6538965577\C,4.6295189539,
0.0000246405,5.7933967641\C,3.3571427994,0.0000512646,6.4066682316\H,3
.2912841052,0.0001437144,7.4926225365\H,1.2187938263,0.000497571,6.11
71387305\H,-0.9868647596,-0.0000531073,1.9443449766\C,-1.2001863519,0.
0001015377,-6.3714497597\H,-1.7221119341,0.8815057497,-6.7667023159\H,
-0.1877081334,0.0000455294,-6.7880817761\H,-1.7222276857,-0.8812156061
,-6.7667420963\C,5.8858391038,-0.000349153,6.6309097457\H,6.7847392438
,0.0037308147,6.005884583\H,5.9332108015,0.8787388995,7.2869737976\H,5
.9369730309,-0.8839671307,7.2806418994\C,2.5022711925,-0.0000379214,-2
.743980078\C,3.1036316099,1.2094350428,-3.0946677703\C,3.1035565948,-1
.2095274988,-3.0946953459\C,4.3080377559,1.2024291627,-3.7970423889\H,
2.6278322694,2.1450185045,-2.8165451298\C,4.3079718489,-1.2025712974,-
3.7970760342\H,2.6277065274,-2.1450928656,-2.8165991064\C,4.928106195,
-0.0000900285,-4.1627141917\H,4.772790475,2.1479408328,-4.0659052127\H
,4.7726679341,-2.1481008893,-4.0659674539\C,6.2153155767,-0.0000894594
,-4.9536769155\H,6.0157463991,0.0013055248,-6.0334269959\H,6.820657204
5,0.88567399,-4.7346877207\H,6.8194081957,-0.8871931549,-4.7367110269\
H,5.6649749089,0.0000648974,3.9165059704\C,4.8442220164,0.0000228602,1
.55333543\C,5.4648932535,-1.209445454,1.238071967\C,5.464840954,1.2095
170776,1.2381055475\C,6.7079550166,-1.2024325311,0.606625365\H,4.97329
10863,-2.1450319783,1.4871879394\C,6.7079108534,1.2025679258,0.6066557
346\H,4.9732051425,2.1450793803,1.4872456531\C,7.3513226863,0.00008896
36,0.2837180667\H,7.1858163833,-2.1479413029,0.3618073716\H,7.18573725
48,2.1481004154,0.361866129\C,8.7137108287,0.0001028549,-0.3692969245\
H,9.5129287332,-0.0009337452,0.3836570675\H,8.857921854,-0.885827775,-
0.9964329416\H,8.8586698914,0.8870400924,-0.9948258313\\Version=IA32L-
G03RevD.02\State=1-A\HF=-1531.5159363\S2=0.\S2-1=0.\S2A=0.\RMSD=4.176e
-09\RMSF=9.780e-06\Thermal=0.\Dipole=3.7261533,-0.0001133,-2.0306816\P
G=C01 [X(C34H28N4)]\\@
```

Table 118. Computational output parameters for triplet 3,9-di-methyl-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91d** (R = Tolyl, X = Me).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H28N4(3)\GAUSSIAN\09-Feb-2013\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\linear tetraazapentacene t
olyl X:CH3 triplet\\0,3\C,0.,0.,0.\C,0.0000000123,0.,1.4065234626\C,1.
1819972922,0.,2.1688820096\C,2.4290803953,0.,1.4665013532\C,2.45528321
42,0.,0.0684432555\C,1.2661975451,0.,-0.6673069974\N,1.2617628975,0.,-
```

```
2.0742733186\N,-1.2000891777,0.,-0.6470096196\C,-1.1648151175,0.,-2.00
63383725\C,0.0463225581,0.,-2.7698302768\H,3.4050474934,0.,-0.44915926
88\C,-2.3902223397,0.,-2.7165895242\C,-0.0112050224,0.,-4.1690527927\C
,-2.4275802635,0.,-4.0985876901\C,-1.2344484898,0.,-4.8469676231\H,-3.
2986955498,0.,-2.1223075851\H,-3.3846990926,0.,-4.6148343052\H,0.90963
46021,0.,-4.7418908004\N,3.6090462196,0.,2.2328267073\N,1.0752556295,0
.,3.5280882853\C,3.5347816079,0.,3.6312470548\C,2.2367111309,0.,4.2352
233757\C,4.679462552,0.0000710753,4.4379927414\C,2.1693923581,0.000075
7758,5.6499831885\C,4.586142239,0.0000699252,5.8334096241\C,3.31053126
85,0.0001577153,6.430443941\H,3.2255944409,0.0002741193,7.5145900301\H
,1.1775700638,0.0001301814,6.0913254103\H,-0.9519006128,0.,1.925290252
8\C,-1.2767564136,0.,-6.3560891224\H,-1.8056741395,0.8813513412,-6.741
342558\H,-0.2707588964,-0.0000642308,-6.7871773668\H,-1.8057885046,-0.
8812816642,-6.7413411623\C,5.8314284715,-0.0003584767,6.6869308766\H,6
.7389628318,0.0044440809,6.0751905312\H,5.8662136671,0.8782472057,7.34
40035371\H,5.8707307541,-0.8843647985,7.3365387022\C,2.5023957476,0.,-
2.7975069138\C,3.108344045,1.2080870451,-3.1519000121\C,3.1082868514,-
1.2080799516,-3.1519777742\C,4.3100859036,1.2022121841,-3.8589110868\H
,2.6351178343,2.1440675547,-2.8701685624\C,4.3100337166,-1.2022078127,
-3.8590006348\H,2.6350240614,-2.1440624408,-2.870314624\C,4.9288775603
,-0.0000053786,-4.2273652067\H,4.7747273147,2.1477766815,-4.1285608136
\H,4.7746292907,-2.1477723113,-4.1287250916\C,6.2134301468,0.000021163
,-5.0229459994\H,6.0110001311,0.0014663521,-6.1022782064\H,6.819723962
5,0.8856869972,-4.8058163508\H,6.8184469933,-0.8870209925,-4.807920974
3\H,5.6599673284,0.0001282874,3.9746360998\C,4.8892717634,0.,1.5822429
242\C,5.5155330441,-1.2080864724,1.2651329532\C,5.5155533307,1.2080805
314,1.2651789833\C,6.7610470609,-1.2022154058,0.6384385482\H,5.0222868
598,-2.1440662994,1.510130349\C,6.7610785525,1.202205598,0.638486393\H
,5.0223286966,2.144063702,1.5102102687\C,7.40607151,-0.0000009323,0.31
81116907\H,7.239503988,-2.1477805212,0.3941427031\H,7.2395564594,2.147
7684765,0.3942316642\C,8.770900535,-0.0000232377,-0.3301674761\H,9.568
2168965,-0.0011158541,0.424964714\H,8.9171839829,-0.8858592737,-0.9570
925217\H,8.9179995598,0.8868497229,-0.9554236165\\Version=IA32L-G03Rev
D.02\State=3-A\HF=-1531.5004048\S2=2.049038\S2-1=0.\S2A=2.001567\RMSD=
8.730e-09\RMSF=2.868e-05\Thermal=0.\Dipole=-0.0000031,-3.4090386,0.000
2045\PG=C01 [X(C34H28N4)]\\@
```

Table 119. Computational output parameters for singlet 3,9-di-fluoro-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91j** (R = Tolyl, X = F).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C32H22F2N4\GAUSSIAN\09-Feb-2013\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\linear tetraazapentacene to
lyl X:F singlet\\0,1\C,-0.0402769015,0.000015473,0.0209101414\C,-0.028
7826474,0.0000004586,1.4224650951\C,1.1437723288,-0.0000144643,2.19032
13475\C,2.4161196073,-0.0000072769,1.4703036999\C,2.4450943961,0.00000
02924,0.0722405816\C,1.253583971,0.0000081272,-0.6596903747\N,1.257022
3664,0.0000058522,-2.0308095017\N,-1.1992548663,0.000031878,-0.6587355
228\C,-1.1581740749,0.0000397575,-2.0133788612\C,0.0559242321,0.000025
4769,-2.7627289009\H,3.3933786803,-0.0000000446,-0.4453262601\C,-2.375
3385454,0.0000618477,-2.7426607021\C,0.0437317472,0.0000322512,-4.1646
077839\C,-2.3955784465,0.0000690003,-4.1251704498\C,-1.1783822076,0.00
00540947,-4.8135563396\H,-3.2934482478,0.0000724213,-2.16462654\H,-3.3
25527803,0.0000857313,-4.6840860391\H,0.955573925,0.0000215482,-4.7479
953257\N,3.5711546343,-0.0000055933,2.2091362538\N,1.0884220226,-0.000
0313557,3.5327387598\C,3.536983531,-0.0000255701,3.6152568192\C,2.2499
632897,-0.000039727,4.2309995178\C,4.7094332256,-0.000032798,4.3838755
561\C,2.2048825791,-0.0000622973,5.6492058131\C,4.5941110095,-0.000055
019,5.7627872707\C,3.3566885805,-0.0000699244,6.4141148147\H,3.3236946
3,-0.0000870273,7.4985980265\H,1.222065775,-0.0000728559,6.1086838138\
H,5.6933619631,-0.0000221913,3.9325647865\H,-0.979796549,0.000000345,1
.9415217233\F,-1.1915579994,0.000061687,-6.1662696273\F,5.7246782152,-
0.0000630352,6.5056362562\C,4.8542988857,0.0000287463,1.5460516753\C,5
.4754774247,-1.2099021148,1.2336758218\C,5.4754469659,1.2099872039,1.2
337559694\C,6.7210508784,-1.2025894485,0.6073163051\H,4.9833816012,-2.
1457320579,1.4809791669\C,6.721028038,1.2027413599,0.6073944584\H,4.98
33333895,2.1457919001,1.481119276\C,7.3658026763,0.0000974283,0.287403
0003\H,7.2001684051,-2.1480216421,0.3651277731\H,7.2001271238,2.148198
4706,0.3652716444\C,2.508840629,-0.0000288025,-2.7512894743\C,3.107598
5413,1.2099022725,-3.1047449865\C,3.1075130101,-1.209987055,-3.1047644
376\C,4.3082046449,1.2025895399,-3.8134928927\H,2.6333998018,2.1457321
976,-2.8246506254\C,4.3081254078,-1.2027412667,-3.8135180504\H,2.63325
34394,-2.1457917798,-2.8246891249\C,4.9260527562,-0.0000977073,-4.1826
990259\H,4.7710817731,2.1480217518,-4.085437231\H,4.7709361501,-2.1481
98361,-4.0854840982\C,8.7314558242,0.0001141084,-0.3583213971\H,8.8799
035344,0.8871204488,-0.9828085854\H,9.5258188265,-0.0008653667,0.39963
84672\H,8.8792065376,-0.8859380269,-0.9843360151\C,6.2079045166,-0.000
1128923,-4.9819640526\H,6.8133972087,-0.8871564386,-4.7690484136\H,6.0
```

```
001458272,0.0009455292,-6.0600883019\H,6.8143743401,0.885901898,-4.767
521517\\Version=IA32L-G03RevD.02\State=1-A\HF=-1651.3452841\S2=0.\S2-1
=0.\S2A=0.\RMSD=2.033e-09\RMSF=3.947e-05\Thermal=0.\Dipole=3.3892373,0
.0000036,-1.8498216\PG=C01 [X(C32H22F2N4)]\\@
```

Table 120. Computational output parameters for triplet 3,9-di-fluoro-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91j** (R = Tolyl, X = F).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C32H22F2N4(3)\GAUSSIAN\09-Feb-201
3\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\linear tetraazapentacene
 tolyl X:F triplet\\0,3\C,0.,-0.0000001247,0.\C,-0.0000000509,-0.00000
01299,1.4067557067\C,1.1831471113,-0.00000005,2.1677582926\C,2.4297066
525,0.0000000329,1.4639992985\C,2.4557820513,0.0000000466,0.0664073362
\C,1.266236357,-0.0000000338,-0.6677071961\N,1.2615219679,-0.000000028
9,-2.075419312\N,-1.1989860891,-0.000000206,-0.6461659462\C,-1.1665306
813,-0.0000001988,-2.0066781947\C,0.0494409069,-0.000000111,-2.7688828
59\H,3.4052385291,0.0000001148,-0.4517992432\C,-2.3952024606,-0.000000
282,-2.7093590697\C,-0.002564644,-0.0000001095,-4.1669656883\C,-2.4487
001009,-0.0000002806,-4.0945332525\C,-1.2430477707,-0.0000001938,-4.79
39905875\H,-3.3000452985,-0.0000003474,-2.1106138194\H,-3.3880684445,-
0.0000003442,-4.6363768807\H,0.8949572848,-0.0000000446,-4.7720357008\
N,3.6111077611,0.0000001193,2.2294841431\N,1.0779959331,-0.0000000624,
3.5257131157\C,3.5386521747,0.0000001091,3.6240386876\C,2.2398072319,0
.0000000161,4.2344030607\C,4.6863718479,0.0000001863,4.4240885152\C,2.
1661280091,0.0000000058,5.6478978776\C,4.5426733272,0.0000001712,5.806
5888108\C,3.3021837447,0.0000000822,6.4422195251\H,3.2497370493,0.0000
000745,7.5253887726\H,1.1730699895,-0.0000000652,6.0850134636\H,5.6807
89829,0.0000002574,3.9965511347\H,-0.9515219232,-0.0000001982,1.926089
5636\F,-1.2712286412,-0.0000001908,-6.1435960097\F,5.6625099902,0.0000
002466,6.5603773807\C,4.8930826919,0.0000002112,1.5800595666\C,5.51986
49938,-1.2085880007,1.2664656995\C,5.5198826439,1.2085800032,1.2665084
716\C,6.7684030683,-1.2023940005,0.6459404284\H,5.02606431,-2.14476300
22,1.5096129566\C,6.7684282225,1.2023850029,0.6459802444\H,5.026100405
,2.1447580009,1.509683257\C,7.4150618006,-0.0000009993,0.3292530196\H,
7.2484796219,-2.1478600025,0.4049793575\H,7.2485225819,2.1478480035,0.
4050538859\C,2.501218957,0.0000000604,-2.802305396\C,3.1040337109,1.20
8587996,-3.1598146081\C,3.1040044912,-1.2085799982,-3.1598556227\C,4.3
013365441,1.2023939959,-3.8742108293\H,2.6324078511,2.1447629982,-2.87
60366219\C,4.301314271,-1.2023849983,-3.874257914\H,2.6323639378,-2.14
```

```
47579991,-2.8761129086\C,4.9175022486,0.0000002344,-4.2467674649\H,4.7
637005118,2.1478599927,-4.1476248364\H,4.7636562826,-2.147847998,-4.14
77100647\C,8.7839389842,-0.0000219996,-0.3100245106\H,8.9353449547,0.8
869149997,-0.9340322784\H,9.5753656858,-0.0010249996,0.451137263\H,8.9
346064044,-0.886011003,-0.9355670489\C,6.1956759814,0.0000239994,-5.05
22315628\H,6.8023648646,-0.886953004,-4.8420651989\H,5.9836358684,0.00
11079992,-6.1296184222\H,6.8033270445,0.885972997,-4.8404964126\\Versi
on=IA32L-G03RevD.02\State=3-A\HF=-1651.3314373\S2=2.04845\S2-1=0.\S2A=
2.001519\RMSD=7.608e-09\RMSF=2.478e-05\Thermal=0.\Dipole=-0.0000006,-3
.030868,-0.0000217\PG=C01 [X(C32H22F2N4)]\\@
```

Table 121. Computational output parameters for singlet 3,9-di-methoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91b** (R = Tolyl, X = OMe).

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C34H28N4O2\GAUSSIAN\11-Feb-2013\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\XOMe singlet\\0,1\C,-0.0520
60719,-0.0001241823,0.026683531\C,-0.0408628334,-0.0000000454,1.428826
3874\C,1.1307864331,0.0001244507,2.1991301834\C,2.4030145186,-0.000147
8039,1.4804232705\C,2.4325327388,0.0000003679,0.0821194671\C,1.2420127
433,0.0001484988,-0.6519016415\N,1.2491199193,0.0006514567,-2.02379908
11\N,-1.210266386,-0.0003614088,-0.655251467\C,-1.1653359382,-0.000308
4383,-2.0101693904\C,0.0490982151,0.0002627979,-2.7605384074\H,3.38132
80888,0.0000000419,-0.4344777187\C,-2.3719360629,-0.0007688197,-2.7488
108563\C,0.0394227936,0.0003501854,-4.1570698359\C,-2.3893847875,-0.00
06960495,-4.133852452\C,-1.1745219058,-0.0001389155,-4.8453990488\H,-3
.2957589523,-0.0011833081,-2.1792393821\H,-3.3398648891,-0.0010657299,
-4.6551475522\H,0.9567504949,0.0007753583,-4.7324631914\N,3.5591927849
,-0.00065132,2.2189385406\N,1.0750546067,0.0003607067,3.542026175\C,3.
526801485,-0.0002636221,3.6266983608\C,2.2374964706,0.000307175,4.2395
576651\C,4.6945636585,-0.0003516297,4.3926782349\C,2.2031329699,0.0007
662886,5.6538752524\C,4.6139548417,0.0001363199,5.7858619993\C,3.35702
59506,0.0006928576,6.4201491008\H,3.2790911565,0.0010615225,7.50139244
18\H,1.2233938071,0.0011802723,6.1207494854\H,5.6756681698,-0.00077662
06,3.9344189868\H,-0.9924948062,-0.0000004519,1.9469680732\O,-1.074121
9401,-0.0000520602,-6.2117274095\O,5.8160824173,0.0000489087,6.4429941
102\C,-2.271159273,-0.0005863672,-6.9696463953\H,-1.9626312775,-0.0004
358238,-8.0170712769\H,-2.8770870116,-0.8952088103,-6.7720302902\H,-2.
8778954354,0.8934839967,-6.772013721\C,5.8031004125,0.0005813904,7.859
7407421\H,6.8503103448,0.0004304903,8.1689975458\H,5.3082956253,0.8952
```

```
032803,8.26144929\H,5.3078430988,-0.8934895165,8.2621169979\C,4.840504
7595,-0.0020087876,1.5542939486\C,5.4605425631,-1.211995709,1.24076292
17\C,5.4623831402,1.2069707719,1.2388331504\C,6.7042312908,-1.20630697
85,0.6102871281\H,4.9684184221,-2.1471035058,1.4905701345\C,6.70571292
87,1.1986966378,0.6085028563\H,4.9713900777,2.1430450457,1.4872592041\
C,7.3486188212,-0.0046879376,0.2872162278\H,7.1819368999,-2.1522854512
,0.367158906\H,7.1846090654,2.1437217905,0.3637757403\C,2.5027135007,0
.0020098029,-2.7393519562\C,3.1025381474,1.211998497,-3.0900054743\C,3
.1051579108,-1.20696799,-3.0905072941\C,4.3070148927,1.2063115899,-3.7
924967839\H,2.62565228,2.1471053946,-2.8122080447\C,4.3093194926,-1.19
86920392,-3.7927773587\H,2.6300475981,-2.1430431594,-2.8129137404\C,4.
9280674302,0.0046922444,-4.1584292458\H,4.7704657299,2.1522908826,-4.0
618034836\H,4.7747600421,-2.1437163385,-4.0622197744\C,8.7120528797,-0
.0051310678,-0.3635036355\H,8.8406355563,0.8571457579,-1.0262562931\H,
9.5092300631,0.042798685,0.3900625241\H,8.8752857909,-0.9138428783,-0.
9519931843\C,6.2145301377,0.005143191,-4.950516718\H,6.014170009,-0.04
25040768,-6.0290511601\H,6.7975362161,0.9137336711,-4.7680584035\H,6.8
408662162,-0.8572773685,-4.6990651897\\Version=IA32L-G03RevD.02\State=
1-A\HF=-1681.9222625\S2=0.\S2-1=0.\S2A=0.\RMSD=9.860e-09\RMSF=4.117e-0
5\Thermal=0.\Dipole=3.0948165,0.0000135,-1.685056\PG=C01 [X(C34H28N4O2
)]\\@
```

Table 122. Computational output parameters for triplet 3,9-di-methoxy-5,7-di-*p*-tolyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **TAP 91b** (R = Tolyl, X = OMe).

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C34H28N4O2(3)\GAUSSIAN\05-Dec-200
8\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\XOMe trplet (from .log f
ile of BS singlet)\\0,3\C,0.,0.,0.\C,0.0000000259,0.,1.4065781676\C,1.
1814509102,0.,2.169882305\C,2.4291459146,-0.0002034638,1.4674065983\C,
2.4555324551,0.000002089,0.0695972616\C,1.2671267893,0.0002057204,-0.6
667868005\N,1.265000489,0.0006931187,-2.0743089701\N,-1.1979878442,-0.
0001362566,-0.6485270056\C,-1.1623291045,-0.000196846,-2.0083757925\C,
0.0535870947,0.000229853,-2.7731152732\H,3.4055589169,0.0000017644,-0.
447670287\C,-2.3817900832,-0.0006139177,-2.7195722297\C,0.0027784621,0
.0001742208,-4.164860382\C,-2.4345857319,-0.0007034958,-4.1070347816\C
,-1.2319965941,-0.0002967518,-4.8309674273\H,-3.2915938701,-0.00086590
62,-2.1276694998\H,-3.3944889388,-0.0010287761,-4.6095836619\H,0.90515
92364,0.0004895732,-4.7633322501\N,3.610236861,-0.0006898668,2.2330108
26\N,1.0760695917,0.0001350504,3.528063784\C,3.539801402,-0.0002287706
```

```
,3.6297531545\C,2.2376216681,0.0001956662,4.2360588709\C,4.6812216215,
-0.0001722924,4.4276853869\C,2.1732270569,0.0006115646,5.6462862334\C,
4.5706433614,0.0002964374,5.8263063097\C,3.3099709894,0.0007010844,6.4
435639287\H,3.2111762067,0.0010254411,7.5225483293\H,1.182338036,0.000
8626838,6.089265798\H,5.6735996601,-0.0004852593,3.9945047449\H,-0.952
1588422,-0.0000016118,1.9250067619\O,-1.1496490788,-0.0003027223,-6.19
33053685\O,5.7596218268,0.0003035252,6.4964365519\C,-2.3559469644,-0.0
00765382,-6.9399760409\H,-2.0573388027,-0.0006836665,-7.9899879664\H,-
2.9579009628,-0.8955375316,-6.7341555488\H,-2.958539647,0.8935945784,-
6.7342316367\C,5.732166414,0.0007640597,7.9148574641\H,6.776166137,0.
0006837197,8.2338512121\H,5.2326262178,0.8955348156,8.3087759144\H,5.2
323456432,-0.8935963003,8.3093510445\C,4.8905647554,-0.0024616198,1.58
25437785\C,5.5164344385,-1.2112387145,1.268587524\C,5.5179500151,1.204
9109651,1.2645026543\C,6.7628774289,-1.2070518385,0.6434396527\H,5.022
6227183,-2.1465482538,1.5148961138\C,6.7639857766,1.1973728716,0.63941
19296\H,5.0250128073,2.1414799582,1.5077744438\C,7.4087759098,-0.00592
15001,0.3220177424\H,7.2414634676,-2.1532206929,0.401888895\H,7.243462
1845,2.1422886146,0.3945085006\C,2.5061519658,0.0024681398,-2.79673047
23\C,3.1094988273,1.2112483143,-3.1520451903\C,3.1137515726,-1.2049013
573,-3.1511158412\C,4.3109945028,1.2070665814,-3.8597423722\H,2.634635
339,2.1465562131,-2.8709278972\C,4.314979576,-1.1973591222,-3.85850156
29\H,2.6419148672,-2.1414719844,-2.869096161\C,4.9314820629,0.00593639
,-4.2278441714\H,4.7735981598,2.1532360216,-4.1306408828\H,4.780883034
,-2.1422732646,-4.1283413781\C,8.7747832788,-0.0067749353,-0.323713663
1\H,8.9051603007,0.8541027901,-0.9880815803\H,9.569970318,0.0431990859
,0.4319919044\H,8.9406486633,-0.9165308236,-0.9100033623\C,6.215149142
,0.0068013106,-5.024801718\H,6.0119102104,-0.0428777056,-6.1028264005\
H,6.7977419665,0.9164304089,-4.8457388112\H,6.8438113495,-0.8542280737
,-4.7739910329\\Version=AM64L-G03RevD.02\State=3-A\HF=-1681.9105928\S2
=2.04718\S2-1=0.\S2A=2.001431\RMSD=6.157e-09\RMSF=6.255e-07\Thermal=0.
\Dipole=-0.0000007,-2.656387,-0.0000014\PG=C01 [X(C34H28N4O2)]\\@
```

