Computational and experimental studies of acenes, starphenes and [60]fullerene derivatives

Ryan Paul Kopreski
University of New Hampshire, Durham

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Computational and experimental studies of acenes, starphenes and [60]fullerene derivatives

Abstract
The computational and experimental studies of acenes, starphenes and [60]fullerene derivatives is described. Acenes are promising organic semiconductors. Hybrid density functional theory applying a triple-zeta valence basis set (B3LYP/6-311+G**) has been used to approximate the HOMO - LUMO excitation gap in various substituted pentacenes. This technique may, in part, synthetically guide substitution patterns of pentacenes and larger acenes. Previous predictions of an open-shell singlet diradical ground state for acenes larger than hexacene have been reproduced and sulfur substitution has been found to alter the electronic ground state to a closed-shell configuration. Substituents that may engage in non-bonding interactions are not well described by the same DFT model, however these shortcomings can be overcome by implementing an appropriate effective-core potential on carbon atoms.

Like acenes, starphenes are a class of polycyclic aromatic hydrocarbon that exhibit interesting electronic characteristics, though synthetically have not been as widely accessible. The synthesis of a soluble precursor to a substituted [4.4.4]tridecastarphene is described. Upon exposure to an excess of [60]fullerene in the presence of a chemical oxidant, the [4.4.4]tridecastarphene PAH is generated and captured in situ by Diels-Alder cycloaddition of the fullerene. Both syn,syn- and syn,anti- diastereomers of the fullerene trisadduct are generated with the syn,syn- formed as the dominant species. Fullerene pi -- pi interactions are believed to drive the formation of the syn,syn- diastereomer.

Understanding intermolecular interactions is critical to the rational design of organic devices. Both electrically conducting and insulating properties are required for the fabrication of such devices. Among these interactions, pi -- pi and CH -- pi interactions dominate the crystal packing in PAHs. Several [60]fullerene derivatives designed to study CH -- pi interactions by variable temperature NMR (VT-NMR) are described. Diels-Alder cycloadducts of [60]fullerene were generated from substituted o-quinodimethane derivatives to give compounds that may or may not engage in an intramolecular CH -- pi interactions. Evaluation of the rate-constant associated with the first-order transition state of a cyclohexene "boat-to-boat" inversion for each fullerene derivative provides evidence for a CH -- pi interaction estimated to be 0.95 kcal/mol.

Keywords
Chemistry, Organic

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COMPUTATIONAL AND EXPERIMENTAL STUDIES OF ACENES, STARPHENES AND [60]FULLERENE DERIVATIVES

BY

Ryan Paul Kopreski
B.S., University of New Hampshire, 2003

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

May, 2010
This dissertation has been examined and approved.

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4/28/10
Date
ACKNOWLEDGEMENTS

Though the work described within the bindings of this document is solely that of the author, there are numerous individuals who have been involved in some way, cosmically or in the flesh, both gainfully helpful and pleasantly distracting, but never discouraging. The time has come to publicly thank those individuals by name.

First and foremost, I need to thank my loving and supportive wife Elia and our three blessings Lucas, Ethan and Gavin for whom this work is dedicated. They are collectively my greatest inspiration. I can only hope the fruits of my labor will be sufficient to repay their selflessness and sacrifice during these trying times.

I would like to acknowledge the exquisite guidance and grace of my advisor Dr. Glen Miller. His patience with my need to balance familial commitments with academics and research has not gone unnoticed. Further, his commitment to financial support has been the sole resource enabling me to continue my program. He has been a powerful force in my transition from an inquisitive young man to an advanced scientific thinker. I have enjoyed our journey together.

I must thank my family; my parents Linda and Paul and my brother Marc. It was the encouragement of my parents alone that started this journey and their continued understanding and support that played a large part in sustaining me. Any discipline, drive, attention to detail and commitment to quality I may have I owe entirely to them. I cannot thank them enough for all that they have done.

I would like to express my sincerest gratitude to all of the members of the UNH Chemistry Department, faculty, staff and fellow graduate students who have been integral
to my education. At the top of the heap is Jon Briggs who has been an advisor, collaborator, and friend to me since 2002. Jon has not only contributed greatly to this work, he has been instrumental in keeping alive my musical interests. I am very grateful to Jon for his instruction and camaraderie. I must also thank members of the Miller Group, past and present. Drew Athans and Jim Rainbolt who helped set various “bars” as PhD candidates in the Miller Group. Mikael Jazdzyk, the most industrious researcher I have ever known who was extremely helpful in much of the success of my own research, was also an inspiration and a good friend. I would also like to thank Jun-Fu Liu for reminding us from time to time that occasionally life gives you the cat, even though you want the dog, Chandrani Pramanik for being like a little sister to me, Joe Dunn for keeping it real and James Mack for leaving a legacy. I must thank graduate students Dannon Stigers and Antoinette Odendaal who were my peers in the program. Dannon was additionally a great friend with whom I shared many a laugh. I am also grateful for the friendship of L. Carsten Nielsen who will always be a reminder that perseverance and positive attitude are useful qualities, but not necessarily sufficient.

Many faculty and staff have both inspired my academic prowess and gone out of their way to be helpful to me. Gary Weisman, Chuck Zercher, Ed Wong and Richard Johnson (alongside Glen Miller) are gifted educators and have all inspired my interest and enjoyment of chemistry. Office administrators Cindi Rohwer and Peggy Torch have been critical to fastening the “nuts-and-bolts” of the roller-coaster that is graduate school. Bob Constantine is a tremendous resource in the chemistry library. Jon Wilderman, Kathy Gallagher, and Pat Wilkinson were always available to manage NMR
instrumentation trouble and Kathy especially must be thanked for training me to use NMR.

Finally, I would like to thank my brethren in Alpha Chi Sigma and all those who would lend me an ear, an eye or a hand, if you are reading this, you know who you are.

Thank You.
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LIST OF EQUATIONS

1
\[ k^{CT} = \sqrt{\frac{\pi}{h}} t^2 \frac{1}{\sqrt{\lambda k_B T}} e^{-\lambda d_4k_T} \]

The rate of charge transport \((k^{CT})\) is a function of temperature \((T)\), electronic coupling between adjacent molecules \((t)\) (Equation 2), and reorganization energy \((\lambda)\) (Equation 3) and closely approximates charge mobility.

2
\[ \lambda = (E_{M^+/M} - E_{M^+/M^+}) + (E_{M^+/M} - E_{M}) \]

The reorganization energy \((\lambda)\) calculated from the energies of four unique electronic configurations of the molecule considered: the geometrically optimized neutral \((E_M)\) and charged \((E_{M^+})\) molecules as well as the energy of the neutral molecule at the cation geometry \((E_{M^+/M^+})\) and of the charged molecule at the neutral geometry \((E_{M^+/M})\).

3
\[ t = \frac{E_{(HOMO)} - E_{(HOMO-1)}}{2} \]

Electronic coupling between adjacent molecules \((t)\) is a function of \(\frac{1}{2}\) the difference in Energy between the HOMO and HOMO-1.

4
\[ \Delta G^f_e = 4.577 T_c \left[c + \log\left(\frac{T_c}{\sqrt{\Delta v_{AB}^2 + 6J_{AB}^2}}\right)\right] \]

Gibbs free energy of activation \((\Delta G^f_e)\) at the coalescence temperature, \(T_c\) is the coalescence temperature in Kelvin, \(\Delta v_{AB}\) is the chemical shift difference for the A and B nuclei in Hz, \(J_{AB}\) is the coupling constant in Hz and \(c\) is a constant dependent on the nature of the exchange (1st or 2nd order).

5
\[ \Delta G^f = R T \left[\ln\left(\frac{T}{k}\right) + \ln\left(\frac{K k_B}{h}\right)\right] \]

The Eyring equation for a molecular transition where \(\Delta G^f\) is Gibbs free energy of activation, \(R\) is the gas constant, \(T\) is temperature in Kelvin, \(k\) is the rate-constant obtained from the simulation, \(K\) is equal to 1 in a first order transition, \(k_B\) is Boltzmann's constant and \(h\) is Planck's constant.
LIST OF STRUCTURES

1  2  3

4  5  6

7  8  9  10
a. R = H
b. R = Me
c. R = Cl

61

62

63

64

65

66

67

68

XXV
ABSTRACT

COMPUTATIONAL AND EXPERIMENTAL STUDIES OF
ACENES, STARPHENES AND [60]FULLERENE DERIVATIVES

by

Ryan P. Kopreski

University of New Hampshire, May, 2010

The computational and experimental studies of acenes, starphenes and [60]fullerene derivatives is described. Acenes are promising organic semiconductors. Hybrid density functional theory applying a triple-zeta valence basis set (B3LYP/6-311+G**) has been used to approximate the HOMO - LUMO excitation gap in various substituted pentacenes. This technique may, in part, synthetically guide substitution patterns of pentacenes and larger acenes. Previous predictions of an open-shell singlet diradical ground state for acenes larger than hexacene have been reproduced and sulfur substitution has been found to alter the electronic ground state to a closed-shell configuration. Substituents that may engage in non-bonding interactions are not well described by the same DFT model, however these shortcomings can be overcome by implementing an appropriate effective-core potential on carbon atoms.

Like acenes, starphenes are a class of polycyclic aromatic hydrocarbon that exhibit interesting electronic characteristics, though synthetically have not been as widely accessible. The synthesis of a soluble precursor to a substituted [4.4.4]tridecastarphene is described. Upon exposure to an excess of [60]fullerene in the presence of a chemical oxidant, the [4.4.4]tridecastarphene PAH is generated and captured in situ by Diels-Alder
cycloaddition of the fullerene. Both syn,syn- and syn,anti- diastereomers of the fullerene trisadduct are generated with the syn,syn- formed as the dominant species. Fullerene $\pi - \pi$ interactions are believed to drive the formation of the syn,syn- diastereomer.

Understanding intermolecular interactions is critical to the rational design of organic devices. Both electrically conducting and insulating properties are required for the fabrication of such devices. Among these interactions, $\pi - \pi$ and CH-$\pi$ interactions dominate the crystal packing in PAHs. Several [60]fullerene derivatives designed to study CH-$\pi$ interactions by variable temperature NMR (VT-NMR) are described. Diels-Alder cycloadducts of [60]fullerene were generated from substituted o-quinodimethane derivatives to give compounds that may or may not engage in an intramolecular CH-$\pi$ interactions. Evaluation of the rate-constant associated with the first-order transition state of a cyclohexene "boat-to-boat" inversion for each fullerene derivative provides evidence for a CH-$\pi$ interaction estimated to be 0.95 kcal/mol.
CHAPTER 1

THEORETICAL STUDY OF THE GROUND-STATE ELECTRONICS OF
ACENES AND SUBSTITUTED ACENES

1.1 Introduction

1.1.1 What are acenes and why are they important?

Acenes are a class of molecule belonging to the polycyclic aromatic hydrocarbon family (PAHs) and are classified as "alternant cata-condensed" polyarenes. Geometrically, acenes are semi-rigid, planar structures constructed by linear benzannellation (benzene ring-fusion) at the 2,3- positions of the growing acene with known derivatives ranging in size from three rings (anthracene) to nine rings (nonacene), collectively referred to as "polyacenes" or simply "acenes" (Figure 1).

Figure 1: The first three members of the polyacene series.
Due to their planarity, and conjugated nature, acenes exhibit extensive \( \pi \) delocalization as evident by their UV-Vis absorption spectra as well as their observable colors in the solid state and in solution.\(^1\) The conjugative effects become optically apparent with tetracene which is orange, pentacene which is a deep blue and hexacene which is green. Although heptacene is also believed to be green in color, it has never been directly observed due to its extremely low stability, and has only recently been isolated for a short time in a polymer matrix.\(^4\) Pentacene has been studied extensively due to its high charge carrier mobility in thin-film electronic devices. A number of reviews discussing pentacene have been published.\(^5\)-\(^10\) Due to the inherent instability and generally poor solubility of unsubstituted acenes larger than tetracene, substituted acenes have received a great deal of attention recently.\(^6\),\(^11\)-\(^14\)

1.1.2 Discovery, Nomenclature and Synthesis

The discovery of benzene is generally attributed to Michael Faraday who isolated it from an oily residue of “illuminating gas” in 1825.\(^3\),\(^15\) The following year, Faraday correctly determined the molecular formula of naphthalene which had been documented by John Kidd\(^16\) in 1821 but not structurally identified until 1866 when Emil Erlenmeyer\(^17\) proposed a two-ring fused structure. The unique \( \text{C}_6\text{H}_6 \) formula determined for benzene was of particular interest to chemists for several decades and structure predictions were not settled upon until one proposed by Kekulé in 1865 suggesting a 6-membered ring with alternating single and double bonds.\(^18\),\(^19\)

The nomenclature of polycyclic aromatic hydrocarbons has been through a few
iterations but ultimately unified through the effort of Eric Clar who provided a detailed description in volume 1 of *Poly cyclic Hydrocarbons*. Here he notes the initial efforts of Scholl and the later refinements of Stelzner and Kuh, and finally Patterson. It is beyond the scope of this text to go into such extensive detail and the reader is encouraged to review Clar's book. However, a few relevant aspects of the nomenclature of PAHs as they pertain to acenes merit discussion.