Table 123. Computational output parameters for singlet 5,7-di-methyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide (R = Methyl).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|RB3LYP|6-31G(d)|C20H16N4|GAUSSIAN|29-Oct
-2012|0||# opt rb3lyp/6-31g(d) geom=connectivity||opt ground state sin
glet vinyl||0,1|C,-1.2355710206,1.2570109492,0.0180205523|C,0.00022748
```

```
84,1.9164803553,0.0000370287|C,1.2359845925,1.2569061448,-0.0179547965
|C,1.2201858481,-0.2048525965,0.0266846121|C,0.0001174163,-0.895299639
5,0.0000238741|C,-1.2198972889,-0.2047492797,-0.0265495922|N,-2.417452
1926,-0.8570343659,-0.1159432692|N,-2.3838689664,1.9515397807,0.050947
0094|C,-3.5519786246,1.2673038322,0.0851318698|C,-3.6320581348,-0.1571
369303,0.0218005885|H,0.000068415,-1.973620625,-0.0000472729|C,-4.7668
654159,1.9924302168,0.1878664746|C,-4.8763551109,-0.800973905,0.110423
5925|C,-5.9872891755,1.3482241952,0.2519670435|C,-6.0446082589,-0.0553
450538,0.2227992623|H,-4.6870061796,3.0742364435,0.2215906231|H,-6.903
4400218,1.9265492368,0.3346495232|H,-6.9989135522,-0.5681947895,0.2962
006781|H,-4.9474359467,-1.8825429398,0.1221619438|N,2.4176808349,-0.85
7247347,0.1160773043|N,2.384316057,1.9513292706,-0.0510906221|C,3.6323
681633,-0.1574407197,-0.0216675341|C,3.5523893856,1.2669949841,-0.0852
08842|C,4.8766483389,-0.8013278338,-0.1101443096|C,4.7672914952,1.9920
537634,-0.1880630268|C,6.0449454644,-0.0557631535,-0.2226037962|H,6.99
92255707,-0.5686842438,-0.2958393864|C,5.987699565,1.3477919552,-0.252
0368003|H,6.9038680158,1.9260705405,-0.3348353387|H,4.6874796552,3.073
8575927,-0.2219637411|H,4.9477624856,-1.8828920182,-0.1216655989|H,0.0
002773411,2.9998498224,-0.000021853|C,-2.4425373009,-2.2992168585,-0.3
601467218|H,-1.6200338559,-2.5690122,-1.0237045869|H,-2.3603655743,-2.
8698965197,0.5725860998|H,-3.3709397142,-2.5630790401,-0.8626737628|C,
2.4425547609,-2.2994297341,0.3602376937|H,1.6200354146,-2.5691444088,1
.0238053543|H,2.3602740162,-2.8700750785,-0.5725148507|H,3.3709163399,
-2.5635007129,0.8627153242||Version=IA32W-G09RevC.01|State=1-A|HF=-990
.7646653|RMSD=4.640e-009|RMSF=8.789e-006|Dipole=-0.0000867,-3.2058788,
0.0001035|Quadrupole=5.3499269,2.9531178,-8.3030447,0.000192,0.4182477
,-0.0003822|PG=C01 [X(C20H16N4)]||@
```

Table 124. Computational output parameters for singlet 5,7-di-ethyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide (R = Ethyl).

```
1|1|UNPC-USER-TOSH|FOpt|UB3LYP|6-31G(d)|C22H20N4|USER|13-Feb-2013|0||#
 opt ub3lyp/6-31g(d) geom=connectivity||linear tetraazapentacene singl
et opt ethyl||0,1|C,1.2374568211,-0.7689384388,-0.0013331774|C,0.00183
22256,-1.4227870327,0.0813235332|C,-1.2346396276,-0.7712400857,-0.0066
606541|C,-1.2229227146,0.6775768906,-0.2083177071|C,0.000123657,1.3621
685434,-0.2784663224|C,1.2242798172,0.6799629076,-0.202822931|N,2.4255
653871,1.3238189163,-0.3200268151|N,2.3831276759,-1.4611229288,0.09858
```

```
40575|C,3.5539962116,-0.7834240271,0.0538872315|C,3.6382281659,0.62896
6143,-0.1389815301|H,-0.0010635043,2.4379427505,-0.3410336178|C,4.7661
088425,-1.5050013111,0.2051963021|C,4.8901071579,1.2663864536,-0.14057
26649|C,5.9914234641,-0.8677169873,0.1863520785|C,6.0559853954,0.52574
55506,0.0188724983|H,4.6796884227,-2.5782888694,0.3409604215|H,6.90553
82083,-1.4424935529,0.3074181312|H,7.0147805864,1.0355216512,0.0177981
974|H,4.9719244136,2.3417578671,-0.2475353035|N,-2.424592415,1.3193788
752,-0.3312392768|N,-2.3796087534,-1.4653009643,0.0881607994|C,-3.6368
774007,0.6228516616,-0.1549904798|C,-3.5513830968,-0.78935886,0.038422
9164|C,-4.8894834691,1.2587124793,-0.1619841554|C,-4.7631511466,-1.512
5652545,0.1844261685|C,-6.0550379926,0.5164853101,-0.0075201299|H,-7.0
145182942,1.0249459805,-0.0126491608|C,-5.9892394394,-0.876900108,0.16
01770788|H,-6.9030747269,-1.4529547486,0.2772278229|H,-4.6759361268,-2
.5857340211,0.3206137644|H,-4.9717969985,2.3341530514,-0.2687621505|H,
0.0025095395,-2.4964397622,0.226039048|C,-2.4687086376,2.7554866274,-0
.6537669474|H,-1.619024762,2.977014814,-1.3024109435|H,-3.359490203,2.
9267360887,-1.25968274|C,-2.4689163765,3.6550591088,0.5850971093|H,-3.
333499163,3.4451137668,1.2218009448|H,-1.566120126,3.5041071874,1.1852
176009|H,-2.5105470432,4.7074773947,0.2832671387|C,2.468983797,2.76068
31674,-0.6394823615|H,3.3624714674,2.9349078175,-1.2404680802|H,1.6221
631586,2.9822179584,-1.2918369797|C,2.461420937,3.6575529632,0.6014351
496|H,1.5564208785,3.5027717486,1.1971832977|H,3.3239956289,3.44823281
7,1.2411004785|H,2.5017457786,4.7107554604,0.3022391899||Version=IA32W
-G09RevC.01|State=1-A|HF=-1069.3969984|S2=0.|S2-1=0.|S2A=0.|RMSD=3.873
e-009|RMSF=2.726e-005|Dipole=-0.0011947,3.2922085,-0.368851|Quadrupole
=6.3084063,0.7465019,-7.0549083,0.0090397,0.0356684,-1.9084367|PG=C01
[X(C22H20N4)]||@
```

Table 125. Computational output parameters for singlet 5,7-di-vinyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide (R = Vinyl).

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|RB3LYP|6-31G(d)|C22H16N4|GAUSSIAN|28-Oct
-2012|0||# opt rb3lyp/6-31g(d) geom=connectivity||opt ground state sin
glet vinyl||0,1|C,-1.2354348322,2.6398933779,0.0084805226|C,0.00007737
79,3.3019056646,0.0002120027|C,1.2356791672,2.6400937187,-0.008250449|
C,1.2140285501,1.1798453651,-0.0308361961|C,0.0002578057,0.4848956971,
-0.0002680691|C,-1.2135955538,1.1796556951,0.0308420741|N,-2.409418431
8,0.514183826,0.0768831648|N,-2.3886989843,3.3278161892,-0.0012395066|
```

```
C,-3.556194391,2.6406165199,0.0415617229|C,-3.6357636927,1.2164068203,
0.0991084043|H,0.0004028244,-0.5959588832,-0.0007839103|C,-4.776577953
4,3.3645651717,0.044949017|C,-4.8769473811,0.5712214529,0.193005643|C,
-5.9959383133,2.7201830567,0.123495495|C,-6.0490366355,1.3175570668,0.
2050183954|H,-4.7017755141,4.4460036586,-0.0076622398|H,-6.9159537023,
3.2983821157,0.1280795337|H,-7.0050963477,0.8077660545,0.278271296|H,-
4.9258958551,-0.5088361112,0.2584270068|N,2.4099441041,0.5146052695,-0
.0768575396|N,2.3888646486,3.3281917853,0.0011747244|C,3.6361622105,1.
2169552719,-0.0990786474|C,3.556445135,2.6411620732,-0.0417514119|C,4.
8773767037,0.5717767196,-0.1925027104|C,4.776782956,3.365187204,-0.045
3768718|C,6.049420831,1.3181790777,-0.2046560456|H,7.0055382654,0.8084
422879,-0.2775186943|C,5.9961837618,2.7208389415,-0.1237053065|H,6.916
1571847,3.2991039043,-0.128469271|H,4.7019381467,4.4466359464,0.006967
3189|H,4.9262773355,-0.5083290071,-0.2571845362|H,-0.0000133388,4.3853
191205,0.0002157225|C,-2.3878350009,-0.914913079,0.2115339555|C,-2.783
7813641,-1.7460742741,-0.747421023|H,-2.0059328574,-1.2700501366,1.167
3190358|H,-2.7636611448,-2.819260751,-0.5852255427|H,-3.1500347213,-1.
3859488116,-1.7040001099|C,2.3889024842,-0.9145006443,-0.2123470121|C,
2.7811076807,-1.7459792396,0.7478436118|H,2.0109188791,-1.2692535642,-
1.1698465775|H,2.7616029714,-2.8191194777,0.5852181267|H,3.1435189726,
-1.3862212128,1.7060286241||Version=IA32W-G09RevC.01|State=1-A|HF=-106
6.9208606|RMSD=6.936e-009|RMSF=1.964e-006|Dipole=0.0006544,-3.3368886,
0.0000248|Quadrupole=3.9800778,2.7880706,-6.7681483,-0.0030561,1.15243
33,-0.0016973|PG=C01 [X(C22H16N4)]||@
```

Table 126. Computational output parameters for singlet 5,7-di-ethynyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide (R = C≡CH).

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C22H12N4\GAUSSIAN\11-Feb-2013\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\linear R=CCH\\0,1\C,0.0114392
456,0.,-0.0060205028\C,0.010521756,0.,1.3959713018\C,1.1775731979,0.,2
.1728707766\C,2.4469435027,0.,1.4575222449\C,2.4961963606,0.,0.0656481
332\C,1.3107525838,0.,-0.6654212471\N,1.3294357417,0.,-2.049478645\N,-
1.1422209161,0.,-0.6976720827\C,-1.0898209957,0.,-2.0514538133\C,0.121
5173991,0.,-2.798984673\H,3.4501132357,0.,-0.4448843869\C,-2.301415451
8,0.,-2.7916774922\C,0.124829556,0.,-4.1963600863\C,-2.29813596,0.,-4.
1731076408\C,-1.0830299731,0.,-4.8829325098\H,-3.2239204963,0.,-2.2202
314549\H,-3.239429262,0.,-4.715763425\H,1.0661131556,0.,-4.7351030556\
N,3.6089267642,0.,2.2096916678\N,1.1131522037,0.,3.5164345496\C,3.5625
```

```
480301,0.,3.6304925059\C,2.2686464269,0.,4.2237561355\C,4.7270866378,0
.,4.4028388318\C,2.2125051307,0.,5.6424669503\C,4.6283759367,0.,5.7886
824493\C,3.3637581888,0.,6.405995867\H,3.2931601916,0.,7.4902118526\H,
1.2253281514,0.,6.0930751417\H,5.697468844,0.,3.9184658601\H,-0.944553
0249,0.,1.9071235284\C,2.5171352814,0.,-2.7075271741\C,3.5698599764,0.
,-3.2974678977\H,4.4982675429,0.,-3.8213892908\C,4.8152615188,0.,1.586
4625582\C,5.8900580024,0.,1.0377624033\H,6.8409656212,0.,0.5558817789\
H,5.5323712585,0.,6.3898508425\H,-1.0818066335,0.,-5.9685703326\\Versi
on=IA32L-G03RevD.02\State=1-A1\HF=-1064.3981948\S2=0.\S2-1=0.\S2A=0.\R
MSD=5.063e-09\RMSF=1.431e-05\Thermal=0.\Dipole=2.3376425,0.,-1.251097\
PG=C02V [C2(H1C1C1H1),SGV(C20H10N4)]\\@
```

Computational Parameters related to Chapter 5

Table 127. Computational output parameters for singlet **180a**

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H2N2S4\GAUSSIAN\11-Sep-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo01\\0,1\C,-1.2141736642,0.
,-0.9012012783\C,-1.2053559245,0.,0.5658455738\C,-0.0139573767,0.,1.28
91993796\C,1.1928227012,0.,0.5918091936\C,1.2334002973,0.,-0.874702885
3\C,0.0170820019,0.,-1.5778112641\N,-2.4050771958,0.,-1.5123088995\N,2
.4372553177,0.,-1.4598839137\S,-3.7461791266,0.,-0.570313907\S,3.75764
84803,0.,-0.4890745343\S,-2.7526858731,0.,1.3292148128\S,2.7232628342,
0.,1.3884995753\H,0.0287972932,0.,-2.6599162069\H,-0.025693391,0.,2.37
32184355\\Version=x86-Linux-G03RevB.05\State=1-A1\HF=-1932.0274688\S2=
0.\S2-1=0.\S2A=0.\RMSD=2.951e-09\RMSF=7.005e-05\Dipole=-0.0164557,0.,1
.5199634\PG=C02V [C2(H1C1C1H1),SGV(C4N2S4)]\\@
```

Table 128. Computational output parameters for triplet **180a**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H2N2S4(3)\GAUSSIAN\08-Mar-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\christos 5 JACS2004\\0,3\C
,-1.2065735465,0.000347108,-0.865188883\C,-1.2127741559,0.0003172943,0
.5754788045\C,-0.0216248395,-0.0000178524,1.300106402\C,1.1929645493,-
0.0003339434,0.6154937645\C,1.2346797427,-0.0003254903,-0.8245832055\C
,0.0257253735,0.0000201903,-1.5466345137\H,-0.039663936,-0.0000320779,
```

```
2.3846344559\H,0.0437386731,0.0000349266,-2.6296116252\N,-2.3739813432
,0.0006792544,-1.5502853755\N,2.4242260659,-0.0006389153,-1.4704761735
\S,-3.7322659936,0.0010277485,-0.6260499087\S,3.7510220069,-0.00101202
98,-0.5015794366\S,-2.8120318282,0.0007424419,1.325617425\S,2.76639015
65,-0.000778727,1.4184040328\\Version=x86-Linux-G03RevB.05\State=3-A\H
F=-1932.0356087\S2=2.042719\S2-1=0.\S2A=2.000943\RMSD=2.257e-09\RMSF=9
.816e-05\Dipole=-0.0118373,-0.0000095,0.7116678\PG=C01 [X(C6H2N2S4)]\\
@
```

Table 129. Computational output parameters for singlet **180b**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H1N3S4\GAUSSIAN\14-Sep-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo012\\0,1\C,-1.2302597696,0
.,-0.5472332782\C,-1.2074247888,0.,0.9163567473\C,-0.0138276294,0.,1.6
356397855\C,1.1917596383,0.,0.9366393508\C,1.239335843,0.,-0.526355421
6\C,0.0105382282,0.,-1.2465437679\N,-2.4137469165,0.,-1.1495741122\N,2
.4328374357,0.,-1.1086012936\S,-3.7531026542,0.,-0.2099596574\S,3.7561
15955,0.,-0.1464770416\S,-2.752546618,0.,1.6825761086\S,2.7237063793,0
.,1.7288721192\H,-0.0229907982,0.,2.7195308137\C,0.0225296123,0.,-2.66
49781451\N,0.0323830526,0.,-3.8305198656\\Version=x86-Linux-G03RevB.05
\State=1-A1\HF=-2024.2722459\S2=0.\S2-1=0.\S2A=0.\RMSD=7.939e-09\RMSF=
1.293e-04\Dipole=-0.0287504,0.,3.4008205\PG=C02V [C2(H1C1C1C1N1),SGV(C
4N2S4)]\\@
```

Table 130. Computational output parameters for triplet **180b**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H1N3S4(3)\GAUSSIAN\18-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo010\\0,3\C,-1.220418893
6,0.,-0.5273943566\C,-1.2227666823,0.,0.911172909\C,-0.0351961457,0.,1
.6401039113\C,1.1825519843,0.,0.9627903374\C,1.2419203941,0.,-0.474553
2825\C,0.0261244284,0.,-1.2173712892\N,-2.3803576178,0.,-1.2088331714\
N,2.4300247516,0.,-1.105603786\S,-3.7387094129,0.,-0.2924490103\S,3.74
78134663,0.,-0.1317904396\S,-2.8235331745,0.,1.6574868398\S,2.74982817
96,0.,1.7770895289\H,-0.0584662163,0.,2.7244650825\C,0.0566381373,0.,-
2.6392784965\N,0.0816131441,0.,-3.8030879255\\Version=x86-Linux-G03Rev
B.05\State=3-B2\HF=-2024.2723603\S2=2.042316\S2-1=0.\S2A=2.000951\RMSD
=6.881e-09\RMSF=1.248e-04\Dipole=-0.0498348,0.,2.3222488\PG=C02V [C2(H
```

```
1C1C1C1N1),SGV(C4N2S4)]\\@
```

Table 131. Computational output parameters for singlet **180c**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4\GAUSSIAN\17-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo04\\0,1\C,-1.2293670829
,0.,-0.1291741862\C,-1.2300156432,0.,1.3359998944\C,-0.0501742527,0.,2
.0765586605\C,1.1640565257,0.,1.3938459761\C,1.2341711068,0.,-0.069649
6517\C,0.0189133376,0.,-0.7827651198\N,-2.4086338346,0.,-0.7537554175\
N,2.4422266393,0.,-0.6365478935\S,-3.7579355602,0.,0.1733888382\S,3.74
51762334,0.,0.3546806237\S,-2.7860365277,0.,2.0827139572\S,2.682198147
2,0.,2.2148386082\H,-0.0763493008,0.,3.1598637392\Br,0.0646074011,0.,-
2.6739024697\\Version=x86-Linux-G03RevB.05\State=1-A1\HF=-4503.1274491
\S2=0.\S2-1=0.\S2A=0.\RMSD=4.971e-09\RMSF=8.409e-05\Dipole=-0.0502688,
0.,2.0804702\PG=C02V [C2(H1C1C1Br1),SGV(C4N2S4)]\\@
```

Table 132. Computational output parameters for triplet **180c**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4(3)\GAUSSIAN\30-Nov-20
06\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\neoklis04\\0,3\C,-0.000
3974848,0.,0.0287396454\C,-0.003341418,0.,1.4698242286\C,1.1799045028,
0.,2.2040170377\C,2.3966592927,0.,1.5268037983\C,2.4621070914,0.,0.087
2031495\C,1.24749193,0.,-0.6427905809\H,1.1541679202,0.,3.2880514876\N
,-1.1645715711,0.,-0.6501541806\N,3.6571872543,0.,-0.5356784881\S,-2.5
220550735,0.,0.2710239733\S,4.9694256808,0.,0.4488828166\S,-1.60269532
29,0.,2.2205849681\S,3.9585829758,0.,2.3526179476\Br,1.2921133288,0.,-
2.5222605246\\Version=AM64L-G03RevD.02\State=3-B2\HF=-4503.1342351\S2=
2.042267\S2-1=0.\S2A=2.000923\RMSD=6.537e-09\RMSF=7.326e-05\Thermal=0.
\Dipole=-0.0248229,0.,1.0455487\PG=C02V [C2(H1C1C1Br1),SGV(C4N2S4)]\\@
```

Table 133. Computational output parameters for singlet **180d**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4\GAUSSIAN\14-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo03\\0,1\C,-1.2223041008
,0.,-0.5072393997\C,-1.2170560261,0.,0.9575721166\C,-0.0348669786,0.,1
.6944490507\C,1.1766342266,0.,1.0068275055\C,1.2421357173,0.,-0.456528
1845\C,0.0240353563,0.,-1.1680589584\N,-2.4030395607,0.,-1.1290463769\
N,2.44745094,0.,-1.0292369736\S,-3.7496495551,0.,-0.197552556\S,3.7546
022511,0.,-0.0431362356\S,-2.7714151508,0.,1.7077861652\S,2.6988161066
,0.,1.820348084\H,-0.0571588222,0.,2.7777775948\Cl,0.0598324453,0.,-2.
9077090731\\Version=x86-Linux-G03RevB.05\State=1-A1\HF=-2391.6168211\S
2=0.\S2-1=0.\S2A=0.\RMSD=8.875e-09\RMSF=1.308e-04\Dipole=-0.0443162,0.
,2.1536556\PG=C02V [C2(H1C1C1Cl1),SGV(C4N2S4)]\\@
```

Table 134. Computational output parameters for triplet **180d**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4(3)\GAUSSIAN\18-Sep-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo03\\0,3\C,-1.2222188
327,0.,-0.4776360632\C,-1.2216041891,0.,0.9632622671\C,-0.036678113,0.
,1.694663212\C,1.1787834108,0.,1.0152145884\C,1.2417398801,0.,-0.42430
7853\C,0.0249718094,0.,-1.1537890907\N,-2.3861644424,0.,-1.1558550873\
N,2.433939597,0.,-1.0515321048\S,-3.7424516872,0.,-0.2331635118\S,3.74
90352881,0.,-0.0710229733\S,-2.820458097,0.,1.7150578747\S,2.743612662
7,0.,1.835482756\H,-0.0601417903,0.,2.7787710756\Cl,0.0623494853,0.,-2
.8807746719\\Version=x86-Linux-G03RevB.05\State=3-B2\HF=-2391.6238611\
S2=2.042697\S2-1=0.\S2A=2.000938\RMSD=6.785e-09\RMSF=9.587e-05\Dipole=
-0.0248901,0.,1.1500151\PG=C02V [C2(H1C1C1Cl1),SGV(C4N2S4)]\\@
```

Table 135. Computational output parameters for singlet **180e**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4\GAUSSIAN\24-May-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis13\\0,1\C,-1.2241619
175,-0.0682393323,-1.2668947242\C,-1.196993096,-0.1214536323,0.1977014
16\C,0.0053728383,-0.0886707382,0.904948877\C,1.2033708073,-0.04434398
15,0.190966431\C,1.2188282198,0.0102617647,-1.2737524256\C,-0.00584103
```

```
56,0.0092928513,-1.962171787\N,-2.4265345585,-0.0984657637,-1.85561430
68\N,2.417307548,0.0572171783,-1.8692883003\S,-3.745053246,-0.19340517
39,-0.8847851295\S,3.7446925836,0.047345876,-0.9058741742\S,-2.7174406
539,-0.2452186899,0.9963215225\S,2.7331540041,-0.0702825909,0.98093035
71\O,0.0118066035,-0.1709512695,2.2774924321\H,-0.0101665012,0.0497680
351,-3.043282809\C,-0.0267586248,1.098267662,2.9558936038\H,-0.9414283
467,1.6485069207,2.7077777288\H,-0.0160347874,0.8664231084,4.021946149
7\H,0.8492197263,1.705933887,2.7023081639\\Version=x86-Linux-G03RevB.0
5\State=1-A\HF=-2046.5449157\S2=0.\S2-1=0.\S2A=0.\RMSD=3.401e-09\RMSF=
1.138e-05\Dipole=-0.0118607,0.5142981,1.6619608\PG=C01 [X(C7H4N2O1S4)]
\\@
```

Table 136. Computational output parameters for triplet **180e**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4(3)\GAUSSIAN\31-May-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis13\\0,3\C,-1.2071
144351,-0.0636843294,-1.2396708751\C,-1.207799692,-0.0620943543,0.1994
423752\C,-0.0103613575,-0.0643101679,0.9173364893\C,1.2013360015,-0.09
39612258,0.22440997\C,1.2304254008,-0.0959253406,-1.2144097724\C,0.019
0406019,-0.074255159,-1.9325897414\N,-2.383237698,-0.0530030214,-1.910
5097687\N,2.4200656628,-0.1165393238,-1.8607346117\S,-3.728473002,-0.0
442020824,-0.9651719547\S,3.7451895655,-0.1430661285,-0.8877280756\S,-
2.7882417557,-0.0882298757,0.977614135\S,2.7640742946,-0.1616873669,1.
035148102\O,-0.0250255534,-0.0952815606,2.2917284961\H,0.0302745889,-0
.0732810863,-3.015304882\C,-0.0143276897,1.1993699601,2.9187514347\H,-
0.8998158458,1.7798109961,2.6353749528\H,-0.0279667766,1.0106304161,3.
993460735\H,0.8919380904,1.7560195322,2.6539373002\\Version=x86-Linux-
G03RevB.05\State=3-A\HF=-2046.5535973\S2=2.042359\S2-1=0.\S2A=2.000926
\RMSD=4.310e-09\RMSF=8.479e-05\Dipole=-0.0007772,0.5769417,0.8144701\P
G=C01 [X(C7H4N2O1S4)]\\@
```

Table 137. Computational output parameters for singlet **180f**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2S4\GAUSSIAN\28-Aug-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis14\\0,1\C,-1.204302193
,-0.0240074944,-1.0958319721\C,-1.1981983566,-0.0184421866,0.371227520
6\C,-0.0153481229,-0.0221885754,1.1228964152\C,1.1875653545,0.00623734
```

```
59,0.404324125\C,1.2344727254,0.0012205669,-1.0619997985\C,0.024784113
3,-0.019430915,-1.7720591968\N,-2.3909506472,-0.0414297045,-1.71615093
59\N,2.4379769364,0.0085235051,-1.6491607493\S,-3.737378003,-0.0394955
814,-0.779821927\S,3.7575869177,0.0380365718,-0.6758463082\S,-2.758937
3046,0.0008975878,1.1183816431\S,2.7262455826,0.0576388914,1.194476039
7\H,0.0399157707,-0.0314941732,-2.8538244033\C,-0.0362861823,-0.021268
736,2.6316345703\H,0.844918545,-0.523601989,3.0439114856\H,-0.05239623
62,1.0012953532,3.0314557308\H,-0.9180212173,-0.5418153416,3.019457839
5\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-1971.3456265\S2=0.\S2-1=
0.\S2A=0.\RMSD=8.145e-09\RMSF=1.079e-04\Dipole=-0.0247759,0.0218678,1.
7696877\PG=C01 [X(C7H4N2S4)]\\@
```

Table 138. Computational output parameters for triplet **180f**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H4N2S4(3)\GAUSSIAN\04-Jun-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis14\\0,3\C,-1.202097
1956,-0.0150756391,-1.0548848453\C,-1.2024264391,-0.0161468268,0.38498
9548\C,-0.015769218,-0.0156729472,1.1300743241\C,1.1911472406,0.010661
2061,0.4187612646\C,1.2314126815,0.0121798209,-1.0205495142\C,0.024646
1486,-0.0042411379,-1.7434251485\N,-2.3690613384,-0.0357903805,-1.7406
42062\N,2.4174286926,0.0178186864,-1.6731073521\S,-3.7270765425,-0.052
845108,-0.8146622349\S,3.74882286,0.0308855302,-0.7091813862\S,-2.8088
049566,-0.0065846948,1.1314766838\S,2.7752107828,0.0559560196,1.210264
2302\H,0.0400138442,-0.0123945215,-2.8261379268\C,-0.0370635894,-0.014
913547,2.6388065179\H,0.8455225228,-0.5150753778,3.0513963611\H,-0.054
1120414,1.0087597592,3.0355026054\H,-0.9195278749,-0.5348215284,3.0264
952954\\Version=x86-Linux-G03RevB.05\State=3-A\HF=-1971.35438\S2=2.043
3\S2-1=0.\S2A=2.000967\RMSD=6.196e-09\RMSF=9.051e-05\Dipole=-0.0133848
,0.0079327,0.9424277\PG=C01 [X(C7H4N2S4)]\\@
```

Table 139. Computational output parameters for singlet **180g**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H1N3S4\GAUSSIAN\13-Sep-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo012\\0,1\C,-1.2095278001,0
.,-1.2199202194\C,-1.2159324737,0.,0.2416821757\C,-0.0125014125,0.,0.9
739139423\C,1.2093282742,0.,0.2728134529\C,1.2404425455,0.,-1.18847176
```

```
33\C,0.0242959931,0.,-1.8927626335\N,-2.3979542657,0.,-1.8377774016\N,
2.4443367802,0.,-1.7756204953\S,-3.7397928322,0.,-0.9001741932\S,3.761
6665597,0.,-0.8038835109\S,-2.7577104978,0.,0.9976403908\S,2.731194150
7,0.,1.0680973974\H,0.0381831166,0.,-2.9746294429\C,-0.0308148153,0.,2
.4006069938\N,-0.045760096,0.,3.5649088124\\Version=x86-Linux-G03RevB.
05\State=1-A1\HF=-2024.2642671\S2=0.\S2-1=0.\S2A=0.\RMSD=9.606e-09\RMS
F=1.262e-04\Dipole=-0.0002031,0.,0.0158239\PG=C02V [C2(H1C1C1C1N1),SGV
(C4N2S4)]\\@
```

Table 140. Computational output parameters for triplet **180g**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H1N3S4(3)\GAUSSIAN\14-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo012\\0,3\C,-1.216435968
4,0.,-1.1708124845\C,-1.2167936173,0.,0.2674877741\C,-0.0050933348,0.,
0.982940595\C,1.2139562509,0.,0.2800832686\C,1.2285039941,0.,-1.158143
4608\C,0.0096593032,0.,-1.8641070484\N,-2.3888771274,0.,-1.8445314233\
N,2.4078640684,0.,-1.8196759958\S,-3.7367583425,0.,-0.9080207797\S,3.7
459676694,0.,-0.8692472987\S,-2.7995101348,0.,1.032728512\S,2.78865744
57,0.,1.0616848989\H,0.0152714428,0.,-2.947169533\C,-0.012495607,0.,2.
41147302\N,-0.0185274799,0.,3.5755380234\\Version=x86-Linux-G03RevB.05
\State=3-B2\HF=-2024.2731939\S2=2.046345\S2-1=0.\S2A=2.001099\RMSD=7.3
02e-09\RMSF=8.117e-05\Dipole=0.0041305,0.,-0.7971347\PG=C02V [C2(H1C1C
1C1N1),SGV(C4N2S4)]\\@
```

Table 141. Computational output parameters for singlet **180h**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4\GAUSSIAN\24-Sep-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo44\\0,1\C,-1.1982335936,
0.0211493663,-1.0909272323\C,-1.2030534319,0.0090105536,0.3799208067\C
,-0.0140085133,-0.0076294118,1.105259929\C,1.1976657875,-0.0154395103,
0.4090238667\C,1.2391320173,-0.0052755082,-1.0526518553\C,0.0318979422
,0.0136172404,-1.7671178183\N,-2.3882235724,0.0382048701,-1.6982101653
\N,2.4526231073,-0.0139039978,-1.6234122019\S,-3.7384453823,0.04726996
62,-0.7774393234\S,3.7542645092,-0.034753029,-0.6296827691\S,-2.754684
6906,0.0159998741,1.1474044587\S,2.7060108218,-0.0369832979,1.23339121
42\O,0.0656253356,-0.0192484757,2.4690718296\H,0.0483301656,0.02248044
95,-2.848581785\H,-0.8188549735,0.0042686549,2.8675402511\\Version=x86
```

```
-Linux-G03RevB.05\State=1-A\HF=-2007.2400024\S2=0.\S2-1=0.\S2A=0.\RMSD
=8.357e-09\RMSF=5.566e-05\Dipole=-0.2365481,0.0028185,1.5150221\PG=C01
 [X(C6H2N2O1S4)]\\@
```

Table 142. Computational output parameters for triplet **180h**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4(3)\GAUSSIAN\25-Sep-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo44\\0,3\C,-1.19851817
4,-0.0127464333,-1.0445617513\C,-1.2069143067,-0.0196489801,0.39613698
51\C,-0.0099422955,-0.0205060218,1.1145677069\C,1.2018852385,0.0224023
252,0.4196894833\C,1.2329544059,0.0530353247,-1.0154456413\C,0.0246580
676,0.0286322518,-1.7388603582\N,-2.3731509969,-0.0521747959,-1.715989
0427\N,2.4246508291,0.0881537109,-1.6575163006\S,-3.7254544827,-0.1134
655966,-0.7914352928\S,3.7451394314,0.0953209688,-0.6764503517\S,-2.80
17855122,-0.0132860234,1.162579183\S,2.7592300894,0.0307999013,1.24056
28792\O,0.0623110032,-0.0373390875,2.4776415108\H,0.0364936492,0.03474
6068,-2.8212212364\H,-0.7942905279,-0.2848045736,2.8613653244\\Version
=x86-Linux-G03RevB.05\State=3-A\HF=-2007.2494483\S2=2.042012\S2-1=0.\S
2A=2.000911\RMSD=3.682e-09\RMSF=1.739e-05\Dipole=-0.4562707,-0.1687903
,0.7221253\PG=C01 [X(C6H2N2O1S4)]\\@
```

Table 143. Computational output parameters for singlet **180i**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4\GAUSSIAN\23-Apr-2007\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\neoklis06\\0,1\C,0.00675793
33,0.,-0.0209879214\C,-0.0099558233,0.,1.4462011702\C,1.183328319,0.,2
.152817358\C,2.4060410067,0.,1.4984419581\C,2.4527629009,0.,0.03190172
86\C,1.2447083916,0.,-0.6858469703\N,-1.1832685522,0.,-0.6334655384\N,
3.6681517869,0.,-0.5285639021\S,-2.5259440977,0.,0.3050963485\S,4.9690
025503,0.,0.4671586132\S,-1.5456272866,0.,2.2161919592\S,3.9069938777,
0.,2.3340932834\H,1.2680929231,0.,-1.7673190598\F,1.1541451883,0.,3.50
2459162\\Version=AM64L-G03RevD.02\State=1-A1\HF=-2031.2560429\S2=0.\S2
-1=0.\S2A=0.\RMSD=8.309e-09\RMSF=1.466e-04\Thermal=0.\Dipole=-0.022932
4,0.,1.0605619\PG=C02V [C2(H1C1C1F1),SGV(C4N2S4)]\\@
```

Table 144. Computational output parameters for triplet **180i**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4(3)\GAUSSIAN\30-Apr-200
7\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\neoklis06\\0,3\C,-0.0013
868788,0.,0.0114612101\C,-0.001881258,0.,1.4519473806\C,1.2057674407,0
.,2.1362851398\C,2.4214703378,0.,1.4663597603\C,2.4381093714,0.,0.0259
696068\C,1.2225526481,0.,-0.6860426094\N,-1.182259493,0.,-0.6488207287
\N,3.6267519542,0.,-0.6202201331\S,-2.5212977028,0.,0.3009378388\S,4.9
543988595,0.,0.3453979896\S,-1.5717167619,0.,2.2438276021\S,3.98177604
17,0.,2.2768558457\H,1.2289912933,0.,-1.7686605756\F,1.1977488431,0.,3
.4845622252\\Version=AM64L-G03RevD.02\State=3-B2\HF=-2031.2655133\S2=2
.041576\S2-1=0.\S2A=2.000894\RMSD=5.463e-09\RMSF=1.027e-04\Thermal=0.\
Dipole=-0.0015128,0.,0.254372\PG=C02V [C2(H1C1C1F1),SGV(C4N2S4)]\\@
```

Table 145. Computational output parameters for singlet **180j**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4\GAUSSIAN\07-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis08\\0,1\C,-1.214410
7426,0.,-1.6207647092\C,-1.2064839272,0.,-0.1539138177\C,-0.0029744433
,0.,0.5485882163\C,1.208081984,0.,-0.14082205\C,1.2319143863,0.,-1.607
5007431\C,0.0124920345,0.,-2.3039547811\N,-2.4085801675,0.,-2.22676688
82\N,2.4325848908,0.,-2.2005181087\S,-3.7419954659,0.,-1.2706997404\S,
3.7555545115,0.,-1.2300480514\S,-2.7432155305,0.,0.6193505178\S,2.7363
382098,0.,0.6490606385\H,0.018357624,0.,-3.3857683878\Br,-0.0132861153
,0.,2.4504101955\\Version=x86-Linux-G03RevB.05\State=1-A1\HF=-4503.129
737\S2=0.\S2-1=0.\S2A=0.\RMSD=4.869e-09\RMSF=1.078e-04\Dipole=-0.00675
53,0.,1.2459035\PG=C02V [C2(H1C1C1Br1),SGV(C4N2S4)]\\@
```

Table 146. Computational output parameters for triplet **180j**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4(3)\GAUSSIAN\11-Sep-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis08\\0,3\C,-1.209
4226631,0.,-1.5842283142\C,-1.2095644329,0.,-0.1431300466\C,-0.0039251
992,0.,0.5537957842\C,1.2114717643,0.,-0.1259702024\C,1.2317574435,0.,
-1.5669256938\C,0.0161448727,0.,-2.2778366028\N,-2.3832333745,0.,-2.25
60576997\N,2.4149733427,0.,-2.2220489228\S,-3.7298880145,0.,-1.3120210
```

```
425\S,3.7481110533,0.,-1.259018407\S,-2.7910292568,0.,0.6294503903\S,2
.7818264436,0.,0.6689497319\H,0.023819389,0.,-3.3606134331\Br,-0.01740
26711,0.,2.4552959851\\Version=x86-Linux-G03RevB.05\State=3-B2\HF=-450
3.1391906\S2=2.043325\S2-1=0.\S2A=2.000966\RMSD=5.825e-09\RMSF=8.556e-
05\Dipole=-0.0028754,0.,0.4056866\PG=C02V [C2(H1C1C1Br1),SGV(C4N2S4)]\
\@
```

Table 147. Computational output parameters for singlet **180k**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4\GAUSSIAN\04-Dec-2006\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\neoklis07\\0,1\C,0.0072525
674,0.,-0.012780566\C,-0.0102550841,0.,1.4539367658\C,1.1832028519,0.,
2.1775368432\C,2.4062731837,0.,1.5051992191\C,2.4509810175,0.,0.039058
892\C,1.2437630251,0.,-0.6772888767\N,-1.1770631781,0.,-0.6382842548\N
,3.6607573657,0.,-0.535658288\S,-2.5267373823,0.,0.2926744572\S,4.9697
378217,0.,0.4516991685\S,-1.5609790574,0.,2.1995151958\S,3.9239840484,
0.,2.315869169\H,1.2667080065,0.,-1.7589225625\Cl,1.1460864998,0.,3.92
72134258\\Version=AM64L-G03RevD.02\State=1-A1\HF=-2391.6175369\S2=0.\S
2-1=0.\S2A=0.\RMSD=9.043e-09\RMSF=2.416e-04\Thermal=0.\Dipole=-0.02336
66,0.,1.1015076\PG=C02V [C2(H1C1C1Cl1),SGV(C4N2S4)]\\@
```

Table 148. Computational output parameters for triplet **180k**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4(3)\GAUSSIAN\21-May-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis07\\0,3\C,-1.212
9277646,0.,-1.2255834848\C,-1.2131665326,0.,0.2157880351\C,-0.00510253
54,0.,0.9131124539\C,1.2106791675,0.,0.229332652\C,1.2265488783,0.,-1.
2119515211\C,0.010736788,0.,-1.9213771491\N,-2.3866097732,0.,-1.897439
4707\N,2.4076661099,0.,-1.8706487264\S,-3.7337917218,0.,-0.9563460572\
S,3.7442464641,0.,-0.9145582642\S,-2.7971591653,0.,0.9855124822\S,2.78
59706002,0.,1.0167113963\H,0.0167871308,0.,-3.004102289\Cl,-0.01488519
6,0.,2.6637459317\\Version=x86-Linux-G03RevB.05\State=3-B2\HF=-2391.62
70347\S2=2.043509\S2-1=0.\S2A=2.000974\RMSD=4.463e-09\RMSF=8.742e-05\D
ipole=-0.0014869,0.,0.2660772\PG=C02V [C2(H1C1C1Cl1),SGV(C4N2S4)]\\@
```

Table 149. Computational output parameters for singlet **180l**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H3N3S4\GAUSSIAN\05-Jun-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis15\\0,1\C,-1.188374259
4,0.1258678809,-1.0967760883\C,-1.19323148,0.1552632535,0.3688893915\C
,-0.0149479472,0.0588715548,1.1235708528\C,1.2253890336,-0.1692733546,
-1.0491486422\C,0.0313623901,-0.0289343227,-1.7706223408\N,-2.36890351
06,0.2584168882,-1.7149941042\N,2.4261115881,-0.3276085397,-1.62062564
02\S,-3.7055207412,0.4442052782,-0.7897617603\S,3.7312413889,-0.465048
4752,-0.6430057914\S,-2.7414527277,0.3141099206,1.122629545\H,0.051231
3497,-0.0412264909,-2.8519012185\N,-0.0418381767,0.0651838327,2.522851
4889\H,0.8243858505,0.3676119484,2.9559561812\H,-0.8250022431,0.570842
3669,2.9232983601\C,1.1801973537,-0.134958191,0.4156699699\S,2.6906961
545,-0.3501538497,1.2296708572\\Version=x86-Linux-G03RevB.05\State=1-A
\HF=-1987.3783974\S2=0.\S2-1=0.\S2A=0.\RMSD=6.128e-09\RMSF=2.273e-05\D
ipole=0.0244455,0.5028397,1.858516\PG=C01 [X(C6H3N3S4)]\\@
```

Table 150. Computational output parameters for triplet **180l**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H3N3S4(3)\GAUSSIAN\11-Jun-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis15 3\\0,3\C,-1.2042
805946,0.0181409205,-1.0412412711\C,-1.2042557208,0.019327083,0.395515
0156\C,-0.0097294952,0.019632637,1.1336760533\C,1.2223256863,-0.038211
766,-1.0194360323\C,0.0154682852,-0.0080100445,-1.742417589\N,-2.37865
73586,0.063330335,-1.7145610476\N,2.409431048,-0.0478464555,-1.6715454
572\S,-3.7285200618,0.1172530711,-0.7818786515\S,3.7433859111,-0.05621
1445,-0.7147652493\S,-2.7994674877,0.0100103599,1.1622450065\H,0.02550
60415,0.0054476533,-2.8245134063\N,-0.0227184937,0.0030232478,2.529852
8209\H,0.8151120003,0.3753934503,2.9636807771\H,-0.8497765548,0.414639
913,2.9486365658\C,1.1965604003,-0.0363915172,0.4170942256\S,2.7756166
868,-0.11929916,1.2123257342\\Version=x86-Linux-G03RevB.05\State=3-A\H
F=-1987.3882439\S2=2.043083\S2-1=0.\S2A=2.000956\RMSD=3.991e-09\RMSF=1
.153e-04\Dipole=0.0011346,0.4682327,1.0961141\PG=C01 [X(C6H3N3S4)]\\@
```

Table 151. Computational output parameters for singlet **180m**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2S4\GAUSSIAN\19-Sep-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo09\\0,1\C,-1.2079588159,-0
.0000000021,-0.6969369188\C,-1.210939477,0.0000000019,0.7705164371\C,-
0.0300428919,0.0000000042,1.5073521542\C,1.1785536541,0.0000000025,0.8
133309875\C,1.225553927,-0.0000000016,-0.6479355409\C,0.0225234334,-0.
0000000038,-1.3854846826\N,-2.4016598062,-0.0000000041,-1.3109228768\N
,2.4330461674,-0.000000003,-1.2328560194\S,-3.7454638735,-0.0000000017
,-0.3770941458\S,3.7499062083,0.,-0.2537914445\S,-2.7630844519,0.00000
00037,1.5257329736\S,2.7050090923,0.000000005,1.6188863207\H,-0.049449
461,0.0000000071,2.5909621529\C,0.0827667321,-0.000000008,-2.888328586
4\H,-0.9216785565,-0.0000000093,-3.3158025141\H,0.6234062571,0.8793830
208,-3.2617648669\H,0.6234062574,-0.8793830386,-3.2617648621\\Version=
x86-Linux-G03RevB.05\State=1-A'\HF=-1971.3460098\S2=0.\S2-1=0.\S2A=0.\
RMSD=9.630e-09\RMSF=8.242e-05\Dipole=-0.0716336,0.,1.3750266\PG=CS [SG
(C7H2N2S4),X(H2)]\\@
```