Among the acene series, some confusion exists which may generally be clarified, specifically regarding acenes with 2, 3 and 4 fused benzene rings. The 2-ring system and 3-ring system in particular have been in existence for more than 100 years and well known by their trivial names “naphthalene” and “anthracene” respectively. The 4-ring system was originally described as the product of the fusion of two equivalents of naphthalene or otherwise the fusion of one equivalent of anthracene and one equivalent of benzene giving the names “naphthacene” and “linear benz-anthracene” (benz[b]anthracene) respectively (Figure 2).

![Naphthacene and Benz[b]anthracene](image)

**Figure 2:** Alternative names for tetracene

Compounding this confusion was still another trivial name for the 4-ring compound “rubene.” Today, acenes with 5 fused rings or more are known systematically by a Greek prefix describing the number of fused rings and the suffix “acene,” which was already a
unique identifier in use for anthracene, thus giving pentacene, hexacene, heptacene and so on. The popularity of this systematic naming is in large part due to Clar's work in this area. Furthermore, Clar recommends referring to the 4-ring acene as "tetracene" to avoid any ambiguity in the name of this compound. Naphthalene and anthracene of course have never suffered from ambiguity in their names and therefore are in continued usage.

As previously mentioned, acenes are a family of compounds formed by successive linear annellation of benzene rings. With the exception of anthracene, the numbering scheme for all of these compounds is consistent, identifying only those sp² carbons bearing a hydrogen or a substituent. The numbering always begins with the last ring in the series, starting with the carbon atom at the "12-o-clock" position as shown in Figure 3. Note the historically based numbering of anthracene is unique from the others in the series.

![Figure 3: The numbering scheme for acenes: anthracene, tetracene and pentacene](image)

A number of different strategies have been employed for the linear construction of the acene scaffold including Friedel-Crafts condensation, double aldol condensation, and most commonly Diels-Alder cyclization, all of which are carefully reviewed in the independent works of Eric Clar¹ and Ronald Harvey.³ In most cases, the synthesis works
through a quinoidal- or keto- precursor to build up the target scaffold and subsequent reduction affords the acene. For a comprehensive picture of the general synthetic strategies or specific synthesis of a target acene, the reader is encouraged to consult the works of both Clar\(^1\) and Harvey.\(^3\)

### 1.1.3 Geometries of Unsubstituted and Substituted Acenes

The time average geometry generally exhibited by unsubstituted acenes in solution is of a two-dimensional (planar) structure with $D_{2h}$ symmetry, and indeed the acene family of molecules are normally flat, rigid structures. In a 2006 review, Pascal surveyed the Cambridge Structural Database (CSD) for examples of substituted acenes exhibiting a twist along the long axis. Though many of the structures described are heavily substituted, Pascal claims “the energy required to bend or twist most polycyclic aromatic hydrocarbons is quite modest, and the crystal structures of most acenes and their derivatives show some deviations from planarity.”\(^{24}\) **Figure 4** depicts decaphenylanthracene minimized with MMFF94 and rendered in “ball-and-stick” omitting phenyl substituents for clarity. The calculated end-to-end twist (63.7°) closely approximates that of the x-ray crystal structure which exhibits a 63° twist.

**Figure 4:** The x-ray crystal structure of decaphenylanthracene exhibits a 63° end-to-end twist. Here minimized by MMFF94 and shown without phenyl rings for clarity.
1.1.4 Electronic Considerations

1.1.4.1 Mobilities in Bulk Material Models

Organic photovoltaic (OPV) devices were first realized in 1986 when Tang reported a device consisting of an organic donor and acceptor layer made by deposition of two small molecules.\textsuperscript{25} Since then, a plethora of organic molecules, oligomers and polymers have been studied in connection with their utility in organic photovoltaics including polymer/fullerene systems, perylene and coronene derivatives, pentacene derivatives, oligothiophenes, triphenylamines and anthradithiophenes.\textsuperscript{26} Pentacene and other acene derivatives have also been examined by numerous researchers for use in other organic electronic devices such as organic field-effect transistors (OFETs)\textsuperscript{27} and for general use as semiconductors.\textsuperscript{6,28-32} For a review on acenes used in organic semiconductor applications, the reader is directed to John Anthony's 2008 review.\textsuperscript{6}

To best understand the electronic properties of materials and devices utilizing acenes one must study the charge carrier mobility (\(\mu\)) of such devices. Charge carrier mobilities may be experimentally determined by time-of-flight (TOF), space-charge-limited current (SCLC), and field-effect transistor (FET) measurements, among other methods.\textsuperscript{6} Although less exacting, computer and mathematical models are often utilized in order to reduce the cost of charge carrier mobility measurements. The cost of the calculation must also be considered with respect to its accuracy. Given that the performance of these devices is complicated by a number of variables including charge injection at the electrode, charge transport, charge recombination or separation, exciton formation or dissociation, energy transfer, supramolecular organization, structure defects,
and absorption or emission properties, high accuracy quantum mechanical models are often prohibitively costly.\textsuperscript{33} Moreover, the model often must be broken into smaller parts. Several researchers have recently published theoretical studies of the electronic properties of various acenes and derivatives in one or more solid morphologies.\textsuperscript{29-33}

Sancho-Garcia and coworkers claim to have accurately calculated charge transport properties of several acenes and derivatives using MP2 and DFT methods, approximating the rate constant of charge transport ($k_{CT}$) using semiclassical Marcus theory.\textsuperscript{33,34} The rate constant, $k_{CT}$ (Equation 1), is a function of temperature ($T$), electronic coupling between adjacent molecules ($t$) (Equation 3), and reorganization energy ($\lambda$) (Equation 2) and closely approximates charge mobility.

$$k_{CT} = \frac{\sqrt{\pi}}{h} t^2 \frac{1}{\sqrt{\lambda k_B T}} e^{-\lambda/4k_B T}$$  

**Eq. 1**

$$\lambda = (E_{M^+/M} - E_{M/M^+/}) + (E_{M/M^-} - E_{M})$$  

**Eq. 2**

$$t = \frac{E_{(HOMO)} - E_{(HOMO-1)}}{2}$$  

**Eq. 3**

The reorganization energy ($\lambda$) in Equation 2 is calculated from the energies of four unique electronic configurations of the molecule considered: the geometrically optimized neutral ($E_M$) and charged ($E_{M^+}$) molecules as well as the energy of the neutral molecule at the cation geometry ($E_{M+/M}$) and of the charged molecule at the neutral geometry ($E_{M^+/M}$).\textsuperscript{33}

A different approach is to apply theoretical electronic models to experimental solid-state organization data, usually either x-ray crystal or powder diffraction data.\textsuperscript{29,32} Yoshida and Sato oriented a set of DFT optimized pentacenes into a lattice based on x-ray
crystal and powder diffraction experiments which was then further refined with a simple force-field minimization to give a bulk phase. The material lattice was further refined and energy bands were calculated with an appropriate materials chemistry computational suite. Similar to this approach is a QM/MM method where the geometric description of the bulk-phase is instead computed directly with an appropriate force-field method and a select sub-space is electronically evaluated using a quantum mechanical method. Bredas and Norton have used this method to compute polarization energies in oligoacene crystals, an indirect measurement that is proportional to charge transport mobility.

1.1.4.2 HOMO-LUMO Energy Gaps and Band Gaps

Condensed (solid-state) matter may be classified into one of three categories with regard to the “band theory of solids” which describes their electronic properties: insulating, semiconducting or conducting. In each case, the material is said to possess a valence band (where the electrons reside) and a conduction band (where the electrons may be excited). Conduction is achieved when an electron is able to move into the higher energy conduction band leaving a “hole” behind in the valence band. This excited state electron and hole pair may then “migrate” through the material.
Si (semiconductor)

Carbon (insulator)

Ge (0.7 eV)

Sn (0.1 eV)

Conduction Band (empty)

Pb (conductor)

Figure 5: Graphic representation (reproduced from Nave\textsuperscript{35}) of band gap energies of solid-state materials from the 4\textsuperscript{th} column of the periodic table as a function of interatomic spacing.

In an insulator, the energy gap between these two bands is sufficiently large that electrons may not be excited to the conduction band under ambient conditions. In conducting materials, such as many bulk metals, the conduction band is said to "mix" with the valence band and as a result the electrons are free to move about even at very low temperatures.

For a bulk material to be semiconducting, the energy gap between the valence and conduction bands, the so-called "band gap," must be sufficiently small that electrons may
be excited into the conduction band under ambient thermal conditions (300 K), typically between 0.5 to 3.0 eV with silicon at 1.1 eV\(^3^5\) and pentacene having a band gap of around 1.8 – 2.0 eV depending upon morphology\(^2^9\).

In loose terms, the band gap of a bulk material may be thought of as the summation of the HOMO-LUMO gaps of discrete molecules in the bulk material. As such, the band gap is expected to be directly proportional to the HOMO-LUMO gap, despite obvious discrepancies in the solid-state organization. Furthermore, the HOMO-LUMO gap may readily be computed using \textit{ab initio} methods and correlated with experimentally derived values\(^1^3\)\(^3^6\). Several studies show a decreased HOMO-LUMO gap as determined using optical (UV-Vis) methods\(^3^7\)\(^4^0\) as well as an increased ionization potential\(^4^1\) as the length of acene increases.

### 1.1.4.3 Aromaticity of Polyacenes

Aromaticity is a convenient concept to describe the unique stability of flat molecules exhibiting cyclic conjugation with \(4n+2\) \(\pi\) electrons. This property is exemplified in benzene with a bond order of 1.5 between carbon atoms as indicated by x-ray crystal data that shows equal bond lengths of 1.4 Å\(^4^2\). Aromatic resonance stabilization energy (RSE) has been quantitatively disputed for decades\(^4^3\)\(^4^6\) but qualitatively, it serves the purpose of demonstrating the special stability of a molecule exhibiting "aromatic" character. The aromatic RSE of benzene is generally believed to be about 30 kcal/mol depending on the method of calculation.
Figure 6: Bond lengths of pentacene, experimental and (calculated).\textsuperscript{40}

Though acenes meet some of the requirements of "classical aromaticity," (they are flat, conjugated molecules) they do not exhibit "aromatic" behavior with respect to chemical reactivity. The perfectly symmetrized delocalization in benzene responsible for its uniform bond lengths is not apparent in acene systems as indicated by the experimental measurements and \textit{ab initio} calculations of pentacene shown in Figure 6.\textsuperscript{40} Instead, acenes are thought to possess "local aromaticity."\textsuperscript{47} However, this aromatic character is not uniquely resistant to reactivity as is the case with benzene, furan, and other more classically "aromatic" molecules that exhibit added stability.

A useful starting point in understanding the aromaticity of polyacenes is E. Clar's "aromatic sextet" concept as will be described in greater detail in chapter 2 of this document. Succinctly put, Clar's sextet concept states that for any given acene, there can be only one sextet of $\pi$-electrons which is increasingly delocalized as the size of the acene increases, suggesting a continual loss in benzenoid (aromatic) character for each subsequent ring addition.\textsuperscript{1} MO calculations of Schleyer agree with Clar's sextet theory, predicting loss of benzenoid character with increasing size of linear acenes.\textsuperscript{48}
As suggested by a number of theoretical models\textsuperscript{48,49} including "ring current" calculations employed by Fowler and coworkers\textsuperscript{50,51}, polyacenes exhibit the greatest amount of electron density, specifically $\pi$ electron density, symmetrically about the center of the ring-system. This is also chemically the most reactive region of acenes. For a review of acene reactivity, the reader is urged to consult the works of Clar\textsuperscript{1} and Harvey.\textsuperscript{3}

1.1.4.4 Tuning Electronics with Substitution

Given the interesting electronic properties of polyacenes, researchers have begun to experiment with substituents that may be used to fine-tune these properties and, in some cases, stabilize the acene. Substitution of pentacene in particular has been considered both theoretically and experimentally.\textsuperscript{6,27,52}

Synthetically, pentacenes have been substituted with aryl,\textsuperscript{53-55} alkyl,\textsuperscript{56,57} silylalkyl,\textsuperscript{58} halo,\textsuperscript{59-62} thio,\textsuperscript{63-65} alkoxy,\textsuperscript{56} and ethynyl\textsuperscript{28,67-75} groups.\textsuperscript{6} Two of the notable advantages of such functionalization include improved solubility (and thus processability) and in some cases enhanced resistance to photooxidation.

Theoretical work has been carried out on substituted pentacenes in just a few cases. Notably, Medina and coworkers compared the calculated HOMO and LUMO energies of pentacenes substituted with fluorine and methoxy groups, considering both frequency and position about the pentacene backbone using the hybrid functional B3LYP and applying a triple-zeta valence (6-311G*) basis set.\textsuperscript{52} In both cases, the substitution had the effect of generally decreasing the energy gap between the HOMO and LUMO energy levels when disubstituted at the 6,13- or tetrasubstituted at the 5,7,12,14-
positions. "Per" substitution was also considered and led to an even greater decrease in the energy of the HOMO-LUMO gap.\textsuperscript{52} Similar work was conducted by Kuo and coworkers, wherein pentacenes with cyano substitution were considered. Here the researchers considered HOMO-LUMO energies, internal reorganization energies ($\lambda$), as well as adiabatic electron affinities (EA) and ionization potentials (IP). The authors note that for device application, high EAs, large intermolecular electronic couplings and small $\lambda$'s are necessary, and that cyanation appears to positively impact all three criteria.\textsuperscript{27}

1.1.4.5 Controversial electronic ground-states of large acenes

It is well established that there are major limitations in the synthesis of polyacenes larger than pentacene, and unsubstituted polyacenes larger than heptacene may never be isolated long enough to be characterized. The isolation of unsubstituted heptacene was reported first by Marschalk\textsuperscript{76-78} and later Clar\textsuperscript{79,80} although in each case no more than visual confirmation of its fleeting existence was offered. Only one other report claims a unique synthesis of heptacene\textsuperscript{81} before recent direct evidence was provided by Neckers and coworkers who carefully trapped the highly reactive compound in a polymer matrix at very low temperatures.\textsuperscript{4}

Theoretical work has been carried out by several researchers to reveal why large polyacenes are so unstable. The relatively recent increase in such work has likely been spurred in part by improvements in computing hardware allowing the use of \textit{ab initio} methods. In 2001, Schleyer and coworkers considered the relationship between aromatic stabilization and reactivity for acenes from benzene to heptacene, finding the more
reactive center rings are actually coincidentally more “aromatic” than the less reactive peripheral rings. The same year Houk and coworkers published an article concerning ground-state triplet energies of the polyacene series benzene to nonacene and compared the geometries and HOMO-LUMO energies to corresponding polyenes, suggesting as acenes increase in length their geometries resemble a pair of delocalized, nonalternating, polyene ribbons joined by relatively long bonds. Later Bendikov, Houk and coworkers refuted the previously accepted triplet ground state for polyacenes larger than hexacene and instead suggested an open-shell singlet diradical species.

Jiang and coworkers pushed the limits of analysis even further by considering extremely long polyacene systems with up to 40 fused benzenoid rings. Their density functional treatment suggested these systems are in fact antiferromagnetic spin systems (i.e. open-shell singlet) that exhibit a build-up of free spins about the edges.

1.2 Results and Discussion

1.2.1 Unsubstituted Acene Series: Naphthalene to Decacene

1.2.1.1 Introduction and Geometric Considerations

Although the series naphthalene to decacene had been previously examined computationally, the principal method utilized was the highly popular hybrid B3LYP density functional with a standard double-zeta valence Pople basis set (6-31G*). Despite its popularity, there has been recent work criticizing its accuracy in predicting energies of organic molecules, specifically in the use of double-zeta valence basis sets. Given this
find and the interest in verifying the methodology, the decision was made to compute the unsubstituted series naphthalene to nonacene, comparing both double-zeta valence (DZV) and triple-zeta valence (TZV) basis sets.

Geometry optimizations were carried out using Wavefunction's Spartan '04 suite of programs (zero-point energies uncorrected), initially with the semiempirical PM3 method and then refined with B3LYP/6-31G* which, despite its reported electronic shortcomings is still considered an accurate method for computing geometries. As expected, the calculated geometries and energies matched those of the literature within experimental error.

Although only closed-shell solutions were evaluated initially, there were suggestions from the literature that open-shell singlet energies were increasingly lower than closed-shell predictions for systems larger than hexacene. Given this, it seemed reasonable to attempt an open-shell geometry optimization with a triple-zeta valence basis to ensure comparable coordinates. The difference in energy between the open-shell and closed-shell singlets for nonacene at the B3LYP/6-311+G** level is approximately 4.5 kcal/mol. Despite this, the geometries for nonacene at a double-zeta valence and triple-zeta valence basis are comparable with no dramatic differences. The bond lengths for nonacene (TZV and DZV) are displayed in Figure 7.
1.2.1.2 Ground State and HOMO-LUMO Energies: DZV vs TZV

Given the insight of Grimme and coworkers\textsuperscript{85} who suggest the use of appropriate triple-zeta valence (TZV) basis sets for examining the energies of organic molecules and given the interest in studying the ground state and MO energies of large polyacenes, both DZV as used by Bendikov, Houk and coworkers\textsuperscript{82} and TZV methods were employed for comparison and validation purposes. A fair comparison of the methods requires analysis of relative energies of spin-states and specific excitation energies. A comparison of HOMO-LUMO energies is shown in Tables 1 and 2 and graphically in Figure 8.
Table 1: HOMO and LUMO energies and gaps compared for unsubstituted acenes evaluated with both DZV and TZV DFT methods. Shaded values are unrestricted calculations.

<table>
<thead>
<tr>
<th>Ring #</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Gap (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Gap (eV)</th>
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The data for the series presented in Table 1 suggests the larger (TZV) basis set is not improving upon the calculations conducted using the more common B3LYP/6-31G* method. However, when predicting the electronic ground state configuration, there does appear to be some discrepancy, albeit minimal. As shown in Figure 8 the HOMO-LUMO gaps predicted for the closed-shell configuration at the B3LYP/6-311+G** (TZV) level of theory are depressed compared to the open-shell solution for polyacenes larger than hexacene. Additionally, the absolute values of the HOMO and LUMO energies predicted by a closed-shell calculation for [n]acenes: 6<n<10 deviate from the trend established by [n]acenes: 1<n<7 as shown in Table 2.
Acene HOMO-LUMO Gaps (B3LYP)

![Graphical depiction of HOMO-LUMO gaps predicted by both DZV and TZV basis sets with open-shell (OS) and closed-shell (CS) configurations considered.]

**Figure 8:** Graphical depiction of HOMO-LUMO gaps predicted by both DZV and TZV basis sets with open-shell (OS) and closed-shell (CS) configurations considered.

<table>
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<th>Ring #n</th>
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<th>LUMO (eV)</th>
<th>Gap (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
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<td>-6.72</td>
<td>-5.56</td>
<td>1.16</td>
<td>-4.62</td>
<td>-3.08</td>
<td>1.54</td>
</tr>
</tbody>
</table>

**Table 2:** HOMO and LUMO energies and gaps predicted by both DZV and TZV basis sets with open-shell (shaded) and closed-shell methods.

Upon careful examination of the relative ground-state energies for [n]acenes (1<n<10), the closed-shell solutions are predicted by 6-31G* to be the lowest energy electronic configuration for [n]acenes where 1<n<6, whereas 6-311+G** predicts hexacene to be a closed-shell configuration as well (Table 3). Nevertheless, this “threshold” around n=6,7 is in agreement with the known instability of acenes.
Table 3: Relative ground-state energies of \([n]\)acenes in singlet (closed-shell \(S(cs)\) and open-shell \(S(os)\)) and triplet (T) states, comparing DZV and TZV basis sets.

<table>
<thead>
<tr>
<th>([n])Acene</th>
<th>(S(cs))</th>
<th>(S(os))</th>
<th>T</th>
<th>(S(cs))</th>
<th>(S(os))</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.00</td>
<td>0.00</td>
<td>71.56</td>
<td>0.00</td>
<td>72.53</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.01</td>
<td>48.79</td>
<td>0.00</td>
<td>49.41</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
<td>0.04</td>
<td>33.49</td>
<td>0.00</td>
<td>33.70</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
<td>0.66</td>
<td>22.71</td>
<td>0.00</td>
<td>22.88</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.00</td>
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<td>14.92</td>
<td>0.12</td>
<td>15.22</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.94</td>
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<td>1.70</td>
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<td>6.16</td>
<td>21.52</td>
<td>6.29</td>
<td></td>
</tr>
</tbody>
</table>

1.2.1.3 Summary

Though the use of triple-zeta valence (TZV) basis sets has been shown in the literature to improve upon energy calculations for organic molecules over the more commonly employed double-zeta valence (DZV) method, this does not seem to be the case for unsubstituted acenes. The only discrepancy noted is in the prediction of the electronic configuration for hexacene, where a TZV basis predicts a closed-shell configuration and a DZV basis predicts an open-shell singlet ground state.

1.2.2 Substituted Acenes: Pentacenes, Heptacenes, Nonacenes

1.2.2.1 Introduction

Although large unsubstituted acenes are of considerable theoretical interest, they are not of practical interest due to their general instability and poor solubility. Appropriate substitution of large acenes enabled the isolation of several acene derivatives.
larger than pentacene.\textsuperscript{11, 36, 86-88} Despite this, pentacene still remains the dominant target organic molecule for use in electronic devices and some theoretical work has been published on cyano,\textsuperscript{27} fluoro,\textsuperscript{52} and methoxy\textsuperscript{52} derivatives of pentacene. Still, there are few if any significant theoretical studies on acene derivatives larger than pentacene. Furthermore, only recently have significant theoretical studies directly compared results to known acene derivatives that have been experimentally isolated and characterized.\textsuperscript{13, 36}

1.2.2.2 Substituted Pentacenes

A critical step in establishing the utility of a particular computational method for a given application is validation of the theory against experimental results or otherwise well known accurate high-level quantum chemical methods. For accurate work predicting the electronic properties of organic molecules, it has been suggested that triple-zeta valence (TZV) basis sets are a minimum requirement.\textsuperscript{85} Given this suggestion, DFT theory utilizing a TZV basis and additional diffuse and polarization functions (B3LYP/6-311+G**) was compared to the more commonly employed B3LYP/6-31G* (DZV) in the ability to predict the experimentally derived HOMO and LUMO energy levels extracted from the corresponding UV-Vis spectra of six uniquely substituted pentacenes shown in Figure 9. The results of these comparisons are shown in Tables 4 and 5.

Geometry optimizations of substituted pentacenes 1-6 (Figure 9) were all carried out at the B3LYP/6-31G* level of theory and energies calculated at both DZV and TZV levels were not zero-point corrected.
<table>
<thead>
<tr>
<th>Pent.</th>
<th>HOMO (Expt.)</th>
<th>LUMO (Expt.)</th>
<th>Gap (Expt.)</th>
<th>HOMO (DFTdzv)</th>
<th>LUMO (DFTdzv)</th>
<th>Gap (DFTdzv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>-4.69</td>
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<td>-4.95</td>
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<td>1.88</td>
<td>-4.43</td>
<td>-2.27</td>
<td>2.16</td>
</tr>
</tbody>
</table>

MAD=0.46  MAD=0.71  MAD=0.25

**Table 4:** Comparison of HOMO – LUMO values for experimental and DFT theory utilizing a double-zeta valence (DZV) basis set by mean absolute deviations (MAD).

![Substituted pentacenes](image)

1. $R_1$=SPH, $R_2$=H
2. $R_1$=S(CH$_2$)$_2$CH$_3$, $R_2$=H
3. $R_1$=CCS(Pr)$_3$, $R_2$=H
4. $R_1$=o,o'-dimethylphenyl, $R_2$=H
5. $R_1$=Ph, $R_2$=H
6. $R_1$=H, $R_2$=Ph

**Figure 9:** Substituted pentacenes (Compounds 1-6) compared in Tables 4 & 5.

<table>
<thead>
<tr>
<th>Pent.</th>
<th>HOMO (Expt.)</th>
<th>LUMO (Expt.)</th>
<th>Gap (Expt.)</th>
<th>HOMO (DFTtzv)</th>
<th>LUMO (DFTtzv)</th>
<th>Gap (DFTtzv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-5.17</td>
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<td>1.81</td>
<td>-5.20</td>
<td>-3.03</td>
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</tr>
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</tr>
<tr>
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<td>1.69</td>
<td>-5.08</td>
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<td>-3.07</td>
<td>1.88</td>
<td>-4.80</td>
<td>-2.59</td>
<td>2.21</td>
</tr>
</tbody>
</table>

MAD=0.07  MAD=0.38  MAD=0.32

**Table 5:** Comparison of HOMO – LUMO values for experimental and DFT theory utilizing a triple-zeta valence (TZV) basis set by mean absolute deviations (MAD).
The data presented in Tables 4 and 5 suggest a vastly improved answer set is achieved in predicting the HOMO and LUMO energy levels of the substituted pentacenes using a TZV method rather than a DZV method. However, the overall HOMO – LUMO gap predicted with a DZV method fares slightly better (MAD_{dev} = 0.25) than that calculated by the TZV method (MAD_{dev} = 0.32). While this initially seems contradictory, upon careful examination it is clear that the TZV HOMO values have improved to a greater extent than that of the LUMO values, resulting in slightly larger HOMO – LUMO gaps.