Table 152. Computational output parameters for triplet **180m**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2S4(3)\GAUSSIAN\21-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo09\\0,3\C,-1.2112552981
,0.,-0.6563538859\C,-1.210502774,0.,0.7846816549\C,-0.0222711631,0.,1.
5109086757\C,1.1866188846,0.,0.8192044104\C,1.2234874157,0.,-0.6192355
957\C,0.0165992973,0.,-1.3674571721\N,-2.3894000037,0.,-1.3242565527\N
,2.4127962896,0.,-1.2630234025\S,-3.7408913354,0.,-0.3917569859\S,3.74
39334084,0.,-0.2985750279\S,-2.8035793848,0.,1.5491375621\S,2.76135500
25,0.,1.6198062002\H,-0.0380605796,0.,2.5952516765\C,0.0587830003,0.,-
2.868566727\H,-0.9491675629,0.,-3.2844500623\H,0.6008074574,0.8781773
389,-3.2383590308\H,0.6008074574,-0.8781773389,-3.2383590308\\Version=
x86-Linux-G03RevB.05\State=3-A'\HF=-1971.3559836\S2=2.043276\S2-1=0.\S
2A=2.000963\RMSD=8.610e-09\RMSF=9.138e-05\Dipole=0.0127585,0.,0.446420
4\PG=CS [SG(C7H2N2S4),X(H2)]\\@
```

Table 153. Computational output parameters for singlet **180n**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4\GAUSSIAN\13-Sep-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo02\\0,1\C,-1.222654293,0
.,-0.7033651375\C,-1.2075001835,0.,0.7588763677\C,-0.0191019432,0.,1.4
881237662\C,1.1876232717,0.,0.7896207946\C,1.2403056274,0.,-0.67174994
42\C,0.0174461594,0.,-1.3591310688\N,-2.401640334,0.,-1.336321698\N,2.
435150123,0.,-1.2742353994\S,-3.7447731386,0.,-0.3972596466\S,3.753736
2685,0.,-0.3010068321\S,-2.762453547,0.,1.5090597913\S,2.7228083758,0.
,1.5794700382\H,-0.0330082932,0.,2.5714884079\F,0.0347378441,0.,-2.706
2278896\\Version=x86-Linux-G03RevB.05\State=1-A1\HF=-2031.2472468\S2=0
.\S2-1=0.\S2A=0.\RMSD=7.404e-09\RMSF=5.113e-05\Dipole=-0.0260465,0.,2.
0291369\PG=C02V [C2(H1C1C1F1),SGV(C4N2S4)]\\@
```

Table 154. Computational output parameters for triplet **180n**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4(3)\GAUSSIAN\14-Sep-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo02\\0,3\C,-1.21757396
53,0.,-0.6825127837\C,-1.2199689132,0.,0.7565477564\C,-0.0345910644,0.
,1.4908044026\C,1.1835666209,0.,0.8123168782\C,1.2479192244,0.,-0.6253
060613\C,0.0310937774,0.,-1.3400784593\N,-2.3697096057,0.,-1.383537706
6\N,2.4313291573,0.,-1.2721394303\S,-3.7350991268,0.,-0.4679825473\S,3
.7527849761,0.,-0.294241525\S,-2.8268520524,0.,1.4904728223\S,2.754680
3422,0.,1.6199808557\H,-0.0597406125,0.,2.57469869\F,0.0619448275,0.,-
2.6696958689\\Version=x86-Linux-G03RevB.05\State=3-B2\HF=-2031.2597118
\S2=2.04239\S2-1=0.\S2A=2.000926\RMSD=5.980e-09\RMSF=8.503e-05\Dipole=
-0.0265947,0.,1.1461763\PG=C02V [C2(H1C1C1F1),SGV(C4N2S4)]\\@
```

Table 155. Computational output parameters for singlet **180o**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4\GAUSSIAN\14-Sep-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis11\\0,1\C,-1.2048671
283,-0.2814887938,-0.4095717146\C,-1.1504855247,-0.0215735619,1.028072
9699\C,0.0511973373,0.2213931536,1.6919636245\C,1.230050015,0.21241108
32,0.9494167359\C,1.2353513844,-0.0349822425,-0.4934008755\C,0.0073654
562,-0.3074079602,-1.1318319288\N,-2.403160097,-0.485595106,-0.9733349
```

```
562\N,2.4106224964,-0.0029399299,-1.1354346774\S,-3.7098565791,-0.4653
744683,0.018897073\S,3.7483618251,0.2825487346,-0.2361705775\S,-2.6723
662113,-0.0336505555,1.8453979344\S,2.7762785665,0.501348729,1.6623721
064\H,0.0680171401,0.4064994506,2.7594845773\O,0.0072524789,-0.6308009
062,-2.4640967993\C,-0.3557237818,0.4433300346,-3.3360702289\H,-0.2950
867696,0.044199581,-4.3513520972\H,-1.3799657498,0.782040591,-3.139086
3913\H,0.3407705858,1.2853635636,-3.2343003354\\Version=x86-Linux-G03R
evB.05\State=1-A\HF=-2046.5376812\S2=0.\S2-1=0.\S2A=0.\RMSD=6.248e-09\
RMSF=9.151e-06\Dipole=-0.048982,0.7296893,1.415346\PG=C01 [X(C7H4N2O1S
4)]\\@
```

Table 156. Computational output parameters for triplet **180o**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4(3)\GAUSSIAN\19-Sep-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis11\\0,3\C,-1.1498
958619,0.1179552031,-0.4909299979\C,-1.1835508179,-0.0659638909,0.9393
52291\C,-0.0302584563,-0.2384959451,1.6979237021\C,1.2032188787,-0.228
0058532,1.0505388466\C,1.3094765723,-0.0375718787,-0.3683934617\C,0.11
96119609,0.1424934591,-1.1442152717\N,-2.3061066213,0.2461733523,-1.17
84922128\N,2.5137070217,-0.0224317695,-0.9697644782\S,-3.6875189451,0.
1949471324,-0.2790643404\S,3.8031711792,-0.2420244948,0.0304496515\S,-
2.7981008042,-0.0738135287,1.6605057985\S,2.7379025348,-0.4371652879,1
.8973331251\H,-0.0911672761,-0.3812894735,2.770786163\O,0.337425925,0.
2879216216,-2.4594818412\C,-0.6530732786,0.7699324154,-3.375731382\H,-
0.1043661205,0.9354242538,-4.3047476676\H,-1.445988435,0.0353923754,-3
.5265474181\H,-1.0915257895,1.7077465988,-3.0246956253\\Version=x86-Li
nux-G03RevB.05\State=3-A\HF=-2046.5512612\S2=2.041382\S2-1=0.\S2A=2.00
0877\RMSD=7.420e-09\RMSF=5.654e-05\Dipole=-0.4646719,0.1622281,0.12206
15\PG=C01 [X(C7H4N2O1S4)]\\@
```

Table 157. Computational output parameters for singlet **180p**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4\GAUSSIAN\21-Sep-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis42\\0,1\C,-1.2061055
69,-0.0097538208,-0.7244958262\C,-1.2300533455,-0.0127286763,0.7393762
53\C,-0.0661697267,-0.003385447,1.5060234395\C,1.1551041332,0.00922608
07,0.8297483221\C,1.2333863078,0.0128184214,-0.6171841035\C,0.04357738
```

```
12,0.0031606095,-1.3647707362\N,-2.3769730722,-0.0192599623,-1.3834688
138\N,2.4355072111,0.0253313778,-1.2221938245\S,-3.7350977103,-0.03229
23161,-0.47816863\S,3.7504433782,0.0330189772,-0.2210383409\S,-2.80463
09725,-0.028770684,1.448756526\S,2.6828900191,0.0217725408,1.640527100
5\H,-0.1069449799,-0.0058689587,2.5883888272\O,0.0974007864,0.00643099
85,-2.7293004819\H,1.0418891979,0.0162417709,-2.9677570871\\Version=x8
6-Linux-G03RevB.05\State=1-A\HF=-2007.2364125\S2=0.\S2-1=0.\S2A=0.\RMS
D=8.565e-09\RMSF=8.443e-05\Dipole=0.0806931,-0.0023835,1.6081029\PG=C0
1 [X(C6H2N2O1S4)]\\@
```

Table 158. Computational output parameters for triplet **180p**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4(3)\GAUSSIAN\24-Sep-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis42\\0,3\C,-1.2277
233538,0.,-0.6807678977\C,-1.2237842301,0.,0.7596239647\C,-0.042744567
8,0.,1.5047168006\C,1.1750084992,0.,0.8273579436\C,1.227356323,0.,-0.6
020237379\C,0.0220906534,0.,-1.3525148296\N,-2.3832874356,0.,-1.372722
0656\N,2.3993828507,0.,-1.2688688993\S,-3.7477584795,0.,-0.4523180701\
S,3.7453984716,0.,-0.3058308835\S,-2.8262679247,0.,1.5009833306\S,2.75
97255589,0.,1.6117573925\H,-0.0743867966,0.,2.5882337458\O,0.060003722
8,0.,-2.6945312563\H,1.002907144,0.,-2.9526687163\\Version=x86-Linux-G
03RevB.05\State=3-A'\HF=-2007.2548371\S2=2.040224\S2-1=0.\S2A=2.000831
\RMSD=4.552e-09\RMSF=8.142e-05\Dipole=0.4958828,0.,0.6627253\PG=CS [SG
(C6H2N2O1S4)]\\@
```

Table 159. Computational output parameters for singlet **180q**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H3N3S4\GAUSSIAN\19-Sep-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo05\\0,1\C,-1.2082969948,0.
0134205464,-0.7641914108\C,-1.201741638,-0.043729275,0.689133697\C,0.0
304977543,-0.0766840415,1.3693504237\C,1.1733942847,0.0288174666,-0.81
63734792\C,-0.0335074282,0.0448121016,-1.5161219885\S,-3.7355680946,-0
.0441081504,0.4209988751\S,3.7506797604,0.004288198,0.2569776602\H,-0.
0574698931,0.0849503928,-2.5979723139\N,0.06182726,-0.2095269296,2.760
0932851\C,1.2312348239,-0.0280008114,0.6358279872\S,-2.7759241505,0.06
01894434,-1.4918311553\S,2.7069137954,0.0956343472,-1.6119583216\N,-2.
3784456131,-0.0448626443,1.3472521026\N,2.4355492888,-0.013741603,1.2
```

```
417790662\H,-0.7748949729,0.1465902471,3.2091662018\H,0.9127425363,0.1
575003177,3.172190622\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-198
7.3779215\S2=0.\S2-1=0.\S2A=0.\RMSD=5.259e-09\RMSF=4.181e-05\Dipole=-0
.026337,0.45022,-1.0692294\PG=CS [SG(C2H1N1),X(C4H2N2S4)]\\@
```

Table 160. Computational output parameters for triplet **180q**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H3N3S4(3)\GAUSSIAN\21-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo05\\0,3\C,-1.2138091816
,-0.0215624383,-0.7735272647\C,-1.2174878098,-0.0148745235,0.660348833
\C,0.0264436193,-0.0095399287,1.3604779784\C,1.1831176979,-0.002301676
6,-0.8199812879\C,-0.0291370005,-0.0167832442,-1.5103647211\S,-3.74607
84904,-0.0150267915,0.4374189888\S,3.7599709062,0.0452888695,0.2919468
027\H,-0.0500986816,-0.0216763113,-2.5939707803\N,0.0529896643,-0.0413
134544,2.7170224104\C,1.2422401276,0.0048908828,0.6126776839\S,-2.8196
713687,-0.029400497,-1.5097852258\S,2.7591669059,0.0154288533,-1.61790
67898\N,-2.3685043561,-0.0069723502,1.3584891656\N,2.4191658005,0.0314
994843,1.2657009614\H,-0.810320745,0.112777479,3.2173456576\H,0.932449
6999,0.1267816969,3.1835696174\\Version=x86-Linux-G03RevB.05\State=3-A
"\HF=-1987.4004828\S2=2.036973\S2-1=0.\S2A=2.000702\RMSD=4.040e-09\RMS
F=6.285e-05\Dipole=0.0020431,0.182715,0.1811748\PG=CS [SG(C2H1N1),X(C4
H2N2S4)]\\@
```

Table 161. Computational output parameters for singlet **182**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C5H1N3S4\GAUSSIAN\16-Nov-2009\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt\\0,1\C,0.,0.,0.\C,0.,0.,1
.47692883\C,1.2105739611,0.,2.1667266181\C,2.3837527233,0.,1.415078396
7\C,2.3072324208,0.,-0.0598671372\S,-2.5288297149,0.,0.3333194922\S,4.
8500229037,0.,0.1419413005\S,-1.5344423523,0.,2.2469364986\S,3.9560657
991,0.,2.1044774482\H,1.2386987385,0.,3.2501886446\N,1.1361258572,0.,-
0.7042322701\N,-1.190452009,0.,-0.5984734817\N,3.4651098246,0.,-0.7192
039143\\Version=AM64L-G03RevD.02\State=1-A'\HF=-1948.0746266\S2=0.\S2-
1=0.\S2A=0.\RMSD=7.087e-09\RMSF=6.699e-05\Thermal=0.\Dipole=0.0000128,
2.1599961,0.\PG=CS [SG(C5H1N3S4)]\\@
```

Table 162. Computational output parameters for triplet **182**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C5H1N3S4(3)\GAUSSIAN\16-Nov-2009\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0.00612
36194,0.,0.0368609547\C,-0.0014296675,0.,1.4820061395\C,1.2106166727,0
.,2.1675956296\C,2.3854940444,0.,1.4200985677\C,2.3030381276,0.,-0.022
7121354\S,-2.5128285608,0.,0.3015411024\S,4.8323227077,0.,0.1110367117
\S,-1.5815213627,0.,2.2566131883\S,4.0036146888,0.,2.1117565622\H,1.23
87376041,0.,3.2518371117\N,1.1367847977,0.,-0.6790768299\N,-1.17750167
18,0.,-0.6318528895\N,3.4504071527,0.,-0.7518836874\\Version=AM64L-G03
RevD.02\State=3-A'\HF=-1948.0697848\S2=2.03304\S2-1=0.\S2A=2.00057\RMS
D=5.013e-09\RMSF=1.122e-04\Thermal=0.\Dipole=0.039264,0.,1.5138871\PG=
CS [SG(C5H1N3S4)]\\@
```

Table 163. Computational output parameters for singlet **183**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C5H1N3S4\GAUSSIAN\16-Nov-2009\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,0.,0.,0.\C
,0.,0.,1.46338914\C,2.2509840884,0.,1.59914399\C,2.4270483013,0.,0.146
4874687\S,-2.5262798287,0.,0.3231102423\S,4.8961857698,0.,0.7708556665
\S,-1.5606933597,0.,2.2186368244\S,3.7094517081,0.,2.5366634229\N,-1.1
801130607,0.,-0.6266420665\N,3.6738455654,0.,-0.3338708086\C,1.2561387
198,0.,-0.6328915609\H,1.3206138481,0.,-1.7131834747\N,1.0832792324,0.
,2.2307038989\\Version=AM64L-G03RevD.02\State=1-A'\HF=-1948.0669449\S2
=0.\S2-1=0.\S2A=0.\RMSD=6.916e-09\RMSF=1.636e-04\Thermal=0.\Dipole=-0.
0005947,0.9202126,0.\PG=CS [SG(C5H1N3S4)]\\@
```

Table 164. Computational output parameters for triplet **183**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C5H1N3S4(3)\GAUSSIAN\17-Nov-2009\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0.00089
3904,0.,0.0323547076\C,-0.0039449652,0.,1.474413457\C,2.2535548626,0.,
1.6105745359\C,2.4220715116,0.,0.1783898332\S,-2.5164479961,0.,0.28039
08255\S,4.8913552162,0.,0.7271982307\S,-1.613243769,0.,2.2253882309\S,
3.7609159076,0.,2.5495380259\N,-1.1581731877,0.,-0.6573300812\N,3.6556
```

```
347436,0.,-0.3669835295\C,1.2546084912,0.,-0.6096301904\H,1.3198588718
,0.,-1.6912082133\N,1.0833773935,0.,2.2293069107\\Version=AM64L-G03Rev
D.02\State=3-A'\HF=-1948.0740874\S2=2.038828\S2-1=0.\S2A=2.000783\RMSD
=3.331e-09\RMSF=1.547e-04\Thermal=0.\Dipole=-0.0048392,0.,0.0802406\PG
=CS [SG(C5H1N3S4)]\\@
```

Table 165. Computational output parameters for singlet **184**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N4S4\GAUSSIAN\26-Jun-2009\0\\#
opt ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,0.0684405428
,0.,0.0266467852\C,0.0041083514,0.,1.4972912489\C,2.2428578993,0.,1.63
23337866\C,2.3558466101,0.,0.1646176662\S,-2.4636768562,0.,0.258845209
4\S,4.8416759294,0.,0.6994997523\S,-1.5705766288,0.,2.2005251031\S,3.7
214841575,0.,2.5198518595\N,-1.087421762,0.,-0.6318930584\N,3.58254494
21,0.,-0.3500844359\N,1.0804692351,0.,2.2774393338\N,1.2540947154,0.,-
0.599487033\\Version=AM64L-G03RevD.02\State=1-A'\HF=-1964.1117536\S2=0
.\S2-1=0.\S2A=0.\RMSD=7.219e-09\RMSF=8.721e-05\Thermal=0.\Dipole=-0.09
54749,0.,1.586234\PG=CS [SG(C4N4S4)]\\@
```

Table 166. Computational output parameters for triplet **184**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N4S4(3)\GAUSSIAN\26-Jun-2009\0\
\# opt ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0.0025103
651,0.,0.0344828324\C,-0.0019682374,0.,1.4813571801\C,2.2441818438,0.,
1.5185250733\C,2.2875590806,0.,0.072290304\S,-2.5051889907,0.,0.305949
0857\S,4.7849496931,0.,0.4265639525\S,-1.5926669935,0.,2.2564441522\S,
3.8083384382,0.,2.3458199725\N,-1.169007286,0.,-0.6399915863\N,3.48079
55175,0.,-0.5630293175\N,1.1095158953,0.,2.2006416851\N,1.1566651322,0
.,-0.6494303788\\Version=AM64L-G03RevD.02\State=3-A'\HF=-1964.1051457\
S2=2.032852\S2-1=0.\S2A=2.000559\RMSD=6.323e-09\RMSF=1.671e-04\Thermal
=0.\Dipole=-0.0145226,0.,0.880914\PG=CS [SG(C4N4S4)]\\@
```

Table 167. Computational output parameters for singlet **181a**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\STO-3G\C6H2N2S4\GAUSSIAN\13-Jun-2007\0\\#
OPT UB3LYP GEOM=CONNECTIVITY\\neoklis21\\0,1\C,-0.6846070616,0.0001001
72,0.1302672633\C,-0.6874612953,0.0002572024,1.5746286759\C,0.52344427
45,0.0001979197,2.283751965\C,1.8423487085,-0.0001648615,0.1947541437\
C,0.6020165996,-0.0001155019,-0.5584218819\N,-1.8402190533,0.000148470
9,-0.6539843484\S,-3.2499565106,0.0004176681,0.3728759411\S,-2.3270368
667,0.0005207618,2.3138278379\C,1.7681258576,-0.0000043246,1.627792498
1\S,0.7166544411,-0.000284941,-2.2901932081\N,3.0982951392,-0.00042628
34,-0.4855196345\S,2.8479538628,-0.0006501964,-2.2165946687\H,2.701004
6402,-0.0000486589,2.1988763316\H,0.5074214332,0.0003170295,3.38236112
92\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-1910.1669698\S2=0.\S2-1
=0.\S2A=0.\RMSD=4.619e-09\RMSF=1.040e-04\Dipole=-0.617915,-0.0000037,-
0.6869034\PG=C01 [X(C6H2N2S4)]\\@
```

Table 168. Computational output parameters for triplet **181a**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H2N2S4(3)\GAUSSIAN\18-Jun-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis21\\0,3\C,-0.682418
8565,0.,0.1027411529\C,-0.6797410277,0.,1.5390382167\C,0.5214478197,0.
,2.2641391084\C,1.7916888316,0.,0.1781053428\C,0.5715073252,0.,-0.5603
721017\N,-1.8385784473,0.,-0.5849523283\S,-3.2046889744,0.,0.342354551
7\S,-2.2759898611,0.,2.2813284314\C,1.7377679034,0.,1.603986099\S,0.71
06736137,0.,-2.3041060437\N,2.9715177811,0.,-0.4748911631\S,2.85342864
76,0.,-2.1225095278\H,2.6735643354,0.,2.1508624781\H,0.4995735401,0.,3
.3491364676\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-1932.0406853\
S2=2.039698\S2-1=0.\S2A=2.000809\RMSD=6.844e-09\RMSF=5.308e-05\Dipole=
-0.2040282,0.,0.6009188\PG=CS [SG(C6H2N2S4)]\\@
```

Table 169. Computational output parameters for singlet **181b**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H3N3S4\GAUSSIAN\07-Sep-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo26\\0,1\C,-1.6351373113,-0
.0123068084,-0.04116351\C,-1.6685902729,-0.015652138,1.3554225975\C,-0
.4688641176,-0.0082705441,2.07241778\C,0.7927536802,0.0060355477,-0.05
```

```
96359239\C,-0.3907920401,-0.0013149419,-0.8006237471\S,3.3174470643,0.
02291371,1.1349499693\C,0.8067086946,0.0030304896,1.3507127282\S,-3.07
37428157,-0.0210269053,-0.9979165642\S,2.4015442687,0.0199906383,-0.83
70808494\N,1.9182870166,0.0101007734,2.066820115\N,-0.4386698097,0.001
1387665,-2.1445840041\S,-1.9408174809,-0.0083408121,-2.8209175415\H,-2
.6145815435,-0.0239383757,1.886905386\N,-0.4125384711,-0.0110968844,3.
4134702595\H,-1.2432628232,-0.0179019968,3.9851451232\H,0.500924835,-0
.004873938,3.850665122\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-198
7.3846802\S2=0.\S2-1=0.\S2A=0.\RMSD=1.116e-09\RMSF=3.410e-05\Dipole=-1
.680146,-0.0160886,1.8169653\PG=C01 [X(C6H3N3S4)]\\@
```