1.2.2.3 Substituted Heptacenes

The popularity of pentacene as a lead candidate in organic electronics is due in part to its relative ease of synthesis and manageable air-stability. Larger polyacenes are likely to exhibit even greater potential based on calculated HOMO-LUMO gaps, but have not been synthetically accessible until very recently. As a result, very little theoretical study has been conducted on heptacene derivatives. Table 6 shows the calculated HOMO – LUMO values and associated gaps for unsubstituted heptacene (7) and 4 other 7,16-disubstituted heptacenes; 7,16-diphenyl (8), 7,16-diethynyl (9), 7,16-dicyano (10) and 7,16-dithiophenyl (11). Geometry optimizations were carried out with B3LYP/6-31G* and energies refined using UB3LYP/6-311+G**.
Table 6: Unrestricted (open-shell) singlet HOMO and LUMO energies for a series of heptacene derivatives (7-11) calculated from UB3LYP/6-311+G**//B3LYP/6-31G*. Spin character before (<S²>) and after (<S²>an) annihilation of the first spin-contaminant also shown.

As is the case with previously published unsubstituted heptacene at the B3LYP/6-31G* level of theory,² the spin character is still expected to be greater than zero at the TZV level calculated here, exhibiting a value of S² = 0.22 after annihilation of the first spin contaminant. Interestingly, spin character appears in all but one in the series from Table 6 without a clear trend. Addition of increasingly more electron withdrawing substituents does appear to have the effect of shrinking the HOMO-LUMO energy gap, however the lowest gap was found for 7,16-dithiophenylheptacene (1.39 eV) which may be the result of additional orbital interactions. Along with this appreciably smaller HOMO-LUMO gap, theory also predicts a closed-shell ground state electronic configuration for 7,16-dithiophenylheptacene suggesting that this compound may have far greater stability than the others in this series.

1.2.3 6,13-Diaryl Substituted Pentacene Oxidation

1.2.3.1 Introduction and scope of problem

Despite utility in numerous areas of organic electronic application, pentacenes and their derivatives still largely suffer from air-instability. Some attempts at better
understanding the mechanism(s) of oxidation have been published, however, the process is decidedly complicated by a number of likely competing pathways. Experimentally, endoperoxides and quinones are two isolable oxidation products of acenes larger than naphthalene. Although it is well established that photo-excited acenes promote triplet oxygen to singlet oxygen which may then be involved in a [4+2] cycloaddition across the acene, transition-state models for this process have eluded researchers. A competing reaction involving direct addition of triplet oxygen to the acene to form a triplet acene peroxide has also been studied. Upon triplet-to-singlet relaxation, the reactive intermediate may rapidly cyclize to form the more stable endoperoxide 12 (Figure 10).

**Figure 10:** Pentacene-6-peroxide diradical intermediate cyclization to form longer-lived pentacene-6,13-endoperoxide (12).

### 1.2.3.2 Computational Results

In an effort to gain a more complete understanding of the oxidation of substituted pentacenes, two experimentally known systems were subjected to computational analysis. The synthesis of 6,13-diphenylpentacene has been known for some years and more recently been used as a platform for diastereoselective addition of [60]fullerene to form a
unique fullerene bis-adduct driven by π-π stacking interactions between fullerenes.\textsuperscript{90,91}

More recently a bulkier derivative, namely 6,13-di(o,o'-dimethylphenyl)pentacene has also been synthesized. Experiments in the Miller research group have shown that the bulkier aryl substituents at the 6,13 positions effectively shut down oxidation at this position which is otherwise favorable, as in the case of unsubstituted pentacene and even 6,13-diphenylpentacene. The UPM3-optimized transition state geometry for triplet 6,13-di(o,o'-dimethylphenyl) pentacene-5-peroxide 13 is shown in Figure 11, and a summary of the computational study is provided in Table 7.

Figure 11: Representative transition-state (TS) showing triplet oxygen addition to the C5 carbon of 6,13-di(o,o'-dimethylphenyl)pentacene 13 in an exo fashion with a bond length of 1.788 Å. The free spin character (isosurface 0.02) is shown in blue.

<table>
<thead>
<tr>
<th>Pentacene Diradical (Triplet)</th>
<th>Rel. E TS (kcal/mol)</th>
<th>Rel. E Prod. (kcal/mol)</th>
<th>dE (kcal) TS - Prod</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,13-diphenyl-6-peroxide</td>
<td>21.36</td>
<td>18.64</td>
<td>2.72</td>
</tr>
<tr>
<td>6,13-diphenyl-5-endo-peroxide</td>
<td>21.84</td>
<td>19.4</td>
<td>2.44</td>
</tr>
<tr>
<td>6,13-diphenyl-5-exo-peroxide</td>
<td>21.85</td>
<td>18.99</td>
<td>2.85</td>
</tr>
<tr>
<td>6,13-di(dimethylphenyl)-6-peroxide</td>
<td>37.62</td>
<td>31.11</td>
<td>6.52</td>
</tr>
<tr>
<td>6,13-di(dimethylphenyl)-5-exo-peroxide</td>
<td>21.63</td>
<td>18.85</td>
<td>2.78</td>
</tr>
<tr>
<td>6,13-di(dimethylphenyl)-5-endo-peroxide</td>
<td>- - -</td>
<td>18.91</td>
<td>- - -</td>
</tr>
</tbody>
</table>

Table 7: Reaction energies for triplet oxygen addition to 6,13-disubstituted pentacenes at the 5- and 6- carbons to form a triplet pentacene peroxide diradical, predicted at the UB3LYP/6-311G*/UPM3 level of theory, relative to starting materials.
From Table 7, it is apparent that 6,13 phenyl substitution minimally impacts addition of triplet oxygen at the C6 position which is still favored over the C5 position by about 0.5 kcal/mol. In contrast to this, \( o,o' \)-dimethylphenyl substitution at the 6,13 carbons dramatically increases the barrier to the transition state for C6 addition, preferring triplet oxygen addition to the C5 position by about 16 kcal/mol. In both pentacene systems analyzed, \textit{exo} addition to C5 is preferred. This preference is negligible for 6,13-di(\( o,o' \)-dimethylphenyl)pentacene which exhibits less than a tenth of a kcal/mol difference between \textit{exo} and \textit{endo} additon of triplet oxygen. The transition state for 5-\textit{endo} addition to 6,13-di(\( o,o' \)-dimethylphenyl) pentacene could not be located. This suggests that the increased bulk from the \( o,o' \)-dimethylphenyl discourages \textit{endo} approach of the oxygen, preferring \textit{exo} addition which in turn requires bond rotation and triplet-to-singlet relaxation before cyclization can be achieved.

\subsection*{1.2.3.3 Summary}

Experiments have shown that bulky aryl substituents at the 6,13 positions of pentacene diminish oxidation at C6 which is otherwise favorable. Calculations at the UB3LYP/6-311G*/UPM3 level of theory corroborate this fact, indicating a 16 kcal/mol preference for 5-\textit{exo} addition of triplet oxygen over addition to C6 in 6,13-di(\( o,o' \)-dimethylphenyl)pentacene. Also in agreement is the bias for addition of triplet oxygen to C6 of 6,13-diphenylpentacene, where the respective transition states differ by about 0.5 kcal/mol. The data suggests that hindered aryl substituents can be implemented with the expectation that they will enhance the oxidative resistance of the resulting acene.
1.2.4 6,13-Diphenethylthiopentacene

1.2.4.1 Introduction and scope of problem

6,13-Diphenethylthiopentacene (Figure 12) is a uniquely persistent pentacene derivative ($t_{1/2} = 2700$ minutes in solution with direct exposure to light and air) that has conformational freedom in solution which could impact its overall electronic characteristics. With a 3-atom bridge connecting the acene backbone to an aryl moiety (in this case phenyl), there are several potential local minima. Initial consideration of possible conformations intuitively lead to two important geometries for consideration. In the first, the aryl groups are as far apart from one another as possible $14a$ (i.e., “stretched” conformation) and in the second, the aryl groups engage in $\pi - \pi$ stacking with the $\pi$ system of the acene $14b$ (i.e., “sandwich” conformation). In theory, $14a$ would minimize any torsional strain over any other conformer while the added torsional strain in $14b$ could be compensated for by the energetic gain expected due to $\pi - \pi$ stacking.

1.2.4.2 Computational Results

A monte carlo conformational search (MMFF94) revealed hundreds of low energy conformers due to 8 bonds with conformational freedom. Among the conformer set, two expected conformations $14a$ and $14b$, plus an additional conformer $14c$ were chosen, giving three symmetric conformers for the theoretical study of non-bonding interactions (Figure 12). Conformer $14c$ benefits from CH – $\pi$ interactions involving the acene (H donor) and the aryl group of the phenethylthio substituent ($\pi$ donor).
Given the stabilizing nature of weak non-bonding interactions such as CH – π and stronger π – π stacking interactions, it was predicted that conformers 14b and 14c would each be favored over conformer 14a in the gas phase. To test this prediction and determine to what extent stabilization was impacted, a variety of theoretical methods were compared, specifically hybrid (B3LYP), non-hybrid (PBEPBE) and effective-core potential modified DFT methods as well as higher accuracy MP2 calculations. A summary of the results of these methods is shown in Tables 8-11.

Table 8 shows relative energies for the three conformers computed by applying a triple-zeta valence basis set including polarization and diffuse functions (6-311+G**) to the hybrid B3LYP density functional. The relative energies are then compared for two differently optimized starting coordinates, a modification of Alinger's MM2 provided by CambridgeSoft's Chem3D package versus a typical hybrid DFT geometry.
Table 8: Comparison of Force-Field and DFT optimizations followed by SPE calculations using a triple-zeta valence basis applied to the hybrid density functional B3LYP.

From Table 8 there are only subtle differences in HOMO and LUMO energies among the conformers and across coordinate groups, however, the relative energies are quite different. There appears to be a much larger discrepancy in energy among the MM2 optimized conformers with an energy difference of 14.27 kcal/mol. DFT optimized conformers show only an energy difference of 5.46 kcal/mol, an intuitively more reasonable conformational potential energy surface (PES). In both cases conformer 14b is predicted to be highest in energy. This suggests π–π stacking interactions are not considered stabilizing by this DFT method.

A similar set of comparisons and thus conclusions is reached for the data presented in Table 9 which replaces the B3LYP single-point energy from Table 8 with a generalized gradient approximated (GGA) non-hybrid DFT method (PBE) applying a basis set with slightly higher polarization functions but now without the presence of diffuse functions (6-311G(2df,2pd)). As with the data-set from Table 8, conformer 14a is predicted to be the lowest in energy. However the conformational PES is diminished with just a 3 kcal/mol separation for the DFT optimized geometries and a 7.75 kcal/mol separation for the MM2 optimized set.
Table 9: Comparison of Force-Field and DFT optimizations followed by SPE calculations using a triple-zeta valence basis applied to a generalized gradient approximation density functional.

The other striking differences with the PBE GGA calculations are the very low HOMO-LUMO gaps, which are not consistent with experimental evidence.

Møller-Plesset perturbation theory provides an electronic correlation term to the standard Hartree-Fock \textit{ab initio} method which generally offers higher accuracy energy predictions. A restricted-localized modification of a second-order Møller-Plesset method was applied with an appropriate triple-zeta valence basis set as suggested from the literature\textsuperscript{85} to provide higher accuracy energies as shown in Table 10.

Table 10: Comparison of Force-Field and DFT optimizations followed by SPE calculations using a triple-zeta valence basis applied to a second-order Møller-Plesset perturbation of Hartree-Fock.
Utilization of MP2 for the conformer set gives results that are more in line with intuition, indicating conformer 14b to be the lowest energy for both MM2 and B3LYP optimized coordinates. However, the HOMO and LUMO energies predicted deviate dramatically from experimentally determined values. With an energy separation of 20 kcal/mol, the MM2 geometries appear to be inaccurate coordinates at this level of theory.

Having exhausted traditional computational models, an effective-core potential (ECP) modified DFT method recently developed by DiLabio\textsuperscript{92} was explored. As noted from the literature, this method is intended to correct notoriously poorly predicted long-range non-bonding interactions inherent in DFT methods. According to the described procedure, the DFT input was easily modified to implement this method and the results are shown in Table 11 where ECP-modified methods are designated with a \textit{signum sectionis} (§).

From Table 11, the ECP-modified method represents the highest accuracy model among those evaluated for this substituted pentacene. As with MP2, the ECP-modified DFT method predicts conformer 14b to be the lowest energy system. However, in contrast to MP2, this method also predicts HOMO and LUMO energies in good agreement with experiment. It should be noted that single-point energies employing this method are of comparable cost to analogous non-modified DFT methods. The use of ECP-modified DFT to produce optimized geometries required up to 7 days on a 3 GHz dual-core processor with 3GB memory. By contrast, MM2 optimizations may be carried out on a desktop computer in about 10-20 minutes and according to Table 11, appear to have equally reliable geometries.
Table 11: Comparison of Force-Field, DFT and ECP modified (§) DFT optimizations followed by SPE calculations using an ECP modified (§) triple-zeta valence basis applied to the B971 functional.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Geometry Optimization</th>
<th>Single Point Energy</th>
<th>Rel. E. (kcal/mol)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>MM2</td>
<td>B971/6-311+G(2d,2p)§</td>
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<td>-4.99</td>
<td>-2.79</td>
<td>2.20</td>
</tr>
<tr>
<td>14c</td>
<td>MM2</td>
<td>B971/6-311+G(2d,2p)§</td>
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<td>-4.89</td>
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</tr>
<tr>
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<td>-4.93</td>
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<td>2.12</td>
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<td>-4.81</td>
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<td>2.12</td>
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<td>0.00</td>
<td>-4.83</td>
<td>-2.71</td>
<td>2.12</td>
</tr>
</tbody>
</table>

1.2.4.3 Summary

6,13-Diphenethylthiopentacene is a uniquely persistent pentacene derivative that can exist in a \(\pi - \pi\) stacking conformation. Given the size of such a chemical system (40 heavy atoms), accurate models are limited to low-level \textit{ab initio}, or modest density functional optimizations at best. DFT energy predictions for systems involved in through-space non-bonding interactions are notoriously poor, and this study is consistent with that conclusion. MP2 methods predict \(\pi - \pi\) stacking geometries to be favorable, but offer very poor HOMO and LUMO energies. DFT methods seem to predict reasonably accurate HOMO and LUMO energies, but do not appreciate the non-bonding interactions unless an appropriate effective-core potential (ECP) is applied to carbon atoms. Application of an ECP modified TZV basis to the B971 functional finds the \(\pi - \pi\) stacking interaction of pentacene conformer 14b to be favorable while also computing reliable HOMO – LUMO energies.
1.3 **Conclusions**

Acenes are a class of polycyclic aromatic hydrocarbon (PAH) which exhibit extensive $\pi$ delocalization. Appropriate substitution has been shown to improve solubility and air-stability, both desirable characteristics for applications in thin-film electronic devices. Fine-tuning the electronic characteristics of substituted acenes may in part be achieved by accurate computational models which may be used to estimate charge carrier mobilities. Density functional theory is a valuable tool for predicting discrete HOMO – LUMO energy gaps for acene derivatives when applying a suitable triple zeta valence (TZV) basis set. Trends in HOMO – LUMO gaps for discrete molecules may be used to approximate valence – conduction band gaps for a bulk material. DFT methods suffer from a poor description of non-bonding interactions such as $\pi$ – $\pi$ and CH – $\pi$ interactions. However application of an effective-core potential (ECP) to the TZV basis set has been shown to correct for this behavior.

1.4 **Experimental**

1.4.1 **Geometry Optimizations**

All semi-empirical and DFT geometry optimizations were computed using Gaussian '03 (Linux) on a Parallel Quantum Solutions (PQS) Quantum Cube 4-node cluster (AMD opteron x86, 64-bit, 2.39 GHz, 3.5 GB memory) operating Novell SuSE 9.0, with the exception of the unsubstituted acenes which were optimized using Spartan '04 (Windows) on a Dell Optiplex GX280 (Intel Pentium 4 x86, 32-bit, 2.79 GHz, 3 GB memory) operating Windows XP. *Monte Carlo* conformational searches were performed using
Spartan '04 with the MMFF94 force-field.

1.4.2 **Single Point Energies**

All single point energies were computed using Gaussian '03 (Linux) on a Parallel Quantum Solutions (PQS) Quantum Cube 4-node cluster (AMD opteron x86, 64-bit, 2.39 GHz, 3.5 GB memory) operating Novell SuSE 9.0.

1.4.3 **Graphical Rendering**

Molecular orbitals were graphically rendered using Avogadro (Linux) on a Dell Optiplex GX280 (Intel Pentium 4 x86, 32-bit, 2.79 GHz, 3 GB memory) operating Ubuntu 9.10.
CHAPTER 2

SYNTHESIS AND STUDY OF SUBSTITUTED STARPHENES

2.1 Introduction

2.1.1 Starphenes

Starphenes are a class of molecule belonging to the polycyclic aromatic hydrocarbon family (PAHs) and are classified as “alternant cata-condensed” polyarenes. Geometrically, they are constructed by linear benzannellation (benzene ring-fusion) of triphenylene at the 2,3-, 6,7-, and 10,11- positions. Each linear polyacene moiety is separated from the adjacent polyacene moiety by 120 degrees giving an overall symmetry of $D_{3h}$. The term “starphene” generally refers to symmetric systems as shown in Figure 13 but a rigorous definition has not been identified and may include asymmetric systems as well. As with all PAHs, starphenes are flat, highly delocalized systems and are expected to pack well in the solid state, thereby significantly limiting solubility. Extensive $\pi$ delocalization suggests starphenes may possess useful electronic properties similar to those of their linear polyacene analogs. Further, their enhanced geometric readiness for $\pi$ stacking interactions bode well for possible integration into organic electronic devices including organic transistors and photovoltaic devices. Several full reviews of polycyclic aromatic hydrocarbons have been authored and the reader is
encouraged to consult volumes including those of Clar, Harvey and Bjorseth for further reading.\textsuperscript{1-3}

![Figure 13: Triphenylene, trinaphthalene ([2.2.2]heptastarphene) and trianthracene ([3.3.3]decastarphene)](image)

2.1.2 Discovery, Nomenclature and Synthesis

2.1.2.1 Discovery: Triphenylene and PAHs

As noted earlier, starphanes are $D_{3h}$ symmetric PAHs built upon the parent triphenylene moiety. Triphenylene itself was isolated as early as 1880\textsuperscript{93} and was identified as an isomer of chrysene, both of which can be extracted from coal tar.\textsuperscript{2,3} The study of these and other small, soluble, isolable PAHs had initially been driven by the interest in quinoid dyes which were of commercial and industrial importance during the industrial revolution.\textsuperscript{3} Access to a large number of such polyarenes soon led to investigation of their physical and chemical properties with special attention to the concept of aromaticity, a theoretical property of the $\pi$ delocalization of a ring of $4n+2$ $\pi$ electrons. Additional interest came from the biomedical community as small-molecule
PAHs became ubiquitous in laboratories where, in the 1930s, several PAHs were found to be procarcinogenic, a discovery which has only furthered investigations of this class of compounds.3

Starphene quinones are a common derivative of, and often a synthetic precursor to, starphenes. Quinones in general have significance in numerous areas of scientific inquiry including their abundance in biological systems as natural facilitators of "RedOx" chemistry in a variety of photosynthetic pathways.94 Two interesting examples of naturally produced starphene quinones trianellinone95 and xylospyrin96 were both coincidently reported in 1970 and are shown in Figure 14.

Figure 14: Natural products: trianellinone and xylospyrin

2.1.2.2 Nomenclature of Phenes and Starphenes

As noted previously in Chapter 1 on the nomenclature of Acenes, the nomenclature of polycyclic aromatic hydrocarbons in general is best described by Eric Clar8 who provides a detailed description in volume 1 of Polycyclic Hydrocarbons.1 The reader is therefore encouraged to review Clar's book, however, a few relevant aspects of
the nomenclature of PAHs as they pertain to phenes and starphenes need mention.

The phene family is a series of angular polycyclic aromatic hydrocarbons derived from the parent phenanthrene. However, the numbering scheme adopted for phenes is not based on that used for phenanthrene. Instead, it is related to the numbering scheme of acenes in that it starts with the ring furthest to the right and begins with the carbon positioned at “10-o-clock” as depicted in Figure 15. Like acenes, the phenes are named by a Greek prefix according to the number of rings in the structure followed by the suffix "phene" as in tetraphene, pentaphene and so on.

\[ \text{Figure 15: The numbering scheme for phenes: tetraphene and pentaphene} \]

Starphenes, derived from the parent triphenylene (Figure 13), are numbered as a derivative of the largest phene moiety present in their structure. This gives the flexibility to consider both symmetric and asymmetric systems under one uniform naming convention. The branch-substituent is numbered with primes and the 2’ and 3’ positions are the conventional site of ring-fusion as shown in Figure 16. As with phenes, starphenes are named by a Greek prefix according to the number of rings in the structure followed by the suffix "starphene." However, an additional qualifier that describes the
number of rings for each branch is also used to eliminate any ambiguity such as [1.2.3]heptastarphene (or heptastarphene-[1.2.3]) shown in Figure 16.

![Figure 16: The number scheme for starphenes: [2.2.2] and [1.2.3] heptastarphenes]

### 2.1.2.3 Synthesis of Unsubstituted Starphenes: [2.2.2]Heptastarphene and [3.3.3]Decastarphene

The synthetic approaches for starphenes are a numbered few. The compound [2.2.2]heptastarphene 16 has been synthesized by the reduction of triphthalylbenzene (15) using either hydriodic acid or by zinc-dust distillation. Compound 15 was first synthesized by cyclotrimerization of 1,4-naphthoquinone\(^1\). In another approach, Hausigk treated benzene with slightly more than 3 equivalents of 1,2-bis(bromomethyl)cyclohexane and a 10 mole percent equivalent of aluminum trichloride to form the starphene ‘backbone’ (17). Compound 17 was then dehydrogenated using Pd/C to generate the target [2.2.2]heptastarphene\(^9\).
Scheme 1: Synthesis of [2.2.2]heptastarphene via cyclotrimerization of naphthoquinone.

Scheme 2: Synthesis of [2.2.2]heptastarphene involving Friedel-Crafts alkylation.

[3.3.3]Decastarphene 18 has also been synthesized via cyclotrimerization utilizing 1,4-anthroquinone\textsuperscript{100} 19 with a 10 mol percent equivalent of 1,4-dihydroxyanthracene to generate the triquinone 20 as shown in Scheme 3.

A second, lengthier approach by Clar begins with a double Friedel-Crafts acylation of phenanthrene using phthalic anhydride in the presence of aluminum trichloride. The resulting bis-ketoacid 21 of phenanthrene was subsequently reduced using zinc-dust forming diacid 22. Another Friedel-Crafts acylation with one equivalent of naphthalene-2,3-dicarboxylic anhydride 23 gives keto-acid 24 followed by a reduction to generate triacid 25 which was converted to [3.3.3]decastarphene 18 in a zinc-dust melt\textsuperscript{101} (Scheme 4).
Scheme 3: Synthesis of [3.3.3]decastarphene by cyclotrimerization of 1,4-anthraquinone

Scheme 4: Clar’s synthesis of [3.3.3]decastarphene
2.1.2.4 Starphene Analogs

Cyclotrimerization chemistry dominates the literature as the preferred synthetic route toward starphene analogs and precursors. The vast majority of this chemical work was carried out in the 1970s by a small collection of organic chemists at the Universität Göttingen in Germany, namely Hans Brockmann, Hartmut Laatsch, and Hartwig Greve. In many cases, the $D_3h$ symmetric cyclotrimer were isolated as byproducts. Polymerization and cyclotrimerization chemistry of naphthazarin and naphthoquinone is described in several papers and isolation of a few cyclotrimers (Figure 17) was achieved.$^{102-105}$

![Figure 17: Quinone and hydroquinone analogs of starphenes](image)

2.1.3 General Reactivity and Electronic Properties

2.1.3.1 Diels-Alder cycloaddition of maleic anhydride

Starphenes and phenes have been shown to exhibit Diels-Alder reactivity toward maleic anhydride.$^{106-108}$ In a series of publications from 1980,$^{106,107}$ Biermann and Schmidt experimentally monitored the reaction kinetics of the Diels-Alder cycloaddition
of maleic anhydride to 90 different PAHs (nearly all of which were obtained from E. Clar's collection) by UV analysis. Based on this set of experiments, it is apparent that the reactivity of phenes and starphenes is less than that of an acene with the same number of linearly annellated rings as are in the longest branch of the phene. For example, tetracene is more reactive toward dienophiles than any phene or starphene containing a tetracene moiety. A few examples of their findings are outlined in Table 12.