Table 170. Computational output parameters for triplet **181b**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H3N3S4(3)\GAUSSIAN\13-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo26\\0,3\C,-1.6367382767
,-0.0002053202,0.0006898258\C,-1.6154435391,-0.0003253256,1.3960344363
\C,-0.4025651435,-0.0002900188,2.0942586606\C,0.7944886426,0.000053621
,-0.0657740725\C,-0.4323107674,-0.000017286,-0.7794645881\S,3.34489407
52,0.0003512501,1.0274510533\C,0.8318199988,-0.0000625698,1.352340577\
S,-3.1263499821,-0.0002653365,-0.9498630359\S,2.3476713385,0.000356628
9,-0.873244187\N,2.0094337779,0.000086975,2.0106976391\N,-0.4638140224
,0.0001084549,-2.123481627\S,-1.9835125608,0.0000221658,-2.7847056011\
H,-2.5460649471,-0.0004975233,1.9556323865\N,-0.3238085544,-0.00064279
92,3.4574351702\H,-1.1494103014,0.0006821596,4.0328811374\H,0.58404541
8,0.0005930109,3.8962074957\\Version=x86-Linux-G03RevB.05\State=3-A\HF
=-1987.3978763\S2=2.035719\S2-1=0.\S2A=2.000655\RMSD=7.773e-09\RMSF=8.
834e-05\Dipole=-0.4009577,0.0015028,1.2893228\PG=C01 [X(C6H3N3S4)]\\@
```

Table 171. Computational output parameters for singlet **181c**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4\GAUSSIAN\27-Sep-2007\0
\\# opt ub3lyp/6-31g(d) guess=mix geom=connectivity\\neo46\\0,1\C,0.01
09156116,0.,0.006848365\C,-0.0016685375,0.,1.4106016314\C,1.1994624002
,0.,2.1895216355\C,2.4232257304,0.,1.485924574\C,2.4560883758,0.,0.079
0747198\C,1.2258403823,0.,-0.6587769667\N,3.6206431484,0.,-0.608891310
1\S,4.9668496803,0.,0.3634966706\S,-1.4867131888,0.,2.3432238685\S,3.9
926490767,0.,2.2852240253\H,-0.9065133252,0.,-0.5702491326\N,1.1510778
184,0.,3.5452824959\S,-0.3714349183,0.,4.1808247322\O,1.2702393384,0.,
```

```
 -2.0045241179\H,2.2140900232,0.,-2.2603013025\\Version=AM64L-G03RevD.0
 2\State=1-A'\HF=-2007.2573714\S2=0.934565\S2-1=0.\S2A=0.080331\RMSD=7.
 241e-09\RMSF=5.120e-05\Thermal=0.\Dipole=-0.2356043,0.,-0.2958471\PG=C
 S [SG(C6H2N2O1S4)]\\@
1\1\GINC-C
```

Table 172. Computational output parameters for triplet **181c**.

```
HEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4(3)\GAUSSIAN\25-Sep-200
 7\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\neo46\\0,3\C,-0.03477640
 23,0.00890619,-0.0078201786\C,-0.0110152782,-0.0068876036,1.3915671821
 \C,1.2179630252,0.0112298257,2.1356311006\C,2.4253085242,0.0461599483,
 1.391116506\C,2.4104591476,0.0622550931,-0.0257850583\C,1.1575877224,0
 .0431307037,-0.7182982744\N,3.5564244682,0.0954052153,-0.7358290517\S,
 4.931200352,0.1147395945,0.1915710656\S,-1.4678430997,-0.0501495999,2.
 3846339132\S,4.0105035012,0.0719143335,2.1329149101\H,-0.9687179116,-0
 .0050458821,-0.5584376114\N,1.2226597873,-0.0042331305,3.480334784\S,-
 0.2756006888,-0.0452113194,4.1812229839\O,1.1501950933,0.0585586513,-2
 .0706937014\H,2.0808989807,0.0821861799,-2.364702035\\Version=AM64L-G0
 3RevD.02\State=3-A\HF=-2007.2610197\S2=2.03725\S2-1=0.\S2A=2.000711\RM
 SD=4.722e-09\RMSF=2.431e-05\Thermal=0.\Dipole=0.0700315,0.0039421,-0.2
 108701\PG=C01 [X(C6H2N2O1S4)]\\@
```

Table 173. Computational output parameters for singlet **181d**.

```
 1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4\GAUSSIAN\10-Sep-2007\0
 \\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo028\\0,1\C,-1.6974408573
 ,-0.0904561031,-1.0642905546\C,-1.6510626441,0.0777470531,0.3260961628
 \C,-0.4038261394,0.1378261767,1.0556218898\C,0.7613306367,0.0184973377
 ,0.2937874865\C,0.7658585677,-0.1530465288,-1.1126289803\C,-0.52496712
 09,-0.2072169057,-1.8012964384\N,1.8994784768,-0.2626295643,-1.7986406
 11\S,3.2751949194,-0.179634553,-0.8591525919\S,-3.0755990885,0.2277112
 156,1.2907242728\S,2.3626843673,0.0771950141,1.0814115282\H,-2.6400260
 303,-0.1335308056,-1.5970307841\N,-0.4157803003,0.300225941,2.39154675
 63\S,-1.9102590887,0.4197792984,3.0842777883\O,-0.7035749783,-0.362741
 7046,-3.1124898213\C,0.3580620831,-0.5046159568,-4.0726398751\H,1.0016
 595108,0.3764097236,-4.0726107108\H,0.9604683353,-1.3884509079,-3.8574
 132615\H,-0.1594541314,-0.60889505,-5.0274437917\\Version=x86-Linux-G0
```

```
3RevB.05\State=1-A\HF=-2046.5395146\S2=0.\S2-1=0.\S2A=0.\RMSD=8.918e-0
9\RMSF=1.453e-05\Dipole=-0.9090179,-0.1433009,-1.3497551\PG=C01 [X(C7H
4N2O1S4)]\\@
```

Table 174. Computational output parameters for triplet **181d**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4(3)\GAUSSIAN\06-Sep-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo028\\0,3\C,-1.6445026
917,0.0005481518,-1.1217806624\C,-1.6544098003,-0.1242516716,0.2688453
135\C,-0.4384043851,-0.0997190357,1.0285851245\C,0.7717082155,0.078509
0437,0.3114335415\C,0.7961931178,0.2295978838,-1.1073963716\C,-0.45279
37021,0.1682987037,-1.8221917201\N,1.9695172792,0.4478321319,-1.735786
3928\S,3.2941026932,0.492932628,-0.7477691249\S,-3.1187389597,-0.33892
77664,1.2262931637\S,2.3162702578,0.1625945829,1.1320569279\H,-2.56327
33092,-0.0283465303,-1.6968632125\N,-0.4496962795,-0.2344585073,2.3662
970589\S,-1.9497206172,-0.429111398,3.0347013341\O,-0.5532911183,0.352
2332027,-3.1639315287\C,0.3133263069,-0.3838016364,-4.0411031033\H,1.3
424440235,-0.0271378453,-3.9767594573\H,0.2766848251,-1.4549236848,-3.
8079971279\H,-0.0855899423,-0.2159703131,-5.0433721823\\Version=x86-Li
nux-G03RevB.05\State=3-A\HF=-2046.5575421\S2=2.038634\S2-1=0.\S2A=2.00
0765\RMSD=4.978e-09\RMSF=2.588e-06\Dipole=-0.1179977,-0.3733938,-0.483
9703\PG=C01 [X(C7H4N2O1S4)]\\@
```

Table 175. Computational output parameters for singlet **181e**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4\GAUSSIAN\20-Jun-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis23\\0,1\C,-0.8794205
314,0.,-0.075704341\C,-0.8683764744,0.,1.3630790528\C,0.3336945487,0.,
2.1214155383\C,1.5959283361,0.,0.0135630578\C,0.3758242314,0.,-0.70341
71836\N,-2.0519510569,0.,-0.7412877673\S,-3.4055601016,0.,0.2120555865
\S,-2.4156510478,0.,2.1185600938\C,1.5269310507,0.,1.4566619449\S,0.52
79999601,0.,-2.4739158013\N,2.7783391926,0.,-0.5900574815\S,2.67336557
4,0.,-2.2428652108\H,0.3215914516,0.,3.2048073251\F,2.6670816084,0.,2.
1377407011\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-2031.24306\S2=
0.\S2-1=0.\S2A=0.\RMSD=2.041e-09\RMSF=1.141e-04\Dipole=-0.3822051,0.,1
.0609793\PG=CS [SG(C6H1F1N2S4)]\\@
```

Table 176. Computational output parameters for triplet **181e**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4(3)\GAUSSIAN\22-Jun-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis23\\0,3\C,-0.8706
555135,0.,-0.0438451141\C,-0.8680494922,0.,1.3914059376\C,0.3297631653
,0.,2.1192857099\C,1.610499365,0.,0.0186570317\C,0.3845315317,0.,-0.70
71489414\N,-2.026136184,0.,-0.7330003018\S,-3.3934925036,0.,0.19355083
12\S,-2.463203551,0.,2.1360635519\C,1.5332297003,0.,1.443763149\S,0.52
67760814,0.,-2.450731668\N,2.7931085835,0.,-0.6223741089\S,2.670301143
3,0.,-2.268971877\H,0.3390710088,0.,3.2033265237\F,2.681123437,0.,2.13
2557145\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-2031.2673269\S2=2
.039098\S2-1=0.\S2A=2.000785\RMSD=5.501e-09\RMSF=1.462e-04\Dipole=-0.5
480552,0.,0.2630728\PG=CS [SG(C6H1F1N2S4)]\\@
```

Table 177. Computational output parameters for singlet **181f**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2S4\GAUSSIAN\29-Aug-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo25\\0,1\C,-1.6165455346,-0
.0000116631,-1.3690401233\C,-1.6048196317,0.0001688456,0.056150244\C,-
0.3919091015,0.0001451638,0.8215371401\C,0.7932541021,-0.0000717262,0.
0685961829\C,0.8044741163,-0.0002618925,-1.347189343\C,-0.4486713766,-
0.0002116928,-2.0878443036\N,1.9499568092,-0.0004836313,-2.0251915751\
S,3.3042861772,-0.0005023439,-1.072456057\S,-3.0613465229,0.0004169801
,0.9772692023\S,2.3770365527,-0.0001473236,0.8669939308\H,-2.569410396
9,0.0000171328,-1.8887582204\N,-0.4321779759,0.0002963061,2.167756225\
S,-1.958512182,0.0005844017,2.8225451297\C,-0.4332269112,-0.0003187563
,-3.5890560774\H,0.0977445857,0.8774405578,-3.9733353675\H,0.098584211
9,-0.8776046366,-3.9732247303\H,-1.4501286114,-0.0007988787,-3.9911918
426\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-1971.335901\S2=0.\S2-1
=0.\S2A=0.\RMSD=7.169e-10\RMSF=7.239e-05\Dipole=-0.9966626,0.0000498,-
1.0383096\PG=C01 [X(C7H4N2S4)]\\@
```

Table 178. Computational output parameters for triplet **181f**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2S4(3)\GAUSSIAN\20-Jul-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo25\\0,3\C,-1.6268438506
,-0.0000066185,-1.358010029\C,-1.6331004204,0.0001597795,0.0441243036\
C,-0.412308446,0.0001230393,0.7957130366\C,0.8014358222,-0.0000826901,
0.0626814146\C,0.8034549599,-0.0002426744,-1.3627984544\C,-0.441509126
6,-0.0002043388,-2.0809232277\N,1.9762175957,-0.0004233974,-2.02816178
41\S,3.3234223514,-0.0004481037,-1.0716709482\S,-3.1003242853,0.000420
8812,1.0186888564\S,2.3639353823,-0.0001495072,0.8502865258\H,-2.56936
33249,0.00001645,-1.8973419663\N,-0.4241891133,0.0002846892,2.14074007
58\S,-1.9292923871,0.0005246102,2.8240390093\C,-0.4233130493,-0.000336
2622,-3.5840873527\H,0.1067139998,0.8777248688,-3.9718536488\H,0.10726
50147,-0.878125559,-3.9716938852\H,-1.4395673834,-0.0006722981,-3.9888
5178\\Version=x86-Linux-G03RevB.05\State=3-A\HF=-1971.3608272\S2=2.039
116\S2-1=0.\S2A=2.000787\RMSD=6.451e-09\RMSF=4.875e-05\Dipole=-0.53994
6,0.0000284,-0.3906179\PG=C01 [X(C7H4N2S4)]\\@
```

Table 179. Computational output parameters for singlet **181g**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4\GAUSSIAN\03-Sep-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo040\\0,1\C,0.,0.,0.\C,-0
.0002701016,-1.4295605534,0.0001779455\C,0.8287621563,-2.2109072096,-0
.878714398\C,1.6948049597,-0.1457386507,-1.7973906713\C,0.8738095465,0
.6076481238,-0.927091107\N,-0.7916540457,0.6833396351,0.8406240742\S,-
1.7324628363,-0.2734088313,1.8363993089\S,-1.0592488061,-2.1887987881,
1.1234200772\C,1.6648925962,-1.586719251,-1.7654385566\S,0.9942897678,
2.3640291269,-1.0547976512\N,2.510273659,0.4581426982,-2.6623778506\S,
2.4526041834,2.1094273467,-2.6016139829\H,2.3087991326,-2.124094439,-2
.4480863458\O,0.6832026731,-3.5507965706,-0.7241119778\C,1.4647264822,
-4.4061006834,-1.5532972714\H,1.1948457631,-5.4229797095,-1.267077757\
H,1.231958125,-4.2457445613,-2.6129790901\H,2.5363112902,-4.2458893036
,-1.3834693702\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-2046.538803
9\S2=0.\S2-1=0.\S2A=0.\RMSD=3.163e-09\RMSF=1.353e-05\Dipole=0.672924,-
0.0006699,1.6163698\PG=C01 [X(C7H4N2O1S4)]\\@
```

Table 180. Computational output parameters for triplet **181g**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2O1S4(3)\GAUSSIAN\20-Aug-200
7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo040\\0,3\C,-0.8060184
408,0.0001377536,-0.4202325677\C,-0.832012085,0.0002982749,1.008277940
6\C,0.3599352527,0.0001121004,1.7665043238\C,1.6593876483,-0.000387167
,-0.2978513052\C,0.4577134355,-0.0002029042,-1.065201957\N,-1.95560783
52,0.0003039393,-1.1214012298\S,-3.327614651,0.0006972991,-0.198869728
9\S,-2.4214325999,0.0007161779,1.7504528775\C,1.5891861025,-0.00022287
84,1.1288357498\S,0.634390831,-0.0004176306,-2.8050171456\N,2.85193367
51,-0.0007104719,-0.9233693887\S,2.7700249976,-0.0008567541,-2.5755748
021\H,2.521536457,-0.0003652891,1.6771348468\O,0.1740425284,0.00029710
94,3.1140195951\C,1.323919999,0.0000422002,3.9526680479\H,0.9437281672
,0.0001829395,4.9749609126\H,1.9345458136,-0.8960488744,3.7876779428\H
,1.9349997392,0.8958103226,3.7876032579\\Version=x86-Linux-G03RevB.05\
State=3-A\HF=-2046.564166\S2=2.037695\S2-1=0.\S2A=2.000719\RMSD=7.654e
-09\RMSF=9.084e-05\Dipole=0.2219348,0.0000218,1.066476\PG=C01 [X(C7H4N
2O1S4)]\\@
```

Table 181. Computational output parameters for singlet **181h**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H3N3S4\GAUSSIAN\31-Aug-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo39\\0,1\C,-1.7392780623,-0
.0086028529,-0.1303800717\C,-1.7630101966,-0.0081785158,1.3054390655\C
,-0.5830806791,-0.0066906022,2.011166118\C,0.7330354315,0.0205738355,-
0.1508471213\C,-0.5061167137,0.02448812,-0.8238823481\N,-0.5401442668,
-0.0725917242,3.4030686312\H,0.184704733,0.4835718705,3.843346387\H,-1
.436280744,0.0722879733,3.8531997926\C,0.6605347777,-0.0129138542,1.27
9763679\H,-2.7252401865,-0.0003034916,1.8053210864\N,1.9172088876,0.00
22711594,-0.7802090404\N,-2.8936380651,-0.0162643762,-0.7994992957\S,-
0.5920987928,0.0304127205,-2.5852986915\S,2.1807535832,-0.0920894654,2
.0976691837\S,-2.7242443605,0.0076518445,-2.4401261612\S,3.2468597553,
0.0539299911,0.2269465902\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-
1987.3680542\S2=0.\S2-1=0.\S2A=0.\RMSD=1.664e-09\RMSF=2.394e-05\Dipole
=-0.5098054,0.4325362,1.5412117\PG=C01 [X(C6H3N3S4)]\\@
```

Table 182. Computational output parameters for triplet **181h**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H3N3S4(3)\GAUSSIAN\09-Aug-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo39\\0,3\C,-1.7504419871
,-0.012869201,-0.1286837575\C,-1.7459088,-0.0122776803,1.2943582582\C,
-0.5566907197,-0.0126818049,2.0160237662\C,0.7150422343,0.0151726942,-
0.1220816078\C,-0.5104470771,0.0130022659,-0.8341449114\N,-0.547957294
,-0.0717406462,3.4124673925\H,0.170945624,0.4891367894,3.8578587297\H,
-1.4517394752,0.1028571725,3.8362366503\C,0.6688573694,-0.0194504999,1
.3094952665\H,-2.7025618636,-0.005708705,1.8061166215\N,1.8969204024,0
.0436556036,-0.7653980937\N,-2.9088712682,-0.0149220532,-0.8172374856\
S,-0.5967426703,0.0394101047,-2.5810738495\S,2.2343198927,-0.099498734
2,2.1118156324\S,-2.74227693,0.0140881391,-2.4608460809\S,3.2284651272
,0.0390873511,0.2101769993\\Version=x86-Linux-G03RevB.05\State=3-A\HF=
-1987.3938806\S2=2.040089\S2-1=0.\S2A=2.000814\RMSD=5.208e-09\RMSF=1.6
00e-05\Dipole=0.0846083,0.4357772,1.1339569\PG=C01 [X(C6H3N3S4)]\\@
```

Table 183. Computational output parameters for singlet **181i**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H4N2S4\GAUSSIAN\30-Aug-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo37\\0,1\C,-0.7266157529,0.
0000000176,-0.1876342371\C,-0.704548358,0.0000000721,1.2484909327\C,0.
5058628368,0.0000000607,2.0264911457\C,1.7386461286,-0.0000000626,-0.0
836050762\C,0.5328760486,-0.0000000496,-0.8168339056\N,-1.8899789863,0
.0000000683,-0.8587358963\S,-3.2521528889,0.0000000964,0.0982725836\S,
-2.2581901186,0.0000001541,2.0027751844\C,1.7000804552,-0.0000000059,1
.3561096032\S,0.6851996356,-0.0000001076,-2.5807203332\N,2.9229807984,
-0.0000001368,-0.6978996257\S,2.8194100515,-0.0000001987,-2.3471350262
\H,2.6451254787,-0.0000000323,1.8883177954\C,0.4437750626,0.0000001346
,3.5325830305\H,-0.0867781222,0.8831809698,3.9101363759\H,-0.086778423
4,-0.8831804872,3.9101364751\H,1.4486929833,-0.0000000039,3.9631705108
\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-1971.3342458\S2=0.\S2-1=0
.\S2A=0.\RMSD=4.734e-09\RMSF=1.078e-04\Dipole=0.2227918,0.,1.3926151\P
G=C01 [X(C7H4N2S4)]\\@
```

Table 184. Computational output parameters for triplet **181i**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H4N2S4(3)\GAUSSIAN\03-Aug-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo37\\0,3\C,-0.7112384141
,0.0000000078,-0.1572018364\C,-0.7078667473,0.0000000628,1.278272249\C
,0.486664202,0.0000000469,2.0281751524\C,1.7549457049,-0.0000000371,-0
.0785648629\C,0.5405026919,-0.0000000421,-0.8230318424\N,-1.866559799,
0.0000000038,-0.8463036278\S,-3.2336208715,0.0000000659,0.0805978662\S
,-2.3081689923,0.0000001334,2.0181220412\C,1.6954411455,0.0000000034,1
.34588807\S,0.6859884831,-0.0000001118,-2.5662170352\N,2.9385903484,-0
.0000000849,-0.7251827042\S,2.8282580219,-0.0000001346,-2.3736963426\H
,2.6338931946,-0.000000004,1.8895194327\C,0.4443619863,0.000000127,3.5
35572453\H,-0.0833670726,0.8832115012,3.9183519302\H,-0.0833677672,-0.
8832107593,3.9183520486\H,1.452458124,-0.0000002495,3.9586201433\\Vers
ion=x86-Linux-G03RevB.05\State=3-A\HF=-1971.3602333\S2=2.04018\S2-1=0.
\S2A=2.000826\RMSD=4.958e-09\RMSF=4.139e-05\Dipole=-0.1912433,0.,0.821
515\PG=C01 [X(C7H4N2S4)]\\@
```

Table 185. Computational output parameters for singlet **181j**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4\GAUSSIAN\06-May-2007\0
\\# opt ub3lyp/6-31g(d) geom=connectivity\\neo48\\0,1\C,0.0082578061,0
.,-0.0225977864\C,-0.0035029483,0.,1.4142260123\C,1.1977582151,0.,2.19
9784231\C,2.4031055924,0.,1.4671517062\C,2.4261818003,0.,0.0510754795\
C,1.2010722842,0.,-0.6971633901\N,3.5884170343,0.,-0.6052080845\S,4.91
54406394,0.,0.3666633224\S,-1.4828998848,0.,2.3122372782\S,3.967808886
,0.,2.2792662397\N,1.1398280021,0.,3.5369037787\S,-0.3910358665,0.,4.1
89381557\H,1.2286824365,0.,-1.7793969205\O,-1.1407758932,0.,-0.7517877
741\H,-1.9214744343,0.,-0.1762530026\\Version=AM64L-G03RevD.02\State=1
-A'\HF=-2007.2268116\S2=0.\S2-1=0.\S2A=0.\RMSD=4.780e-09\RMSF=7.928e-0
5\Thermal=0.\Dipole=-0.6875625,0.,-0.390407\PG=CS [SG(C6H2N2O1S4)]\\@
```

Table 186. Computational output parameters for triplet **181j**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2O1S4(3)\GAUSSIAN\28-Sep-200
7\0\\# opt ub3lyp/6-31g(d) geom=connectivity\\neo48\\0,3\C,-0.01696484
```