**2.1.3.2 Electronic Properties and Theoretical Study**

Most knowledge of the electronic properties of polycyclic aromatic hydrocarbons (PAHs) has come from the careful analysis of the ultraviolet and visible absorption spectra of some 150 compounds from Clar's collection as detailed in volume 1 of *Poly cyclic Hydrocarbons*.\(^1\) It is also in this work that several concepts regarding the nature of aromaticity in these compounds is presented. Clar's "aromatic sextet," "the annellation principle," and "asymmetric annellation effects" are elegant albeit simple qualitative theories that correlate well with experiment and can be utilized to describe and predict the general reactivity and likely absorptive bands of new PAHs.\(^1\) The significance of the aromtic sextet is portrayed pictorially in Figure 18. Here a series of heptacene 'benzologues' are depicted with a circle drawn in each six-membered ring that contains a sextet of \(\pi\) electrons. Inspection of the \(\lambda_\pi\) and \(\lambda_\sigma\) bands along the series reveals consistent blue-shifting in benzologues as a function of increasing aromatic sextets. This property is visually evident when directly comparing the color of each compound in its pure form.\(^1\)

The annellation principle builds upon the aromatic sextet concept whereby linear
<table>
<thead>
<tr>
<th>Compound Structure</th>
<th>Compound Name</th>
<th>2°-Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>pentacene</td>
<td>1,640,000</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>tetracene</td>
<td>94,200</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>1,2-benzotetracene</td>
<td>17,000</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>heptaphene</td>
<td>9,320</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>7,8-benzoheptaphene</td>
<td>7,930</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>hexaphene</td>
<td>6,670</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>1,2:3,4-dibenzotetracene</td>
<td>5,910</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>anthracene</td>
<td>2,270</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>1,2-benzanthracene</td>
<td>136</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>1,2:3,4-dibenzanthracene</td>
<td>67.4</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>6,7-benzopentaphene</td>
<td>60</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>naphtho(2',3':6,7)pentaphene</td>
<td>58</td>
</tr>
</tbody>
</table>

**Table 12:** Rate constants for general reactivity of maleic anhydride with various PAHs.
annellation of benzene rings, which introduces no additional aromatic sextets, has the effect of shifting the absorption toward the red as in the polyacene series naphthalene to heptacene. Conversely, asymmetric annellation effects may also be observed in non-linear benzannellation. Whereas linear benzannellation produces constant successive spectral shifts, non-linear benzannellation spectral shifts are, not surprisingly, more varied and complex. For a complete description of these concepts the reader is directed toward Clar's *Polycyclic Hydrocarbons*.¹

In particular, strong asymmetric annellation effects have been noted in the series of linear benzologues of triphenylene.¹⁰⁹ From spectral evidence it was concluded that only two branches of these systems participate in extended $\pi$ delocalization whilst the third branch is "insulated" from the system by the double bond present in the central ring. This phenomenon is demonstrated in [Figure 19]. When comparing benzene to anthracene and anthacene to pentaphene, the $\beta$-bands undergo a substantial red-shift of 66 nm and 63 nm respectively. However, addition of the third naphthalene branch to the pentaphene causes a slight 2 nm blue-shift. According to Clar, this behavior is not due to the introduction of a third aromatic sextet, but instead results from the "fixation of the central double bond in [the] pentaphene." The central $\pi$ bond may only contribute to the delocalization of two of the three branches at any given moment, "cutting off the third branch from aromatic conjugation."¹⁰⁹ This work was theoretically corroborated by Goodwin and Morton-Blake in a simple modification of a Hückel molecular orbital (MO) study of the $\beta$, $\alpha$- and $\rho$- bands.¹¹⁰ Clar's final demonstration of this effect was published in 1968 with his syntheses of [2.3.3]nonastarphene and [3.3.3]decastarphene. These
compounds completed the benzologue series of the parent heptaphene ([0.3.3]heptastarphene) and benzheptaphene ([1.3.3]octastarphene) and the absorption spectra of each shows only very small shifts in the absorption bands again indicating that the heptaphene moiety is the dominant chromophore and the third branch is shielded from conjugation.\textsuperscript{101}

Figure 18: A series of heptacene 'benzologues' demonstrating the concept of the aromatic sextet as it pertains to absorption bands and compound color

Figure 19: Asymmetric annellation effects observed in phenes and starphenes
2.2 Results and Discussion

2.2.1 Synthesis and Reactivity of [3.3.3]Decastarphene

2.2.1.1 Brockman and Laatsch cyclotrimerization approach

Two synthetic methods which have been used to synthesize the known [3.3.3]decastarphene were identified from the literature. The cyclotrimerization reaction between 1,4-anthraquinone and 1,4-dihydroxyanthracene (Scheme 5) as reported by Brockman and Laatsch\textsuperscript{100} was chosen due to its relative simplicity over the more laborious approach of Clar and coworkers\textsuperscript{101}.

The 1,4-anthraquinone 19 can be readily accessed in high yield by sodium borohydride reduction of commercially available quinizarin. Subsequent reduction of 1,4-anthraquinone with sodium dithionite generates the needed 1,4-dihydroxyanthracene 26. The cyclotrimerization is then catalyzed via acidic (acetic acid) media at reflux for 16 to 20 hours and the [3.3.3]decastarphene triquinone 20 is obtained. The triquinone has extremely poor solubility and could not be characterized by NMR spectroscopy. Despite this limitation, treatment of the triquinone with a mixture of hydriodic acid and acetic acid under a nitrogen atmosphere for 5 days according to the procedure of Miller and coworkers\textsuperscript{111} gives a mixture of hydrogenated products in which hexahydro decastarphene 27 is believed to be the dominant isomer. Treatment of the mixture with DDQ in refluxing benzene cleanly gave [3.3.3]decastarphene 18 which was purified by solvent washing and characterized by $^1$H NMR, UV-Vis, and MALDI-TOF MS.
Scheme 5: Cyclotrimerization of 1,4-anthraquinone and 1,4-dihydroxyanthracene for the synthesis of [3.3.3]decastarphene 18

### 2.2.1.2 Attempted Derivatization of Decastarphene with [60]Fullerene

The [3.3.3]decastarphene showed no reactivity with [60]fullerene in refluxing CS$_2$, toluene, or o-dichlorobenzene. It was assumed that solubility of the two reactants was a critical limitation. Also the limited reactivity of this relatively small starphene was considered. As shown in Table 12, the Diels-Alder reactivity of anthracene is significantly less than that of tetracene and by analogy a similar trend is expected for starphenes. Therefore, the synthesis of the larger, decidedly more reactive [4.4.4]tridecastarphene was pursued.

### 2.2.2 Attempted Synthesis of [4.4.4]Tridecastarphene

Despite some limitations regarding the cyclotrimerization chemistry utilized for the synthesis of [3.3.3]decastarphene, it was still believed to be a useful direct approach
for constructing a starphene scaffold. In order to construct a [4.4.4]tridecastarphene in this way it was necessary first to synthesize 1,4-tetracenequinone 28 and 1,4-dihydroxytetracene 29. The synthesis of 28 reported by Patney\textsuperscript{112} was subsequently followed (Scheme 6).

\begin{center}
\includegraphics[width=\textwidth]{scheme6.png}
\end{center}

**Scheme 6:** Synthesis of 1,4-tetracenequinone following the procedure of Patney\textsuperscript{112}

The synthesis relies on a key condensation step between naphthalene-2,3-dicarboxyhydride 23 (synthesized from dehydration of diacid 30) and 1,4-hydroquinone to construct the four-ringed tetracene scaffold. The reaction proceeds under relatively harsh conditions at 220-250 °C in a molten aluminum trichloride and sodium chloride slurry followed by a cold water quench and overnight digestion into 20% hydrochloric acid. Soxhlet extraction into xylenes cleanly affords 1,4-dihydroxytetracene-5,12-quinone 31 (nicknamed tetrazarin) as a brilliant orange powder. Tetrazarin may then be converted directly to 1,4-tetracenequinone 28 by sodium borohydride reduction followed by mild acid workup. Simple sodium dithionite reduction of the quinone generated the 1,4-dihydroxytetracene 29 needed to complete the
cyclotrimerization reaction. Subsequent chemistry to convert the crude cyclotrimerized product into [4.4.4]tridecastarphene was unsuccessful, presumably due to extremely poor solubility. Successful synthesis of a starphene larger than [3.3.3]decastarphene therefore relied on strategies that incorporated substituents designed to enhance the solubility of this large class of polycyclic aromatic hydrocarbon.

2.2.3 Synthesis of Soluble 1,4-Acenequinone Precursors

2.2.3.1 Synthesis of 6,11-Diphenyl Tetrazarin

Phenyl substitution has been utilized extensively in the Miller labs for the purpose of enhancing the solubility of acenes.90,91,113 Solubility enhancement combined with ease in characterization made phenyl substitution of starphene systems an attractive strategy, and several useful synthetic precursors were synthesized. Initially a simple and effective target was identified as 1,4-dihydroxy-6,11-diphenyltetracene-5,12-quinone 32 (also called 6,11-diphenyltetrazarin) due to commercially available starting materials 1,3-diphenylisobenzofuran and 5,8-dihydroxy-1,4-naphthalenequinone (naphthazarin). Here a one-pot, two-step reaction proceeds in refluxing benzene whereby a Diels-Alder cycloadduct forms the carbon skeleton followed by catalytic p-toluenesulfonic acid dehydration and azeotropic removal of water utilizing a Dean-Stark trap to form the final product (Scheme 7). Attempts at reducing 32 to 6,11-diphenyl-1,4-tetracene-quinone utilizing sodium borohydride, potassium borohydride or lithium aluminum hydride were unsuccessful.
Scheme 7: Synthesis of 6,11-diphenyltetrazarin 32 in one pot via Diels-Alder cycloaddition, acid-catalyzed dehydration followed by azeotropic removal of water using a Dean-Stark (D-S) trap.

2.2.3.2 Synthesis of 7,10-Diphenyl Tetrazarin

Synthetic efforts by Rainbolt and Miller\textsuperscript{114} allowed easy access to another useful phenyl substituted synthon 4,7-diphenylisobenzofuran which could be utilized \textit{in situ} to form the 7,10-diphenyltetrazarin 33 in one pot as shown in Scheme 8. However the reaction did not proceed cleanly, resulting in a significant proportion of a competing product 34. Although separation could be achieved, this route was abandoned in favor of cleaner chemistry.

Scheme 8: Synthesis of 7,10-diphenyltetrazarin 33 in one pot via Diels-Alder cycloaddition, acid-catalyzed dehydration and subsequent azeotropic removal of water
2.2.3.3 Synthesis of Diphenyl Pentazarin

The synthesis of 1,3-diphenylisonaphthofuran by Cava and coworkers\textsuperscript{115} was undertaken in order to carry out construction of another useful phenyl substituted starphene precursor identified as 1,4-dihydroxy-6,13-diphenyl-5,14-pentacenequinone 35 or 6,13-diphenylpentazarin as a trivial name. This novel compound was generated again in a one-pot, two-step reaction via Diels-Alder cycloaddition followed by catalytic dehydration and azeotropic removal of water (Scheme 9).

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme_9.png}
\end{center}

\textit{Scheme 9}: Synthesis of 6,13-diphenylpentazarin in one pot via Diels-Alder cycloaddition and subsequent azeotropic removal of water.

The product was generated cleanly and purified by chromatography to give deep red solids which were isolated and fully characterized. This system was subjected to a variety of reductive conditions intended to generate 6,13-diphenyl-1,4-pentacenequinone, but all such attempts failed.

2.2.3.4 Synthesis of 9,10-Diphenylanthracene-1,4-quinone

A useful phenyl substituted 1,4-quinone identified from the literature, 9,10-diphenylanthracene-1,4-quinone 36, was reported to be constructed through direct
phenylmagnesium bromide addition into the 9,10- carbonyls of quinizarin\textsuperscript{116-118} followed by acid mediated double dehydration. However, this method resulted in a low-yielding mixture of products. A less direct, higher-yielding, cleaner synthesis was subsequently devised (Scheme 10). The strategy invoked methylation of quinizarin in order to enhance the electrophilicity of the 9,10- carbonyls by shutting down tautomerization (Figure 20). This was followed by phenyl addition into the carbonyls to form a diastereomeric mixture of cis and trans diols 38 which was aromatized by the action of potassium iodide in refluxing acetic acid. The vibrant green, fluorescent anthracene 39 was then oxidatively demethylated at room temperature using N-bromosuccinimide according to the procedure of Kim and coworkers\textsuperscript{119} to give the target quinone 36.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure20.png}
\caption{Thermodynamically controlled methylation of quinizarin to prevent tautomerization.}
\end{figure}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme10.png}
\caption{Synthesis of 9,10-Diphenylanthracene-1,4-quinone from quinizarin}
\end{scheme}
2.2.3.5 **Synthesis of 9,10-Di(p-t-butyphenyl)anthracene-1,4-quinone**

Using the same strategy as for the synthesis of quinone 36, the synthesis of 9,10-di(p-t-butyphenyl)anthracene-1,4-quinone 40 was carried out (Scheme 11). This novel compound would likely further enhance the solubility of a starphene or starphene-precursor due to the p-t-butyphenyl aryl substitution. Furthermore, this aryl substituent simplifies the aromatic region in the 'H NMR spectrum and adds a large indicative resonance from the t-buty methyl groups. The p-t-butyphenyl magnesium bromide was readily synthesized under typical Grignard conditions in dry THF.