```
36,0.,0.0200717457\C,-0.0295718284,0.,1.4283488442\C,1.1903965715,0.,2
.1770399259\C,2.4155847637,0.,1.462206859\C,2.4220619514,0.,0.03533153
2\C,1.1825008924,0.,-0.6702301661\N,3.5933212503,0.,-0.6286838674\S,4.
9374879945,0.,0.3342373915\S,-1.5105782479,0.,2.3682203533\S,3.9751763
372,0.,2.2539560813\N,1.1594811554,0.,3.5224684529\S,-0.3560132394,0.,
4.1818052274\H,1.2081430773,0.,-1.7553553257\O,-1.2378892714,0.,-0.588
2100156\H,-1.1191224201,0.,-1.5511102967\\Version=AM64L-G03RevD.02\Sta
te=3-A'\HF=-2007.2566303\S2=2.037891\S2-1=0.\S2A=2.000729\RMSD=7.382e-
09\RMSF=9.207e-05\Thermal=0.\Dipole=-0.5466933,0.,-0.6167112\PG=CS [SG
(C6H2N2O1S4)]\\@
```

Table 187. Computational output parameters for singlet **181k**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4\GAUSSIAN\20-Jun-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis24\\0,1\C,-1.449759
5992,0.,-0.5320508544\C,-1.4447345319,0.,0.9023234049\C,-0.2443021929,
0.,1.6674052493\C,1.0324659553,0.,-0.4167265543\C,-0.1835806761,0.,-1.
142600163\N,-2.6103670097,0.,-1.2108477226\S,-3.9763106077,0.,-0.26592
50936\S,-2.9979151305,0.,1.6504342085\C,0.9673602838,0.,1.0316202449\S
,-0.0364139837,0.,-2.9100862358\N,2.2078443342,0.,-1.0368203986\S,2.09
89801136,0.,-2.6840945957\H,-0.2907810066,0.,2.7499595631\Br,2.5608656
581,0.,2.0365324796\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-4503.
1145994\S2=0.\S2-1=0.\S2A=0.\RMSD=3.669e-09\RMSF=8.355e-05\Dipole=-0.1
406492,0.,0.9318931\PG=CS [SG(C6H1Br1N2S4)]\\@
```

Table 188. Computational output parameters for triplet **181k**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4(3)\GAUSSIAN\25-Jun-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis24\\0,3\C,-1.442
9011248,0.,-0.4872946319\C,-1.4398796622,0.,0.9485208689\C,-0.24385078
26,0.,1.6748031978\C,1.0413531455,0.,-0.4189714539\C,-0.187359589,0.,-
1.1460377271\N,-2.5972854617,0.,-1.174803057\S,-3.964179669,0.,-0.2486
932083\S,-3.035106885,0.,1.6919736101\C,0.9727851073,0.,1.0111072408\S
,-0.0585616477,0.,-2.8909774049\N,2.2118832166,0.,-1.0791530897\S,2.08
36024326,0.,-2.722709933\H,-0.2561724065,0.,2.7585360154\Br,2.58117251
03,0.,2.0072258006\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-4503.1
411236\S2=2.038873\S2-1=0.\S2A=2.000779\RMSD=6.340e-09\RMSF=5.238e-05\
```

```
Dipole=-0.5703053,0.,0.2193137\PG=CS [SG(C6H1Br1N2S4)]\\@
```

Table 189. Computational output parameters for singlet **181l**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4\GAUSSIAN\15-Jun-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo22\\0,1\C,-0.8235164865
,0.0001319769,-0.2934156384\C,-0.8431344755,0.0001297311,1.1226128769\
C,0.4259296118,-0.0000915751,1.8270636885\C,1.603254175,-0.0002651742,
1.1280616782\C,1.5791989098,-0.0002541955,-0.2951391674\C,0.3605735545
,-0.0000638116,-1.0510526587\H,2.5486514885,-0.0004037269,1.657447876\
N,-1.9859937282,0.0003134038,1.7996964921\N,0.3899189938,-0.0000765139
,-2.3952865681\S,1.9112361784,-0.000292266,-3.0631855382\S,-3.33263741
3,0.0005042671,0.8447854975\S,3.0305639595,-0.000449191,-1.2259842858\
S,-2.4063336574,0.0003971759,-1.0931921546\Cl,0.4449867551,-0.00007858
75,3.5578895105\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-2391.60473
9\S2=0.\S2-1=0.\S2A=0.\RMSD=2.117e-09\RMSF=1.267e-04\Dipole=0.8957725,
-0.0001369,0.2550834\PG=C01 [X(C6H1Cl1N2S4)]\\@
```

Table 190. Computational output parameters for triplet **181l**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4(3)\GAUSSIAN\20-Jun-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo22\\0,3\C,-0.8343529
185,0.,-0.2830780545\C,-0.8342903541,0.,1.1445061622\C,0.4329436442,0.
,1.8143008958\C,1.6235845229,0.,1.1033921251\C,1.6061596607,0.,-0.2956
103083\C,0.3715706836,0.,-1.0285373883\H,2.5622889841,0.,1.6454948793\
N,-1.9971022515,0.,1.8172983141\N,0.3667119553,0.,-2.3722370654\S,1.85
93990333,0.,-3.0780556037\S,-3.3471973314,0.,0.8715705377\S,3.05779088
09,0.,-1.2907996428\S,-2.4025441156,0.,-1.0587070017\Cl,0.4692691872,0
.,3.5532413621\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-2391.63126
29\S2=2.039168\S2-1=0.\S2A=2.00079\RMSD=9.527e-09\RMSF=5.159e-05\Dipol
e=0.4919509,0.,-0.4671549\PG=CS [SG(C6H1Cl1N2S4)]\\@
```

Table 191. Computational output parameters for singlet **181m**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4\GAUSSIAN\30-Aug-2007\0
\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis34\\0,1\C,-0.7335877
578,0.,-0.1642726206\C,-0.7071354905,0.,1.2687270075\C,0.5229551981,0.
,1.9903014708\C,1.7451855085,0.,-0.0728127136\C,0.5291715638,0.,-0.796
3931577\N,-1.9038764918,0.,-0.8166922242\S,-3.2523604179,0.,0.16437774
74\S,-2.2299184038,0.,2.0653957045\C,1.7319314431,0.,1.3684991459\S,0.
6675004994,0.,-2.5586548579\N,2.9199624665,0.,-0.7041059511\S,2.798391
9478,0.,-2.3483315812\H,2.6612618989,0.,1.9237084849\F,0.4396883866,0.
,3.3325546383\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-2031.243814
9\S2=0.\S2-1=0.\S2A=0.\RMSD=1.361e-09\RMSF=1.692e-04\Dipole=0.2566956,
0.,0.5197625\PG=CS [SG(C6H1F1N2S4)]\\@
```

Table 192. Computational output parameters for triplet **181m**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1F1N2S4(3)\GAUSSIAN\30-Jul-200
 7\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis34\\0,3\C,-0.7157
 051906,0.,-0.1332974004\C,-0.7130796411,0.,1.301191382\C,0.5020247697,
 0.,1.9956697652\C,1.7592654472,0.,-0.0702624947\C,0.5339434114,0.,-0.8
 045698771\N,-1.8822907342,0.,-0.8024073038\S,-3.2326471761,0.,0.146478
 6123\S,-2.2822583847,0.,2.0796168904\C,1.7211716694,0.,1.3562159093\S,
 0.6669362039,0.,-2.5484879392\N,2.9337279851,0.,-0.7286490852\S,2.8091
 701255,0.,-2.374587697\H,2.6442507359,0.,1.9221021176\F,0.454528157,0.
 ,3.3419212263\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-2031.270853
 2\S2=2.038614\S2-1=0.\S2A=2.000763\RMSD=5.412e-09\RMSF=6.069e-05\Dipol
 e=-0.275769,0.,0.0674351\PG=CS [SG(C6H1F1N2S4)]\\@
```

Table 193. Computational output parameters for singlet **181n**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4\GAUSSIAN\30-Aug-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo35\\0,1\C,-0.7582144681
,0.,-0.4113670323\C,-0.7349192816,0.,1.0247803812\C,0.4969572295,0.,1.
7543942898\C,1.7138305166,0.,-0.3299472044\C,0.4997478857,0.,-1.048375
2851\N,-1.9233569908,0.,-1.0753457917\S,-3.2788226402,0.,-0.1033708682
\S,-2.2747906679,0.,1.7956061862\C,1.7000633035,0.,1.1097114507\S,0.63
```

```
30296995,0.,-2.812716532\N,2.8919090148,0.,-0.9582119606\S,2.766689479
9,0.,-2.603491532\H,2.6404888421,0.,1.6462633996\Cl,0.4433624668,0.,3.
5045308943\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-2391.6047737\S
2=0.\S2-1=0.\S2A=0.\RMSD=2.492e-09\RMSF=8.372e-05\Dipole=0.1978772,0.,
0.5253901\PG=CS [SG(C6H1Cl1N2S4)]\\@
```

Table 194. Computational output parameters for triplet **181n**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Cl1N2S4(3)\GAUSSIAN\31-Jul-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo35\\0,3\C,-0.7360525
725,0.,-0.3946544219\C,-0.7560253324,0.,1.042609005\C,0.4476964167,0.,
1.7634591383\C,1.7347103837,0.,-0.2982918308\C,0.5219880204,0.,-1.0482
083266\N,-1.8855644354,0.,-1.0917654349\S,-3.258153627,0.,-0.173176266
2\S,-2.3516646247,0.,1.773986536\C,1.675246353,0.,1.1259533376\S,0.678
0002426,0.,-2.7892794481\N,2.9208799066,0.,-0.9379917357\S,2.818164176
2,0.,-2.5860234237\H,2.5994365987,0.,1.6897854013\Cl,0.3909668715,0.,3
.5155997068\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-2391.6326213\
S2=2.04031\S2-1=0.\S2A=2.000831\RMSD=7.578e-09\RMSF=1.075e-04\Dipole=-
0.2733401,0.,-0.0208548\PG=CS [SG(C6H1Cl1N2S4)]\\@
```

Table 195. Computational output parameters for singlet **181o**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4\GAUSSIAN\07-Sep-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo35\\0,1\C,-0.7944584789
,0.,-0.8811979645\C,-0.7923814644,0.,0.5544103878\C,0.4249507837,0.,1.
3033580962\C,1.676160019,0.,-0.7594254122\C,0.4736625915,0.,-1.4975585
713\N,-1.949954127,0.,-1.5625661918\S,-3.3186848614,0.,-0.6084923185\S
,-2.3420594203,0.,1.3040415504\C,1.6386821378,0.,0.6804783651\S,0.6353
457957,0.,-3.2599186862\N,2.864558951,0.,-1.3681644978\S,2.7658109488,
0.,-3.0154806432\H,2.5702832839,0.,1.2320880263\Br,0.3263197146,0.,3.2
045782558\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-4503.1153877\S2
=0.\S2-1=0.\S2A=0.\RMSD=4.957e-09\RMSF=5.785e-05\Dipole=0.1928,0.,0.67
48717\PG=CS [SG(C6H1Br1N2S4)]\\@
```

Table 196. Computational output parameters for triplet **5181o**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C6H1Br1N2S4(3)\GAUSSIAN\11-Sep-20
07\0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo36\\0,3\C,-0.7911281
738,0.,-0.8425504063\C,-0.7879152958,0.,0.5940756732\C,0.4231104017,0.
,1.2980669034\C,1.6819222537,0.,-0.7790841677\C,0.4586212445,0.,-1.512
4850571\N,-1.9510611531,0.,-1.5216742728\S,-3.3087847887,0.,-0.5789408
183\S,-2.3692418508,0.,1.3536801128\C,1.6424049457,0.,0.6467411284\S,0
.5910089401,0.,-3.2558765955\N,2.8589325695,0.,-1.4355458459\S,2.73452
09755,0.,-3.0815164804\H,2.5749675537,0.,1.1964199019\Br,0.3699367959,
0.,3.2022284853\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-4503.1432
843\S2=2.04015\S2-1=0.\S2A=2.000825\RMSD=5.696e-09\RMSF=5.848e-05\Dipo
le=-0.2414082,0.,0.1049185\PG=CS [SG(C6H1Br1N2S4)]\\@
```

Table 197. Computational output parameters for singlet **181p**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H1N3S4\GAUSSIAN\31-Aug-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis38\\0,1\C,-0.744201663
3,0.,-0.332613957\C,-0.7231427586,0.,1.0996867657\C,0.5104246813,0.,1.
8444647899\C,1.7305147759,0.,-0.2537648774\C,0.5141001576,0.,-0.969653
7096\N,-1.9109166688,0.,-0.9962098165\S,-3.2641490865,0.,-0.0279681824
\S,-2.2612537304,0.,1.870369607\C,1.7152187836,0.,1.1809508418\S,0.644
0900552,0.,-2.7348807288\N,2.9095710411,0.,-0.8829371525\S,2.782749652
9,0.,-2.5268498412\H,2.6566333419,0.,1.7170764134\C,0.4753542918,0.,3.
2765214722\N,0.4371694549,0.,4.4389529632\\Version=x86-Linux-G03RevB.0
5\State=1-A'\HF=-2024.2500085\S2=0.\S2-1=0.\S2A=0.\RMSD=4.155e-09\RMSF
=6.632e-05\Dipole=0.1249539,0.,-0.5507447\PG=CS [SG(C7H1N3S4)]\\@
```

Table 198. Computational output parameters for triplet **181p**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H1N3S4(3)\GAUSSIAN\07-Aug-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neoklis38\\0,3\C,-0.727919
6747,0.,-0.3032974025\C,-0.7245061169,0.,1.1310444385\C,0.4920335093,0
.,1.8490746192\C,1.7472636861,0.,-0.2488266946\C,0.5204679968,0.,-0.97
67370483\N,-1.8882322135,0.,-0.9828165128\S,-3.2460980969,0.,-0.047239
2677\S,-2.3084084794,0.,1.8839156972\C,1.7124700242,0.,1.1718533612\S,
```

```
0.643314062,0.,-2.7184154075\N,2.9221419429,0.,-0.9116613839\S,2.78978
49012,0.,-2.5547991559\H,2.6473611929,0.,1.7183847925\C,0.473960159,0.
,3.2806127175\N,0.442167858,0.,4.4436038117\\Version=x86-Linux-G03RevB
.05\State=3-A'\HF=-2024.2785874\S2=2.042048\S2-1=0.\S2A=2.000903\RMSD=
8.139e-09\RMSF=1.247e-04\Dipole=-0.332974,0.,-1.1491588\PG=CS [SG(C7H1
N3S4)]\\@
```

Table 199. Computational output parameters for singlet **181q**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C7H1N3S4\GAUSSIAN\29-Aug-2007\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo27\\0,1\C,-1.6000016166,0.
,-1.2103697699\C,-1.5901341281,0.,0.2110026118\C,-0.3797121392,0.,0.98
52046984\C,0.8151888023,0.,0.2192326971\C,0.8335096938,0.,-1.189955968
7\C,-0.4216932384,0.,-1.9253921183\N,1.9840255408,0.,-1.8619484456\S,3
.3181359862,0.,-0.9057237818\S,-3.0505897171,0.,1.1351853861\S,2.38895
15154,0.,1.0153866807\H,-2.546680777,0.,-1.7390275438\N,-0.4056533494,
0.,2.3130576064\S,-1.940321724,0.,2.9880210358\C,-0.4286267163,0.,-3.3
492071276\N,-0.4759893538,0.,-4.5125336929\\Version=x86-Linux-G03RevB.
05\State=1-A'\HF=-2024.2515991\S2=0.\S2-1=0.\S2A=0.\RMSD=1.485e-09\RMS
F=2.220e-04\Dipole=-0.2661169,0.,0.9081476\PG=CS [SG(C7H1N3S4)]\\@
```

Table 200. Computational output parameters for triplet **181q**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C7H1N3S4(3)\GAUSSIAN\03-Jul-2007\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\neo27\\0,3\C,-1.6202911978
,0.,-1.200830702\C,-1.6226202731,0.,0.1933256796\C,-0.3943521437,0.,0.
9461733495\C,0.8241592699,0.,0.2216219211\C,0.8406346777,0.,-1.2034526
192\C,-0.4153520803,0.,-1.9099034625\N,2.0076747026,0.,-1.8628469173\S
,3.3485564375,0.,-0.9051887926\S,-3.0845480058,0.,1.1699816372\S,2.382
7736452,0.,1.0146229671\H,-2.5526701524,0.,-1.7540321982\N,-0.41453383
69,0.,2.2865369719\S,-1.9149901567,0.,2.9700968635\C,-0.4317338027,0.,
-3.3340265408\N,-0.4843790474,0.,-4.4973495342\\Version=x86-Linux-G03R
evB.05\State=3-A'\HF=-2024.2802697\S2=2.039005\S2-1=0.\S2A=2.000805\RM
SD=7.706e-09\RMSF=9.285e-05\Dipole=-0.4672368,0.,1.7523461\PG=CS [SG(C
7H1N3S4)]\\@
```

Table 201. Computational output parameters for singlet **185**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C5H1N3S4\GAUSSIAN\09-Nov-2009\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\azo1 opt\\0,1\C,-0.7316565224
,0.,0.027028553\C,-0.6864526756,0.,1.4562380733\C,0.5566059678,0.,2.17
27587866\C,1.7450203974,0.,0.235769966\C,0.5675115596,0.,-0.5574440347
\S,-3.2488021051,0.,0.3247656304\S,-2.2264842988,0.,2.2413204814\S,0.7
795206197,0.,-2.2931622076\S,2.8882192371,0.,-1.9906009636\H,0.5318861
191,0.,3.260976052\N,1.7396482937,0.,1.6142033837\N,-1.8672400238,0.,-
0.6496753659\N,2.9394040549,0.,-0.3622781846\\Version=x86-Linux-G03Rev
B.05\State=1-A'\HF=-1948.0475766\S2=0.\S2-1=0.\S2A=0.\RMSD=6.190e-09\R
MSF=1.248e-04\Dipole=0.125318,0.,0.0031261\PG=CS [SG(C5H1N3S4)]\\@
```

Table 202. Computational output parameters for triplet **185**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C5H1N3S4(3)\GAUSSIAN\12-Nov-2009\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\azo1 opt triplet\\0,3\C,-0
.7005518956,0.,0.040768343\C,-0.7404780437,0.,1.4739161955\C,0.4606321
841,0.,2.2064743308\C,1.7420478186,0.,0.2895609432\C,0.582855559,0.,-0
.5523842901\S,-3.2218127665,0.,0.2144333913\S,-2.3478191657,0.,2.17567
47079\S,0.8440923784,0.,-2.2763945867\S,2.9744380453,0.,-1.9193281504\
H,0.4358860347,0.,3.2941497875\N,1.6599146073,0.,1.6485981114\N,-1.837
064511,0.,-0.6786346669\N,2.9649648133,0.,-0.2777246894\\Version=x86-L
inux-G03RevB.05\State=3-A'\HF=-1948.0753448\S2=2.034587\S2-1=0.\S2A=2.
00061\RMSD=8.293e-09\RMSF=8.295e-05\Dipole=-1.0535803,0.,0.0709889\PG=
CS [SG(C5H1N3S4)]\\@
```

Table 203. Computational output parameters for singlet **186**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C5H1N3S4\GAUSSIAN\10-Nov-2009\0\\
# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\azo2 opt\\0,1\C,-0.7151285993
,0.,0.0305411811\C,-0.6652390699,0.,1.4659945423\C,1.7259493843,0.,0.1
881517591\C,0.5486720108,0.,-0.5860512777\S,-3.2241433841,0.,0.3893165
224\S,-2.2033306851,0.,2.2611567696\S,0.7722358326,0.,-2.3459917644\S,
2.905735777,0.,-2.0179873333\N,-1.8918590869,0.,-0.6154304402\N,2.9406
631812,0.,-0.3628178312\N,0.4498808181,0.,2.241810352\C,1.604414287,0
```

```
.,1.6251898048\H,2.5092368851,0.,2.2282022706\\Version=x86-Linux-G03Re
vB.05\State=1-A'\HF=-1948.0482229\S2=0.\S2-1=0.\S2A=0.\RMSD=9.257e-09\
RMSF=1.375e-04\Dipole=0.0379826,0.,0.4511727\PG=CS [SG(C5H1N3S4)]\\@
```

Table 204. Computational output parameters for triplet **186**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C5H1N3S4(3)\GAUSSIAN\12-Nov-2009\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\azo2 opt triplet\\0,3\C,-0
.7017638151,0.,0.0343336918\C,-0.7115490425,0.,1.4741901023\C,1.740195
3252,0.,0.2614603526\C,0.5804870008,0.,-0.5652999158\S,-3.2192822111,0
.,0.2514640306\S,-2.3314926352,0.,2.1945086299\S,0.8475266793,0.,-2.28
993933\S,2.9754164065,0.,-1.9454609197\N,-1.8410424015,0.,-0.672342273
8\N,2.969250401,0.,-0.2940691907\N,0.3599513239,0.,2.2540732691\C,1.55
86099186,0.,1.6777955084\H,2.4323165827,0.,2.3223303592\\Version=x86-L
inux-G03RevB.05\State=3-A'\HF=-1948.0764468\S2=2.036778\S2-1=0.\S2A=2.
000703\RMSD=9.413e-09\RMSF=1.290e-04\Dipole=-0.181276,0.,-0.2653129\PG
=CS [SG(C5H1N3S4)]\\@
```

Table 205. Computational output parameters for singlet **187**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C4N4S4\GAUSSIAN\10-Nov-2009\0\\#
OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\azo3 opt\\0,1\C,-0.7152735766,0
.,0.0369202758\C,-0.622911979,0.,1.4860795787\C,1.7343726635,0.,0.2574
705974\C,0.5579212459,0.,-0.6030590643\S,-3.2060882892,0.,0.3625340011
\S,-2.2472371891,0.,2.2864257889\S,0.7891616805,0.,-2.2857131221\S,2.8
92688899,0.,-2.0100682667\N,-1.857609066,0.,-0.6142131241\N,2.93147833
63,0.,-0.4052811987\N,0.4660212945,0.,2.1866272304\N,1.6913877577,0.,1
.5878209859\\Version=x86-Linux-G03RevB.05\State=1-A'\HF=-1964.0516979\
S2=0.\S2-1=0.\S2A=0.\RMSD=2.849e-09\RMSF=1.860e-04\Dipole=-0.4438337,0
.,-2.1570986\PG=CS [SG(C4N4S4)]\\@
```

Table 206. Computational output parameters for triplet **187**.

```
1\1\GINC-CHEM40\FOpt\UB3LYP\6-31G(d)\C4N4S4(3)\GAUSSIAN\12-Nov-2009\0\
\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\azo3 opt triplet\\0,3\C,-0.7
146014661,0.,-0.0171122426\C,-0.7336355658,0.,1.4219380425\C,1.6861689
674,0.,0.3303355123\C,0.5778861367,0.,-0.5727581169\S,-3.2260837677,0.
,0.1913022448\S,-2.3480571755,0.,2.1354101666\S,0.9274050109,0.,-2.278
4241931\S,3.0416680709,0.,-1.8018429633\N,-1.8503384105,0.,-0.72670280
35\N,2.9411469518,0.,-0.1676847549\N,0.3311454428,0.,2.2153592989\N,1.
5474999228,0.,1.6908077951\\Version=x86-Linux-G03RevB.05\State=3-A'\HF
=-1964.0756847\S2=2.035028\S2-1=0.\S2A=2.000633\RMSD=8.075e-09\RMSF=8.
753e-05\Dipole=-1.0437424,0.,-0.9606857\PG=CS [SG(C4N4S4)]\\@
```