![Scheme 11: Synthesis of 9,10-Di(p-t-butyphenyl)anthracene-1,4-quinone 40](image)

2.2.4 **Synthesis and Study of [4.4.4]Hexa-p-t-butyphenyltridecastarphene**

2.2.4.1 **New approach using a [6]radialene hub**

Although interesting and synthetically challenging targets, radialenes have yet to prove practical utility in chemical synthesis. In 1977-1978 a buzz of activity revolved around the synthesis and isolation of [6]radialene, specifically by the three independent
research laboratories of K.P.C. Vollhardt, Virgil Boekelheide, and that of Peter Schiess and Markus Heitzmann. A summary of synthetic methods is depicted in Figure 21.

It was Vollhardt and coworkers who first isolated [6]radialene from pyrolysis of 1,5,9-cyclododecatriyne and obtained a ¹H NMR spectrum showing evidence of a methylene singlet resonating at 64.69.¹²⁰ Heitzmann and Schiess studied the pyrolysis products of 2,4,6-tris(chloromethyl)mesitylene finding that at sufficiently high temperatures (660 °C) the compound loses three equivalents of hydrochloric acid to cleanly give [6]radialene which was carefully isolated and characterized by ¹H and ¹³C NMR at -40 °C.¹²¹ In a separate communication, it was noted by Boekelheide that the relatively low temperature pyrolysis of 2,4,6-tris(chloromethyl)mesitylene to generate [6]radialene was the most attractive synthesis. In addition, he and coworkers isolated [6]radialene from pyrolysis of hexamethylbenzene-tris-sulfone at 900 °C.¹²²

In an earlier communication, Vollhardt had found that 1,5,9-cyclododecatriyne when combined with dimethyl maleate (solvent, b.p. 207 °C) and heated to 230 °C in a sealed tube gave tris-adduct 41 (Scheme 12) as a mixture of isomers in good yield.¹²⁰
Figure 21: Various synthetic methods of [6]radialene

Scheme 12: Synthesis of [6]radialene dimethyl maleate tris-adduct 41 from 1,5,9-cyclododecatriyne and dimethyl maleate at 230 °C in a sealed tube
The question arose concerning the possible intermediacy of benzo[1,2:3,4:5,6]tricyclobutene during the course of the reaction. Calculations suggested this benzenoid compound to be 11 kcal/mol higher in energy than [6]radialene, but its formation could not be ruled out.

The reactive radialene has subsequently been trapped via triple Diels-Alder cycloaddition chemistry on two occasions. Though a demonstration of proof-of-concept, this method of synthesis is not very practical nor amenable to general synthetic strategies.

Coincident to the isolation of [6]radialene in 1978 by Hart and coworkers was the mention of the molecular ion of [6]radialene appearing in the mass spectrum of hexamethylbenzenetrisulfone. Hart suggests that hexamethyl-benzenetrisulfone may therefore be a useful precursor to [6]radialene under appropriate conditions, but no work in this area has since been explored. Interestingly, utilization of benzosulfone as a thermal precursor to o-quinodimethane in solution at temperatures above 210 °C has been reported. It was therefore conceivable that similar solution-phase chemistry could be employed to generate [6]radialene in situ from hexamethylbenzenetrisulfone and that it could be trapped on three sides with an appropriate dieneophile to form a trisadduct precursor to a starphene.

2.2.4.2 Synthesis of hexamethylbenzenetrisulfone and derivatives

The synthesis of hexamethylbenzenetrisulfone 42 was carried out following a modified procedure of Hart and coworkers and is outlined in Scheme 13.
The synthesis relies on the generation of hexakis(bromomethyl) benzene 43 which may be accomplished by one of several methods. Direct bromination may be carried out by addition of molecular bromine to a hot solution of hexamethylbenzene in 1,2-dibromoethane followed by reflux under a halogen lamp for 4 days.

![Scheme 13: Synthesis of hexamethylbenzenetrisulfone 42](image)

Another method starting from commercially cheap mesitylene was found to be more efficient and is a modification of a synthesis by Zavada et al. which describes bromomethylation of mesitylene followed by direct bromination of the remaining three free methyl positions using molecular bromine. In the synthesis presented in Scheme 13, 2,4,6-tris(chloromethyl) mesitylene 44 was generated as previously published and subsequently brominated with molecular bromine in refluxing 1,2-dibromoethane for 48 hours during which time $S_N$ displacement of chloride was achieved. Hexakisbromomethylbenzene was recrystalized from 1,2-dibromoethane.

The $D_3h$ symmetry imposed on all symmetric starphenes may be initiated by converting hexakisbromomethylbenzene into hexamethylbenzene trisulfide 45 (CA Index
Name: Benzo[1,2-c:3,4-c':5,6-c"]trithiophene, 1,3,4,6,7,9-hexahydro- (9CI)) following
the procedure of Hart and coworkers.\textsuperscript{124} Subsequently 45 could be oxidized to the
 corresponding hexamethylbenzene trisulfone 42 (CA Index Name: Benzo[1,2-c:3,4-
c':5,6-c"]trithiophene, 1,3,4,6,7,9-hexahydro-, 2,2,5,5,8,8-hexaoxide (9CI)) using 32%
peracetic acid stirring at room temperature for 18 hours and collecting the clean
precipitate by filtration.

Once in hand, trisulfone 42 was heated in an appropriate solvent to temperatures
greater than 230 °C in the presence of three different dienophiles to generate three unique
derivatives as shown in Figure 22.

[60] Fullerene was introduced to the hexamethylbenzene trisulfone in refluxing
$alpha$-chloronaphthalene under nitrogen to generate a fullerene tris-adduct 46 with very
poor solubility. Despite significant efforts, characterization of this unique compound was
limited only to $^1$H NMR which showed a dynamically broadened AB multiplet centered
around $\delta$5.25 ppm. Freshly recrystallized tetracyanoethylene was also used to generate
novel trisadduct 47 that again, but more surprisingly, suffered from poor solubility.
Attempts at full characterization again only produced a $^1$H NMR in DMSO-d$_6$ that
showed a single resonance at $\delta$4.26 ppm.
Maleic anhydride was introduced to the trisulfone in refluxing diphenyl ether (~250 °C) to generate trisadduct 48 which was characterized by $^1$H and $^{13}$C NMR. This provided a “proof of principle” demonstration that hexamethylbenzene trisulfone can be utilized as a precursor to hexaradialene at relatively low temperatures in solution. The $^1$H NMR indicated a diastereoselective cycloaddition process giving the syn-anti product exclusively. This product has two separate spin-systems due to its $C_5$ symmetry. The anti- addend contains an ABX system while each of the syn- addends possesses identical ABMNXY systems as depicted in Figure 23. Although no further chemistries were carried out with this novel compound, it may provide a useful platform for a plethora of triphenylene derivatives upon oxidative aromatization. Triphenylenes have been found to form interesting lamellar columns due to $\pi-\pi$ interactions.
2.2.4.3 Synthesis of Hexa-(p-t-butylphenyl)[4.4.4]tridecastarphene

Using trisulfone 42 in the "low-temperature" bench-top synthesis of three novel hexaradialene trisadducts suggested its general utility for the purpose of constructing starphenes. With this useful "starphene-hub" precursor in hand, one need only utilize an appropriate 1,4- acene quinone dienophile to rapidly build up the starphene scaffold. To this end, 9,10-di(p-t-butyphenyl)-1,4-anthraquinone 40 was selected. Combined with trisulfone 42 in nitrogen-purged diphenyl ether and heated to reflux for 16 hours, the p-t-butyphenyl substituted [4.4.4]tridecastarphene triquinone 49 was obtained as shown in

Figure 23: Pople analysis of hexaradialene maleic anhydride trisadduct 48
Scheme 14. Structural analysis of the triquinone 49 utilized $^1$H NMR and MALDI-TOF MS, and the compound could not be completely isolated from minor bi-product impurities. Reduction of the triquinone was successfully achieved using a 1:10 mixture of hydriodic acid and acetic acid which was heated to 140 °C for 2 hours in a sealed tube by microwave radiation. The reduced starphene 50 was cleanly extracted from the crude reaction mixture with dichloromethane and characterized by $^1$H and $^{13}$C NMR. Oxidation of the hexa-aryl substituted hexahydro[4.4.4]tridecastarphene to generate hexa-(p-t-butylphenyl)-[4.4.4]tridecastarphene 51 was carried out by the action of 10% palladium on carbon in refluxing o-dichlorobenzene for 4 days (Scheme 15). The red-orange compound exhibited an intense “day-glow” orange fluorescence under short-wave UV light.

Scheme 15: Synthesis of hexa-(p-t-butylphenyl)[4.4.4]tridecastarphene from triquinone precursor 49

2.2.4.4 Synthesis of a [60]fullerene Trisadduct of Hexa-(p-t-butylphenyl)[4.4.4]Tridecastarphene

Diels-Alder cycloaddition chemistry between [60]fullerene and acenes larger than tetracene has been readily accomplished utilizing the “over-reduced” hydrogenated form of the acene and generating the reactive acene diene \textit{in situ} in the presence of [60]fullerene.\textsuperscript{90, 91, 113, 131-134} This strategy avoids isolating any highly reactive acene species having more than 4 rings. The same strategy could be employed for the synthesis of [60]fullerene adducts of starphenes. In this manner, the hexahydro-hexa-(p-t-butylphenyl)[4.4.4]tridecastarphene 50 was combined with [60]fullerene and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and heated to 90 °C in o-dichlorobenzene for 20 hours. Column chromatography on silica gel with carbon disulfide as eluent was used to separate two [60]fullerene trisadduct diastereomers, the \textit{syn,syn-} 52a and \textit{syn,anti-} 52b adducts shown in Figure 24.
2.2.4.5 Theoretical Electronic Predictions of Starphenes

Starphenes are expected to have interesting electronic characteristics due to extensive π delocalization. Given recent improvements in computational chemistry, it seemed reasonable to computationally explore these systems via density functional theory (DFT). As noted in Chapter 1, B3LYP/6-311+G** energies have shown promise in predicting accurate trends in HOMO – LUMO gaps among polycyclic aromatic hydrocarbons and therefore is a useful method for evaluating starphenes. Single-point energies for the closed-shell singlet (Scs), open-shell singlet (Sos) and triplet (T) states of [nnn]starphenes (n = 3-5, 7,9) were evaluated using B3LYP/6-311+G**. Geometries for each starphene were obtained from the PM3 semi-empirical method. The results of the study are shown in Tables 13-16 in Figure 25. [nnn]Starphenes are predicted to have a closed-shell for n < 5 and an open-shell singlet configuration for n > 4 (Table 16), in contrast to [n]acenes where an open-shell electronic configuration is true for n > 6 (see Chapter 1). The data suggests that [nnn]starphenes will have remarkably low HOMO – LUMO gaps for n > 5 as compared with [n]acenes.
Table 13: Closed-shell H-L gaps
(R)DFT B3LYP/6-311+G**//PM3 - S(cs)

<table>
<thead>
<tr>
<th>Starphene</th>
<th>Homo (eV)</th>
<th>Lumo (eV)</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333</td>
<td>-5.26</td>
<td>-2.54</td>
<td>2.72</td>
</tr>
<tr>
<td>444</td>
<td>-4.96</td>
<td>-2.84</td>
<td>2.12</td>
</tr>
<tr>
<td>555</td>
<td>-4.75</td>
<td>-3.04</td>
<td>1.72</td>
</tr>
<tr>
<td>777</td>
<td>-4.5</td>
<td>-3.28</td>
<td>1.23</td>
</tr>
<tr>
<td>999</td>
<td>-4.36</td>
<td>-3.42</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Figure 25: Tabulated results of DFT study of different sized [nnn]starphenes. Tables 13-15 show HOMO - LUMO energies for closed-shell (Table 13) and open-shell (Table 15) singlets as well as triplet (Table 14) electronic configurations. Table 16 shows the relative energies for each starphene as a function of electronic configuration.

2.3 Conclusions

Starphenes are an interesting class of polycyclic aromatic hydrocarbons that, by analogy to acenes, are expected to have interesting properties, both physical and chemical. Despite this, there are very few known examples of starphenes from the literature. In their unsubstituted form they are marked by very poor solubility and as a result are challenging to characterize and process in the usual ways. Hybrid density functional theory (B3LYP) calculations have shown remarkably low HOMO-LUMO energy gaps in starphenes due to extensive π delocalization making them attractive compounds for use in organic electronic applications. The synthesis of a hexa-hydro...
precursor to hexa-(p-t-butylphenyl)-[4.4.4]tridecastarphene has been described and represents the largest, soluble starphene derivative known. Oxidation of the hydrogenated starphene, upon crude work-up gives a compound that exhibits characteristic “day-glow orange” fluorescence in solution, which bleaches after a few days. Although isolation of the starphene remains elusive, it may be formed \textit{in situ} and is reactive towards an excess of [60]fullerene, forming a mixture of \textit{syn,syn}- and \textit{syn,anti-} tris adducts.