Table 207. Computational output parameters for singlet **189a**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4H1N3S4\GAUSSIAN\22-Aug-2009\0\\
# opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,-0.0
272297893,-0.0360615999,-0.0389130636\C,0.0052194948,-0.0108236233,1.3
945997565\C,1.4381260699,0.0052397917,1.7667562259\C,2.162168425,-0.21
08666882,0.5478593618\S,-1.5762232784,-0.3792865554,-0.7937998618\S,-2
.4672944994,-0.3463711066,1.2469015357\S,3.6846277097,0.4196585376,2.7
812609341\N,-1.0652499725,-0.1810179675,2.1234522447\S,3.8963639424,0.
0677285005,0.5924561185\N,2.0277082094,0.3432488355,2.8822111696\N,1.2
594969269,-0.1904758108,-0.4819944618\H,1.5136032354,-0.2791510044,-1.
4565473685\\Version=AM64L-G03RevD.02\State=1-A\HF=-1909.9150512\S2=0.\
S2-1=0.\S2A=0.\RMSD=8.161e-09\RMSF=5.831e-07\Thermal=0.\Dipole=0.35814
03,-0.1249794,-1.373543\PG=C01 [X(C4H1N3S4)]\\@
```

Table 208. Computational output parameters for triplet **189a**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4H1N3S4(3)\GAUSSIAN\23-Aug-2009\
0\\# opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0
.0096904068,-0.1599216644,0.036892666\C,0.0151435884,-0.0456426935,1.4
442961327\C,1.4077272961,0.0459821717,1.8331059551\C,2.1531249995,-0.0
366407575,0.6366822619\S,-1.5005344561,-0.3945079948,-0.7861771437\S,-
2.473929404,-0.2145926833,1.1945673509\S,3.6641031723,0.2768537016,2.9
```

```
016840603\N,-1.125444167,-0.1167975582,2.1500704123\S,3.8786851102,0.1
406440885,0.7019982804\N,2.0123723213,0.2597533257,3.0132869004\N,1.30
30453816,-0.1572597948,-0.4431442602\H,1.5778332504,-0.2303818356,-1.4
101088026\\Version=AM64L-G03RevD.02\State=3-B\HF=-1909.9302112\S2=2.01
9355\S2-1=0.\S2A=2.000202\RMSD=2.562e-09\RMSF=2.516e-06\Thermal=0.\Dip
ole=0.4900067,-0.1303926,-1.7243088\PG=C02 [C2(N1H1),X(C4N2S4)]\\@
```

Table 209. Computational output parameters for singlet **189b**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N2O1S4\GAUSSIAN\29-Jun-2009\0\\
# opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,0.02
55698427,0.2282581916,0.1051787114\C,-0.0262693644,0.072111993,1.52063
05888\C,1.3832698789,-0.0730613549,1.9309512479\C,2.0993304129,-0.2283
884667,0.708779497\S,-1.466260079,0.0639469221,-0.7841703085\S,-2.4937
955936,-0.0900825016,1.1872402206\S,3.6441228525,0.0887992242,2.974248
2273\N,-1.152033256,-0.1184143139,2.1627935565\O,1.2838313634,0.000155
7747,-0.3534283751\S,3.8353782676,-0.0638698672,0.7592714709\N,1.98839
16148,0.116854433,3.0771515578\\Version=AM64L-G03RevD.02\State=1-A\HF=
-1929.7532977\S2=0.\S2-1=0.\S2A=0.\RMSD=2.059e-09\RMSF=2.331e-06\Therm
al=0.\Dipole=0.135398,0.0001336,-0.4647958\PG=C01 [X(C4N2O1S4)]\\@
```

Table 210. Computational output parameters for triplet **189b**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N2O1S4(3)\GAUSSIAN\30-Jun-2009\
0\\# opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0
.0123437497,-0.2247959118,0.0462380657\C,0.0105168189,-0.071574731,1.4
359548781\C,1.4161385777,0.0718157147,1.7894115239\C,2.0946565334,-0.0
123751343,0.5698549821\S,-1.4823786094,-0.4299118488,-0.8066002165\S,-
2.4638673678,-0.286094106,1.1573577403\S,3.7223628368,0.3450158345,2.7
12939119\N,-1.1309337234,-0.0792206071,2.1349658337\O,1.2652895729,-0.
1924912179,-0.5042128592\S,3.822808716,0.1112834352,0.5274381925\N,2.0
75027327,0.247855482,2.9411318769\\Version=AM64L-G03RevD.02\State=3-A\
HF=-1929.7771997\S2=2.020627\S2-1=0.\S2A=2.000217\RMSD=6.669e-09\RMSF=
9.480e-07\Thermal=0.\Dipole=0.2216092,-0.0773325,-0.8499212\PG=C01 [X(
C4N2O1S4)]\\@
```

Table 211. Computational output parameters for singlet **189c**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N2S5\GAUSSIAN\30-Jun-2009\0\\#
opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,-0.138
1957536,-0.1086032047,-0.0906518736\C,0.0250142728,-0.0483415103,1.326
761634\C,1.4553560322,0.0298358629,1.6925972088\C,2.2873820992,-0.1432
85268,0.5449511129\S,-1.7733572004,-0.345548433,-0.6836827945\S,-2.463
9549434,-0.3237765843,1.4006556112\S,3.6062158042,0.4232548912,2.91542
85515\N,-0.9940814766,-0.1519419183,2.1458187045\S,4.0137493596,0.0618
339699,0.7881867187\N,1.9534124073,0.315252988,2.8718430082\S,1.370423
8311,-0.2291737349,-0.9074287587\\Version=AM64L-G03RevD.02\State=1-A\H
F=-2252.7537939\S2=0.\S2-1=0.\S2A=0.\RMSD=8.434e-09\RMSF=3.799e-06\The
rmal=0.\Dipole=0.1973672,-0.0688713,-0.7569547\PG=C01 [X(C4N2S5)]\\@
```

Table 212. Computational output parameters for triplet **189c**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N2S5(3)\GAUSSIAN\30-Jun-2009\0\
\# opt=tight ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,-0.
1336619062,-0.0000015959,-0.1005545924\C,0.0254232845,0.0000014243,1.2
947890863\C,1.4378732433,0.0000035221,1.660647805\C,2.2543594558,0.000
0020695,0.5180007272\S,-1.7524485725,-0.000004214,-0.7338407555\S,-2.4
843612976,-0.0000007729,1.3265087471\S,3.6166531389,0.0000079713,2.906
8191224\N,-1.0287631053,0.0000022154,2.1166066304\S,3.9770288999,0.000
0039807,0.7502325554\N,1.9605228684,0.0000063474,2.8909040342\S,1.3738
467137,-0.0000018962,-1.001580605\\Version=AM64L-G03RevD.02\HF=-2252.7
743248\S2=2.020902\S2-1=0.\S2A=2.000226\RMSD=4.183e-09\RMSF=2.355e-06\
Thermal=0.\Dipole=-0.9034262,-0.0000013,-0.2340094\PG=C02 [C2(S1),X(C4
N2S4)]\\@
```

Table 213. Computational output parameters for singlet **189d**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N2O2S5\GAUSSIAN\29-Aug-2009\0\\
# opt=tight ub3lyp/6-31g(d) geom=connectivity\\singlet opt\\0,1\C,0.01
35466293,-0.1259063537,-0.0077677794\C,0.015214635,-0.0262358367,1.401
2044237\C,1.3879907469,0.0221929325,1.9249495064\C,2.3328475016,-0.044
1510403,0.8771022591\S,-1.5235695466,-0.1932116042,-0.7783444983\S,-2.
```

```
4733634374,-0.0623291395,1.1828599479\S,3.3869352328,0.1444686352,3.41
86922733\N,-1.0889065325,0.0140231582,2.1001025377\S,3.9932829247,0.00
14482878,1.3264568202\N,1.7419305501,0.113976412,3.180124921\S,1.62956
56141,-0.1653559823,-0.7540822316\O,1.889608659,1.0405492376,-1.547156
4518\O,1.9103606742,-1.4664563177,-1.3697839082\\Version=AM64L-G03RevD
.02\State=1-A\HF=-2403.1230209\S2=0.\S2-1=0.\S2A=0.\RMSD=8.817e-09\RMS
F=4.632e-06\Thermal=0.\Dipole=-0.3416816,0.0601408,0.8900128\PG=C02 [C
2(S1),X(C4N2O2S4)]\\@
```

Table 214. Computational output parameters for triplet **189d**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C4N2O2S5(3)\GAUSSIAN\29-Aug-2009\
0\\# opt=tight ub3lyp/6-31g(d) geom=connectivity\\triplet opt\\0,3\C,-
0.0254379856,-0.0000548108,-0.010508848\C,0.0008472691,-0.0000000811,1
.3917855635\C,1.3854436939,0.0000008888,1.9240276288\C,2.3442562603,-0
.0000548622,0.9004070964\S,-1.5660107671,-0.0000641657,-0.7881209696\S
,-2.4901693149,0.0000260623,1.1875921835\S,3.371839621,0.0000341982,3.
4409619655\N,-1.1097379258,0.0000429637,2.1049389615\S,4.009023351,-0.
0000598084,1.3549350296\N,1.7323820882,0.0000481165,3.1974564623\S,1.6
149883482,-0.0001072089,-0.7402133947\O,1.8796450179,1.2649215684,-1.4
287000951\O,1.8796062806,-1.2651966928,-1.4286034109\\Version=AM64L-G0
3RevD.02\State=3-A\HF=-2403.1315058\S2=2.023853\S2-1=0.\S2A=2.000287\R
MSD=5.107e-09\RMSF=3.450e-06\Thermal=0.\Dipole=-0.3028934,0.0000345,0.
7879596\PG=C01 [X(C4N2O2S5)]\\@
```

Table 215. Computational output parameters for singlet **191**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2S4\GAUSSIAN\28-Sep-2010\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt\\0,1\C,-0.095099015,0.,0.
0002144284\C,0.0278822048,0.,1.4685065687\C,1.2435664772,0.,2.08198659
48\C,2.4487612051,0.,1.2928459228\C,2.3258405783,0.,-0.175569869\S,-2.
5932615294,0.,0.4424229676\S,4.9468817494,0.,0.8516339499\S,-1.5195853
844,0.,2.3106956449\H,1.3528063569,0.,3.1602292401\N,-1.2745912422,0.,
-0.5620881413\C,1.1099476724,0.,-0.7890474378\H,1.0007316989,0.,-1.867
3158865\N,3.6279355518,0.,1.8555135157\S,3.8733544028,0.,-1.0174209617
\\Version=AM64L-G03RevD.02\State=1-A'\HF=-1932.058867\S2=0.\S2-1=0.\S2
```

```
A=0.\RMSD=4.727e-09\RMSF=7.634e-05\Thermal=0.\Dipole=0.0003999,0.,0.00
03791\PG=CS [SG(C6H2N2S4)]\\@
```

Table 216. Computational output parameters for triplet **191**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2S4(3)\GAUSSIAN\01-Oct-2010\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0.01104
34534,0.,0.0048411833\C,-0.0012339297,0.,1.4345326065\C,1.1793087625,0
.,2.1690056317\C,2.4159709686,0.,1.4957747143\C,2.4282514245,0.,0.0660
80011\S,-2.5141625541,0.,0.2415608921\S,4.9411845726,0.,1.2590657542\S
,-1.6024068365,0.,2.185056702\H,1.1807751061,0.,3.2530205358\N,-1.1684
649813,0.,-0.6953953628\C,1.2477037122,0.,-0.6683888545\H,1.2462355894
,0.,-1.7524039797\N,3.5954836212,0.,2.1959764781\S,4.0294045564,0.,-0.
6844642598\\Version=AM64L-G03RevD.02\State=3-A'\HF=-1932.0277973\S2=2.
010729\S2-1=0.\S2A=2.000062\RMSD=4.545e-09\RMSF=1.975e-04\Thermal=0.\D
ipole=0.0000397,0.,0.0000601\PG=CS [SG(C6H2N2S4)]\\@
```

Table 217. Computational output parameters for singlet **192**.

```
1\1\GINC-CHEM53\FOpt\UB3LYP\6-31G(d)\C6H2N2S4\GAUSSIAN\10-May-2010\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,-0.0415966
308,0.,0.1402068075\C,-0.0696483267,0.,1.5059938916\C,1.1441325231,0.,
2.2682666149\C,2.3619757067,0.,1.6493712793\C,2.473910034,0.,0.1906806
593\S,4.967028028,0.,0.5880603563\H,1.0728058631,0.,3.3507789873\C,1.2
235808232,0.,-0.5944081908\H,-1.0137389079,0.,2.0405124318\S,-0.216413
5989,0.,-2.6681939637\N,1.24694612,0.,-1.8959931835\S,-1.4699266985,0.
,-0.912359671\N,3.6362852679,0.,-0.3956744862\S,3.9312875639,0.,2.4775
820641\\Version=AM64L-G03RevD.02\State=1-A'\HF=-1932.0454605\S2=0.\S2-
1=0.\S2A=0.\RMSD=7.355e-09\RMSF=1.092e-04\Thermal=0.\Dipole=-0.4771042
,0.,0.7639066\PG=CS [SG(C6H2N2S4)]\\@
```

Table 218. Computational output parameters for triplet **192**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2S4(3)\GAUSSIAN\01-Oct-2010\
0\\# opt ub3lyp/6-31g(d) geom=connectivity\\opt triplet\\0,3\C,0.04161
72256,0.,-0.014603957\C,0.0110478384,0.,1.396568036\C,1.1970899105,0.,
2.1077427957\C,2.4274163738,0.,1.415962567\C,2.4964033341,0.,-0.001397
95\S,4.9975999691,0.,0.3571073901\H,1.1801624759,0.,3.1921360563\C,1.2
593540483,0.,-0.7431452147\H,-0.9375007229,0.,1.9223375798\S,-0.234907
2747,0.,-2.780698147\N,1.2619399908,0.,-2.0951652841\S,-1.4216486221,0
.,-0.9900371926\N,3.687820755,0.,-0.6405685933\S,3.9771299333,0.,2.247
2938113\\Version=AM64L-G03RevD.02\State=3-A'\HF=-1932.0313828\S2=2.015
03\S2-1=0.\S2A=2.000113\RMSD=3.353e-09\RMSF=7.665e-05\Thermal=0.\Dipol
e=-0.6427159,0.,1.0718037\PG=CS [SG(C6H2N2S4)]\\@
```

Table 219. Computational output parameters for singlet **193**.

```
1\1\GINC-CHEM54\FOpt\UB3LYP\6-31G(d)\C6H2N2S4\GAUSSIAN\01-Oct-2010\0\\
# opt ub3lyp/6-31g(d) geom=connectivity\\opt singlet\\0,1\C,0.00758585
03,0.,0.0208665064\C,0.0037252685,0.,1.4715065573\C,1.1609271851,0.,2.
1711059567\C,2.4438498322,0.,1.4940057904\C,2.46192462,0.,0.0329707684
\S,4.968125944,0.,1.2918716222\H,1.1733758373,0.,3.2555437161\N,-1.109
3804407,0.,-0.6538009426\C,1.2937721303,0.,-0.6734262402\N,3.559346335
6,0.,2.1714475981\S,4.0786685947,0.,-0.6802484259\S,1.1760728309,0.,-2
.4362385254\H,-0.9624340615,0.,1.9641676087\S,-0.9845367193,0.,-2.3090
355821\\Version=AM64L-G03RevD.02\State=1-A'\HF=-1932.057755\S2=0.\S2-1
=0.\S2A=0.\RMSD=3.249e-09\RMSF=1.186e-04\Thermal=0.\Dipole=-0.0995695,
0.,0.1603043\PG=CS [SG(C6H2N2S4)]\\@
```

Table 220. Computational output parameters for triplet **193**.

```
1\1\GINC-CHEM39\FOpt\UB3LYP\6-31G(d)\C6H2N2S4(3)\GAUSSIAN\01-Oct-2010\
0\\# OPT UB3LYP/6-31G(D) GEOM=CONNECTIVITY\\opt triplet\\0,3\C,-1.7918
548825,0.,0.2335764871\C,-1.79671678,0.,1.6514748933\C,-0.6162964263,0
.,2.3614510731\C,0.6338494795,0.,1.6923933687\C,0.6588151144,0.,0.2684
689007\S,3.1643005762,0.,1.4616063762\H,-0.6132678916,0.,3.4457021131\
N,-2.960005029,0.,-0.479712079\C,-0.5459474588,0.,-0.4561288128\N,1.81
```

```
16374668,0.,2.3897594799\S,2.2480126637,0.,-0.4824948893\S,-0.62785483
65,0.,-2.2119598094\H,-2.7559271579,0.,2.1569844905\S,-2.7746662967,0.
,-2.1096787943\\Version=x86-Linux-G03RevB.05\State=3-A'\HF=-1932.02937
66\S2=2.013205\S2-1=0.\S2A=2.000084\RMSD=6.936e-09\RMSF=4.199e-05\Dipo
le=0.2035239,0.,-0.3390914\PG=CS [SG(C6H2N2S4)]\\@
```

Table 221. Computational output parameters for 1,2,3-dithiazole radical.

```
1|1|UNPC-CHEM40-OTNBTO7T|FOpt|UB3LYP|6-31G(d)|C2H2N1S2(2)|GAUSSIAN|02-
Jan-2013|0||# opt ub3lyp/6-31g(d) geom=connectivity||SSN||0,2|C,0.,1.2
472344921,0.8381997609|C,0.,1.1819887368,-0.5460604338|N,0.,2.41274400
74,1.4892649346|S,0.,3.7429050433,0.4880553995|S,0.,2.7046202191,-1.39
85587956|H,0.,0.2686146147,-1.1268166196|H,0.,0.3460083566,1.446438363
9||Version=IA32W-G09RevC.01|State=2-A"|HF=-928.4928535|S2=0.766534|S2-
1=0.|S2A=0.750081|RMSD=8.445e-009|RMSF=2.280e-004|Dipole=0.,-0.5557846
,-0.4714556|Quadrupole=-2.2110738,4.1570711,-1.9459973,0.,0.,-0.257222
8|PG=CS [SG(C2H2N1S2)]||@
```

Table 222. Computational output parameters for benzo-1,2,3-dithiazole radical.

```
1|1|UNPC-CHEM39-KPDQ5T27|FOpt|UB3LYP|6-31G(d)|C6H4N1S2(2)|GAUSSIAN|02-
Jan-2013|0||# opt ub3lyp/6-31g(d) geom=connectivity||benzoSSN||0,2|C,0
.,1.2270339196,0.8550320425|C,0.,1.1998684928,-0.5778679178|C,0.,-0.01
27014907,-1.2694582853|C,0.,-1.2088303775,-0.5531954853|C,0.,-1.200265
0744,0.8527182869|C,0.,-0.0070191514,1.5534071801|N,0.,2.4102953991,1.
5161572609|S,0.,3.7471418415,0.5546460659|S,0.,2.7791858357,-1.3657152
83|H,0.,0.0190275567,2.637874359|H,0.,-0.0254390289,-2.3548763979|H,0.
,-2.1408640123,1.3958343325|H,0.,-2.1524135703,-1.0904423087||Version=
IA32W-G09RevC.01|State=2-A"|HF=-1082.1434179|S2=0.768688|S2-1=0.|S2A=0
.750247|RMSD=6.960e-009|RMSF=5.332e-005|Dipole=0.,-0.6277805,-0.418965
2|Quadrupole=-4.0180208,4.1943627,-0.1763419,0.,0.,-0.9455499|PG=CS [S
G(C6H4N1S2)]||@
```

II Crystallographic Data

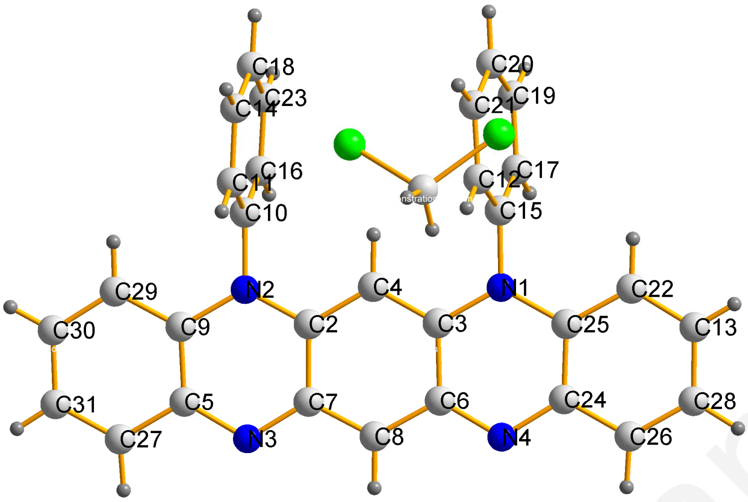


Figure 60 X-ray structure of 5,7-di-phenyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **116**.

Space Group: P -1

Cell Lenghts (Å): a 10.6913(7), b 10.7388(7), c 11.0400(7)

Cell Angles (^{o}): α 79.393(5), β 88.577(5), γ 78.677(5)

Cell Volume (Å^3): 1221.53(14)

Z: 2

R factor (%): 3.99

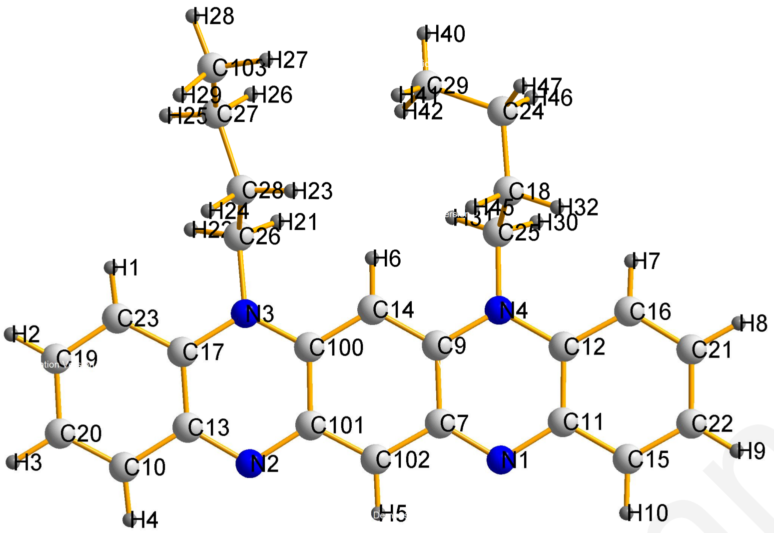


Figure 61 X-ray structure of 5,7-di-*n*-butyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **117**.

Space Group: P -1

Cell Lenghts (Å): a 8.2937(4), b 8.9994(4), c 14.1540(5)

Cell Angles (^{o}): α 79.277(3), β 79.434(3), γ 83.042(4)

Cell Volume (Å^3): 1016.23(7)

Z: 2

R factor (%): 6.30

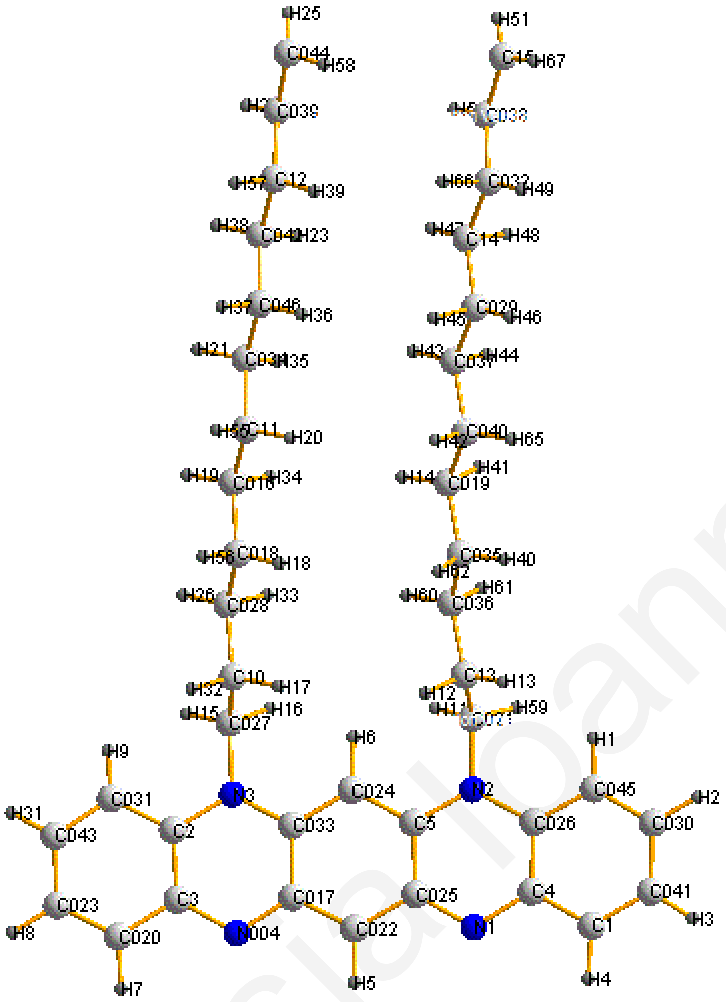


Figure 62 X-ray structure of 5,7-di-*n*-dodecyl-7,13-dihydroquinoxalino[2,3-*b*]phenazin-5-ium-13-ide **118**.

Space Group: P 2(1)/c

Cell Lenghts (Å): a 21.4795(10), b 9.3618(4), c 17.9078(6)

Cell Angles (^{o}): α 90.000, β 93.816(4), γ 90.000

Cell Volume (Å^{3}): 3593.04(30)

Z: 4

R factor (%): 6.93

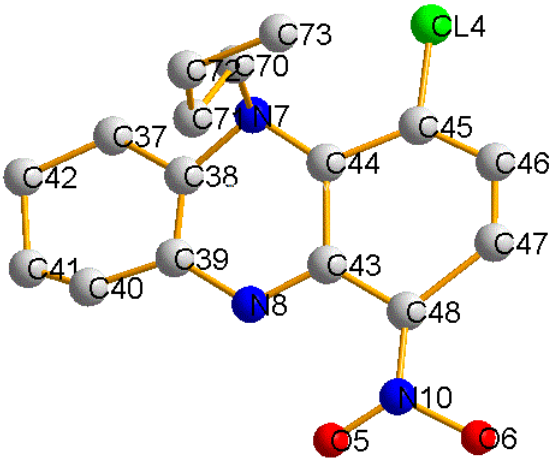


Figure 63 X-ray structure of 5-butyl-4-chloro-1-nitro-5,10-dihydrophenazine **146**.

Space Group: C 2/c

Cell Lenghts (Å): a 30.1757(16), b 28.9029(38), c 21.2557(20)

Cell Angles (^{o}): α 89.900, β 127.505(8), γ 90.041

Cell Volume (Å^3): 14706.56(296)

Z: 8

R factor (%): 31.65

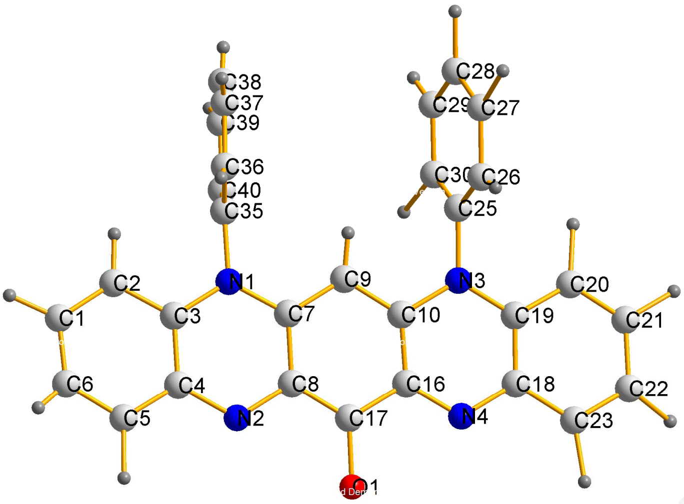


Figure 64 X-ray structure of tetraazapentacene oxy radical **158**.

Space Group: C 2/c

Cell Lenghts (Å): a 20.544(2), b 14.5427(18), c 17.625(4)

Cell Angles (^{o}): α 89.996, β 102.027(14), γ 90.041

Cell Volume (Å^3): 5150.15(150)

Z: 8

R factor (%): 11.83

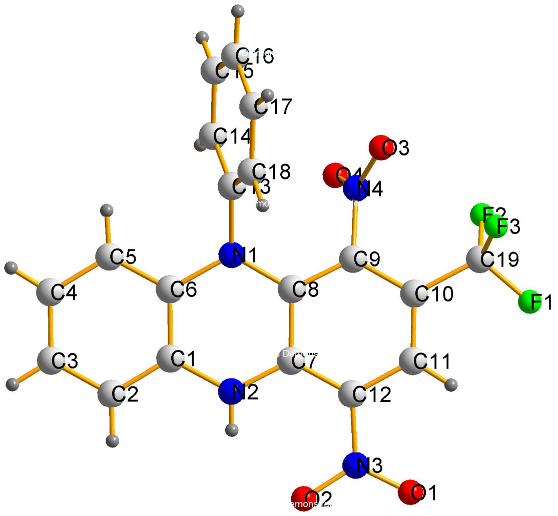


Figure 65 X-ray structure of 1,4-dinitro-10-phenyl-2-(trifluoromethyl)-5,10-dihydrophenazine **176**.

Space Group: C 2/c

Cell Lenghts (Å): a=26.0989(19), b=10.6474(8), c=14.0452(10)

Cell Angles (^{o}): α 90.000, β 107.6700, γ 90.000

Cell Volume (Å^3): 3718.82(50)

Z: 4

R factor (%): 3.16

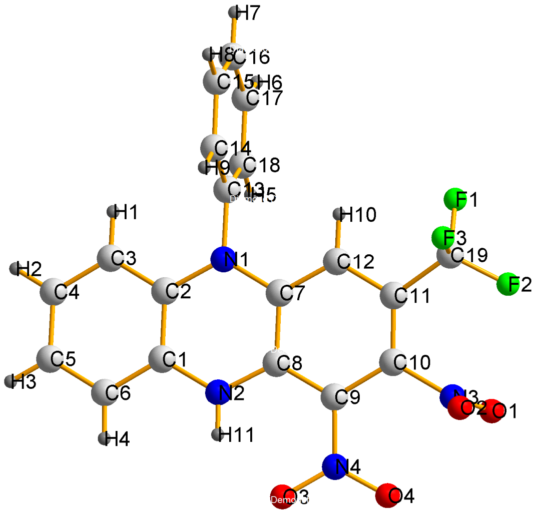


Figure 66 X-ray structure of 1,2-dinitro-5-phenyl-3-(trifluoromethyl)-5,10-dihydrophenazine **177**.

Space Group: P 2(1)/n

Cell Lenghts (Å): a 13.1420(6), b 7.3928(4), c 17.9303(9)

Cell Angles (^{o}): α 90.013, β 106.319(4), γ 90.048

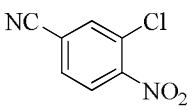
Cell Volume (Å^{3}): 1.65389

Z: 4

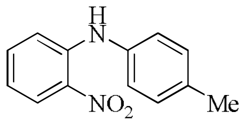
R factor (%): 3.21

LIST OF COMPOUNDS PREPARED

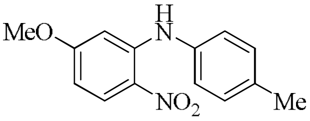
Compound number in bold followed by page number where compound appears in Chapter 6 (Experimental).



95f
p 187



94a
p 188



94b
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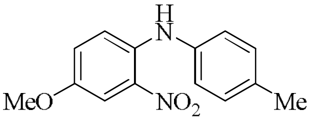

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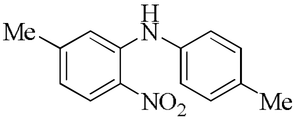

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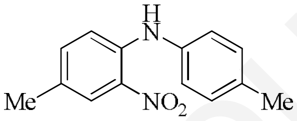

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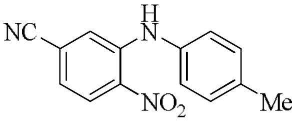

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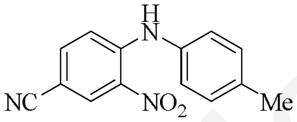

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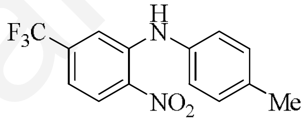

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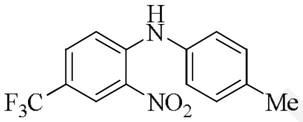

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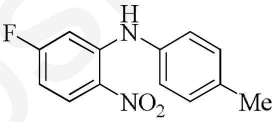

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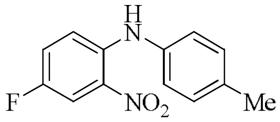

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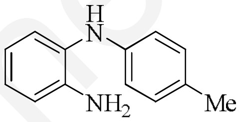

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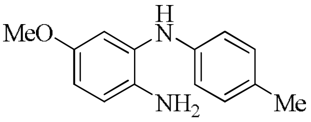

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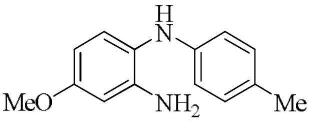

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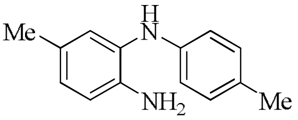

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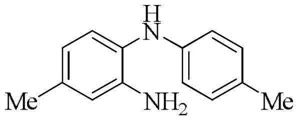

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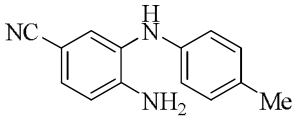

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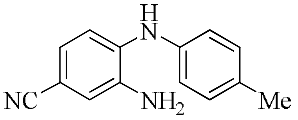

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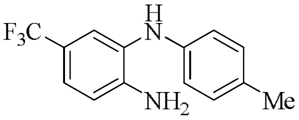

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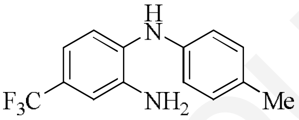

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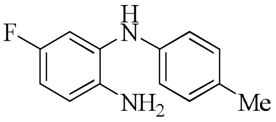

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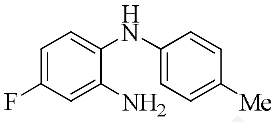

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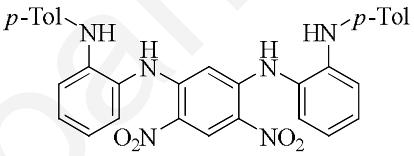

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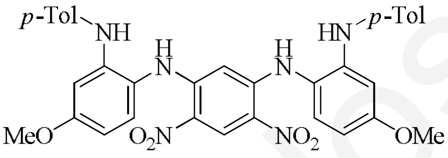

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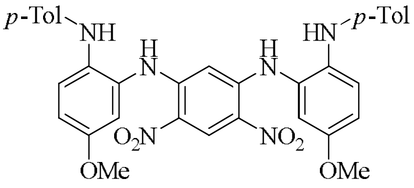

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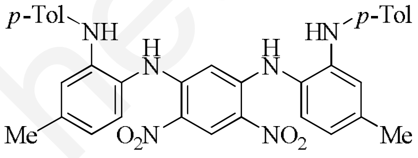

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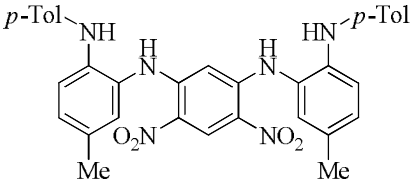

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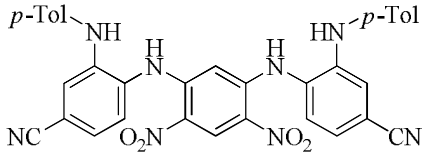

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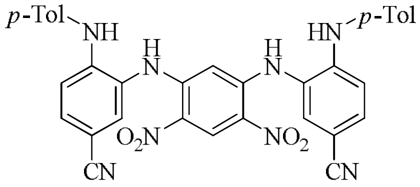

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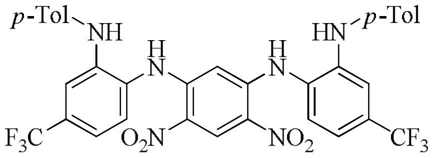

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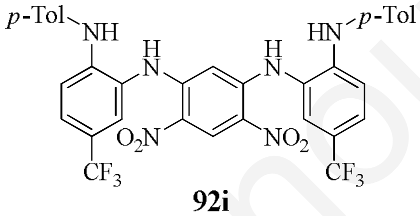

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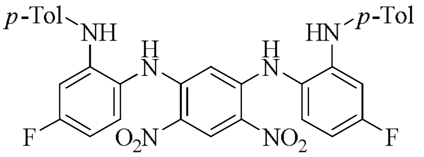

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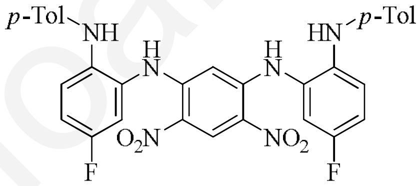

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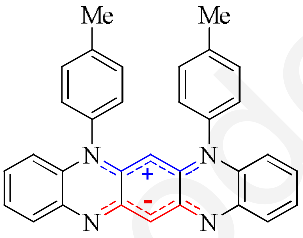

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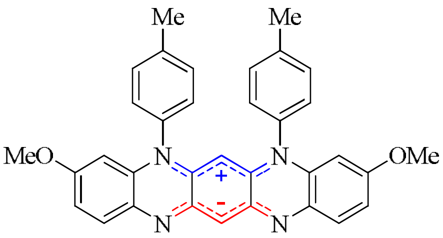

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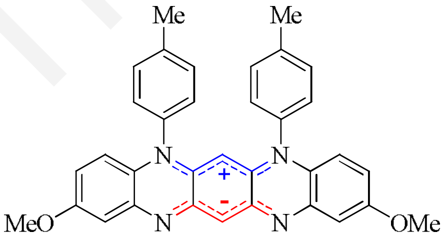

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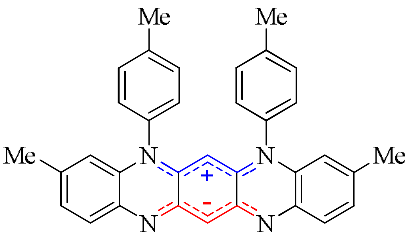

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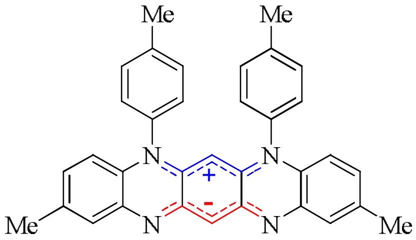

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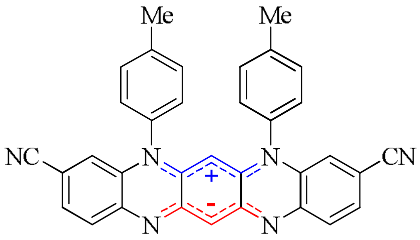

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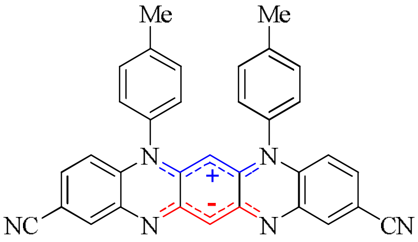

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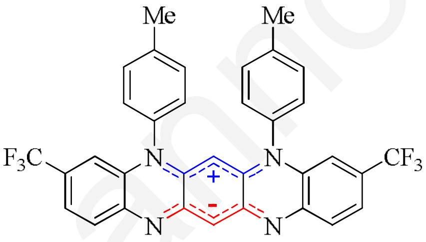

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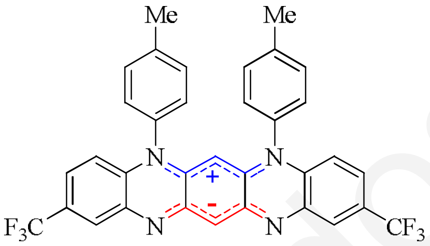

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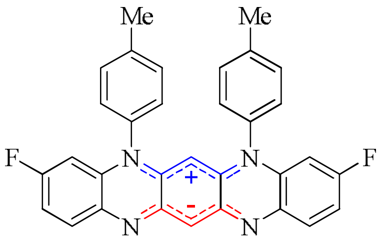

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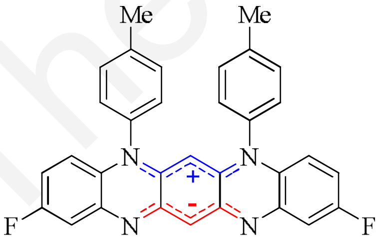

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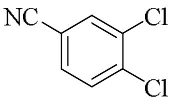

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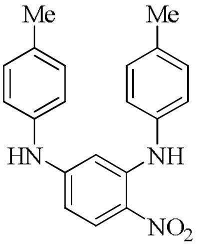

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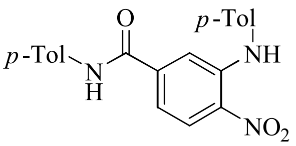

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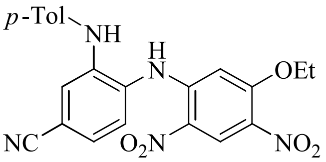

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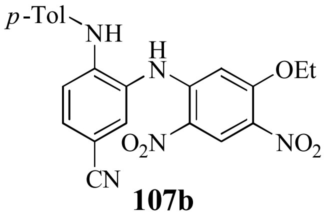

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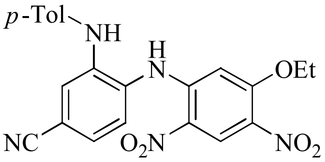

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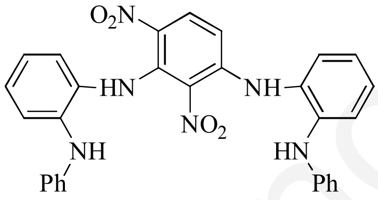

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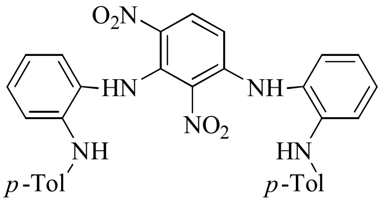

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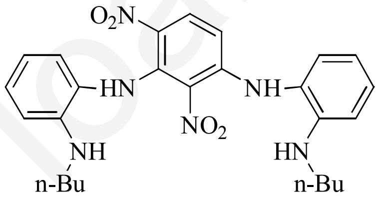

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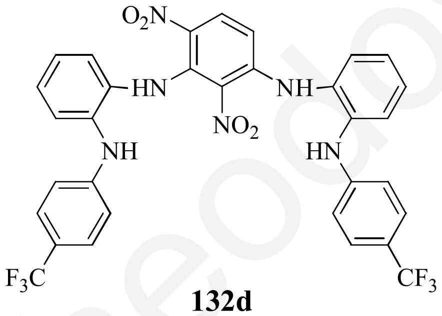

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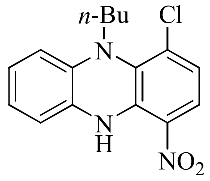

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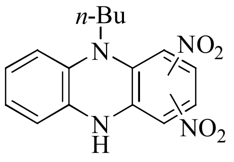

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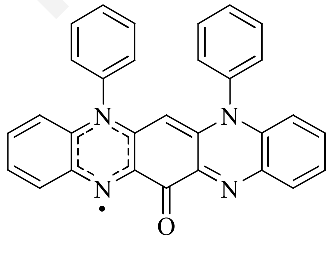

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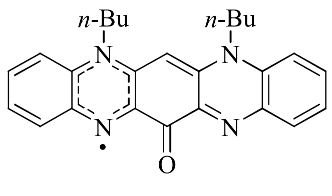

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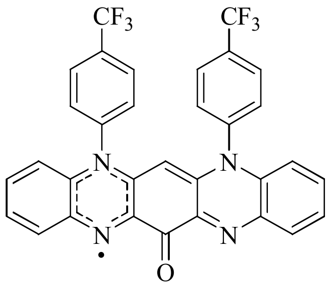

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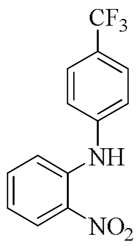

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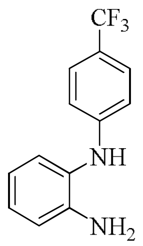

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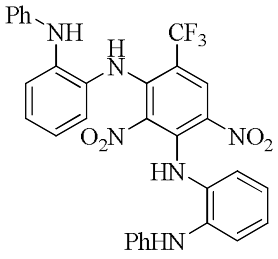

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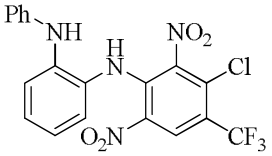

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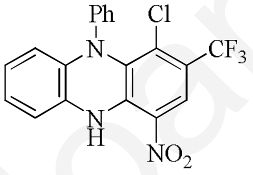

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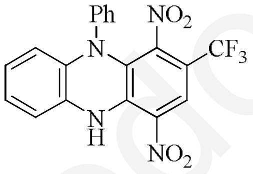

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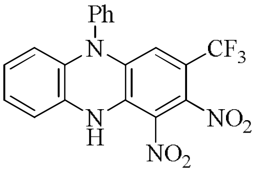

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