2.4 \textbf{Experimental}

2.4.1 \textbf{Analytical Instrumentation}

2.4.1.1 \textit{\textsuperscript{1}H NMR Spectra}

\textit{\textsuperscript{1}}H NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 399.768 MHz or a Varian INOVA 500 FT-NMR operating at 499.763 MHz. All chemical shift (\(\delta_{\text{H}}\)) values are reported in parts per million (ppm) relative to \((\text{CH}_{3})_{4}\text{Si}(\text{TMS})\) unless otherwise noted.

2.4.1.2 \textit{\textsuperscript{13}C NMR Spectra}

\textit{\textsuperscript{13}}C NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 100.522 MHz or a Varian INOVA 500 FT-NMR operating at 125.666 MHz. All chemical shift (\(\delta_{\text{C}}\)) values are reported in parts per million (ppm) relative to \((\text{CH}_{3})_{4}\text{Si}(\text{TMS})\) unless otherwise noted.
2.4.1.3 **Mass Spectrometry**

Time-of-flight matrix assisted laser desorption ionization (MALDI-TOF) mass spectrometry was performed on a Shimadzu Kratos Axima-CFR running in reflectron mode.

2.4.2 **Chromatography**

Sand was obtained from Fisher Scientific Co.
Silica Gel (230-400 mesh) was obtained from Natland International Co.
Glass Wool was obtained from Fisher Scientific Co.
Thin Layer Chromatography Plates obtained from Fisher Scientific Co.

2.4.3 **Solvents**

*Note: All solvents were used without further purification unless otherwise noted.* Solvent drying was carried out for tetrahydro furan, toluene, methylene chloride, ethyl ether and dimethyl formamide as needed by distillation from sodium metal (THF, toluene) or by passing through a silica column in a dry-solvent delivery system.

Acetic Acid (CH₃CO₂H) was obtained from VWR Chemical Co.
Acetic Anhydride ((CH₃CO)₂O) was obtained from Fisher Scientific Co.
Acetone (reagent grade) was obtained from Pharmco.
Benzene (C₆H₆) was obtained from EM Science.
Carbon Disulfide (CS₂) was obtained from EM Science.
Carbon Tetrachloride (CCl₄) was obtained from Aldrich Chemical Co.

Chloroform (CHCl₃) was obtained from Fisher Scientific Co.

Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories.

1,2-Dichlorobenzene (ODCB) was obtained from Aldrich Chemical Co.

Dichloromethane (CH₂Cl₂) was obtained from Fisher Scientific Co.

Diethyl Ether ((CH₃CH₂)₂O) was obtained from Pharmco.

N,N-Dimethylformamide (HCON(CH₃)₂) was obtained from Fisher Scientific Co.

Dimethylsulfoxide (DMSO) (anhydrous) was obtained from Alfa Aesar Chemical Co.

1,4-Dioxane ((CH₂CH₂)₂O) was obtained from Aldrich Chemical Co.

Ethanol (anhydrous) was obtained from Pharmco.

Ethanol (95%) was obtained from Pharmco.

Ethyl Acetate (CH₃CO₂CH₂CH₃) was obtained from Fisher Scientific Co.

Hexanes were obtained from Fisher Scientific Co.

Methanol (CH₃OH) was obtained from Pharmco.

Nitrobenzene (PhNO₂) was obtained from Fisher Scientific Co.

Pyridine (C₅H₅N) was obtained from Aldrich Chemical Co.

1,1,2,2-Tetrachloroethane (Cl₂CHCHCl₂) was obtained from Aldrich Chemical Co.

Tetrahydrofuran (THF) was obtained from Fisher Scientific Co.

Toluene (PhCH₃) was obtained from Fisher Scientific Co.

Triglyme (CH₂O(CH₂CH₂O)₅CH₃) was obtained from Fisher Scientific Co.

Xylenes were obtained from Fisher Scientific Co.
2.4.4 Reagents

*Note: All reagents were used without further purification unless otherwise noted.*

Aluminum foil (Al°) was obtained from Reynolds.

Aluminum trichloride (AlCl₃) was obtained from Aldrich Chemical Co.

Ammonium chloride (NH₄Cl) was obtained from Fisher Scientific Co.

1,4-Benzquinone (C₆H₄O₂) was obtained from Acros Organics Co.

Benzoyl peroxide (BPO) was obtained from Aldrich Chemical Co.

Benzyl bromide (C₆H₅CH₂Br) was obtained from Aldrich Chemical Co.

Borane THF Complex (BH₃:THF) was obtained from Acros Organics Co.

Boric Acid (H₃BO₃) was obtained from Fisher Scientific Co.

Bromine (Br₂) was obtained from Acros Organics Co.

N-Bromosuccinimide (NBS) was obtained from Aldrich Chemical Co.

n-Butanol (C₄H₁₀O) was obtained from Fisher Scientific Co.

p-tert-Butylbromobenzene (C₆H₅BrC₄H₉) was obtained from Alfa Aesar Chemical Co.

Calcium chloride (CaCl₂) was obtained from Fisher Scientific Co.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was from Aldrich Chemical Co.

1,4-Dihydro-1,4-epoxynaphthalene (C₁₀H₈O) was obtained from Aldrich Chemical Co.

Diisobutylaluminum hydride (DIBAL-H) was obtained from Aldrich Chemical Co.

Dimethylacetylene dicarboxylate (DMAD) was obtained from Aldrich Chemical Co.

1,3-Diphenylisobenzofuran (C₂₀H₁₄O) was obtained from Aldrich Chemical Co.

[60] Fullerene (C₆₀) was obtained from MER Chemical Co.
Hydriodic Acid (HI) was obtained from Aldrich Chemical Co.

Hydrochloric Acid (HCl) was obtained from EM Science.

Hydroquinone (C₆H₄O₂) was obtained from Fisher Scientific Co.

Iodine (I₂) was obtained from Aldrich Chemical Co.

Lithium aluminum hydride (LiAlH₄) (LAH) was obtained from Aldrich Chemical Co.

Manganese sulfate (MgSO₄) was obtained from Fisher Scientific Co.

Maleic Anhydride (C₄H₂O₃) was obtained from Alfa Aesar Chemical Co.

Mercury (II) chloride (HgCl₂) was obtained from Fisher Scientific Co.

1,4-Naphthoquinone (C₁₀H₆O₂) was obtained from Aldrich Chemical Co.

Nitric Acid (HNO₃) was obtained from EM Science.

Palladium on activated carbon (10% Pd/C) was obtained from Aldrich Chemical Co.

Phenyllithium (C₆H₅Li) was obtained from Aldrich Chemical Co.

Phenylmagnesium bromide (C₆H₅MgBr) was obtained from Aldrich Chemical Co.

Phthalic anhydride (C₈H₄O₃) was obtained from Aldrich Chemical Co.

Potassium borohydride (KBH₄) was obtained from Aldrich Chemical Co.

Potassium carbonate (K₂CO₃) was obtained from Fisher Scientific Co.

Potassium hydroxide (KOH) was obtained from EM Science.

Potassium iodide (KI) was obtained from Acros Organics Co.

Quinizarin (C₁₄H₁₄O₄) was obtained from Aldrich Chemical Co.

Rongalite (HOCH₂SO₂Na:2H₂O) was obtained from Acros Organics Co.

Sodium (Na°) was obtained from Aldrich Chemical Co.

Sodium bicarbonate (NaHCO₃) was obtained from Fisher Scientific Co.
Sodium bisulfite (NaHSO₃) was obtained from EM Science.

Sodium borohydride (NaBH₄) was obtained from Aldrich Chemical Co.

Sodium carbonate (Na₂CO₃) was obtained from Fisher Scientific Co.

Sodium chloride (NaCl) was obtained from J.T. Baker Chemical Co.

Sodium dithionate (Na₂S₂O₄) was obtained from Acros Organics Co.

Sodium hydroxide (NaOH) was obtained from EM Science.

Sodium Iodide (NaI) was obtained from Acros Organics Co.

Sodium Nitrite (NaNO₂) was obtained from Aldrich Chemical Co.

Sulfuric Acid (H₂SO₄) was obtained from EM Science.

1,2,4,5-Tetrabromobenzene (C₆H₂Br₄) was obtained from Aldrich Chemical Co.

Tetrabutylammonium bromide (TBAB) was obtained from Aldrich Chemical Co.

Tetrabutylammonium fluoride (TBAF) was obtained from Aldrich Chemical Co.

Thionyl chloride (SOCl₂) was obtained from Aldrich Chemical Co.

Tin (II) chloride (SnCl₂) was obtained from Aldrich Chemical Co.

Titanium (IV) chloride (TiCl₄) was obtained from Aldrich Chemical Co.

Trifluoromethanesulfonic anhydride (Tf₂O) was obtained from Acros Organics Co.

Trimethylsilyl chloride (TMSCl) was obtained from Aldrich Chemical Co.

p-Toluenesulfonic acid (CH₃C₆H₄SO₃H) was obtained from Aldrich Chemical Co.

Zinc (Zn⁰) was obtained from Aldrich Chemical Co.
2.4.5 Syntheses

Note: All routine solvent evaporations were conducted on a standard rotary evaporator using vacuum pump pressure unless otherwise noted.

[3.3.3]Decastarphene (18). To a 50 ml round-bottomed flask equipped with a reflux condenser was added 15 ml toluene followed by hexahydro[3.3.3]starphene 27 (50 mg, 0.09 mmol) and DDQ (184 mg, 0.81 mmol). The mixture was brought to reflux and stirred continuously for 18 hours at which point the toluene was removed under reduced pressure and the crude product washed with ethanol on a glass fritted funnel until the washings were colorless. The product 18 was dried under vacuum and obtained as a shiny black amorphous solid (47.5 mg, 0.09 mmol, 95% yield). UV-Vis (λ max. nm, CHCl₃): 303, 338, 352, 367. MALDI-TOF MS (m/z): 358.5, 528.8, 542.7, 580.4. ¹H NMR (380 MHz, benzene-ᵈ) δ (ppm): 9.27 (s, 6H), 8.63 (s, 6H), 8.10-8.01 (m, 6H), 7.50-7.40 (m, 6H).

1,4-Anthraquinone (19). 10.0g (41.66 mmol) of commercially available quinizarin was suspended in 150 mL of methanol. The suspension was cooled to 0 °C and to it was added sodium borohydride (9.45g, 250 mmol, 6eq.) portion wise over 20 min. The reaction continued for 1 hour and was carefully quenched at 0 °C with water. During the quench the crude product precipitated. The precipitate was collected by vacuum filtration, washed with water, ethanol and hexanes and dried under vacuum to give 8.4 g (95%) of clean product 19. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.60 (s, 2H), 8.08-8.02
(m, 2H), 7.72-7.65 (m, 2H), 7.06 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 184.91, 140.29, 135.05, 130.45, 129.83, 129.10, 128.58.

[3.3.3]Decastarphene-5,6,14,15,22,23-quinone (20). To a 100 ml round-bottomed flask equipped with a reflux condenser was added 40 ml glacial acetic acid followed by anthracene-1,4-quinone 19 (200 mg, 0.96 mmol) and anthracene-1,4-hydroquinone 26 (20 mg, 0.09 mmol). The reaction mixture was stirred continuously at reflux for 18 hours before cooling and quenching with 20 ml cold water. The crude product precipitated and was collected by vacuum filtration and washed with water, ethanol and hexanes and then dried under vacuum to give 20 as a brown amorphous solid with terrible solubility such that the material could not be characterized and was carried on without further purification (162 mg, 80% crude yield).

Naphthalene-2,3-dicarboxylic acid anhydride (23). To a 100 ml round-bottomed flask was added a mixture of glacial acetic acid (45 ml) and acetic anhydride (10 ml) followed by naphthalene-2,3-dicarboxylic acid 30 (1.5 g, 7.6 mmol). The mixture was heated to reflux with magnetic stirring for 24 hours. Upon cooling, the crystalline product precipitated and was collected by vacuum filtration and dried $\textit{in vacuo}$ (1.4 g, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.56 (s, 2H), 8.19-8.14 (m, 2H), 7.86-7.81 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 163.15, 136.24, 130.69, 130.65, 128.01, 126.08.
4,8,13,16,21,24-Hexahydro[3.3.3]decastarphene (27). To a 50 ml round-bottomed flask equipped with a reflux condenser was added a mixture of glacial acetic acid (30 ml) and hydriodic acid (8 ml) which was purged with nitrogen gas for 5 minutes before addition of triquinone 20 (100 mg, 0.16 mmol). The reaction mixture was brought to reflux under a blanket of nitrogen gas for 5 days. The crude reaction product was extracted into methylene chloride and washed successively with saturated aqueous sodium bisulfite to remove halogen ions (2 x 50 ml), water (2 x 100 ml) and brine (50 ml). The organic phase was separated and evaporated under reduced pressure to give 27 as the dominant product in an inseparable mixture of hydrogenated starphenes. The mixture was used in the following step without further purification.

Tetracene-1,4-quinone (28). To a 50 ml round-bottomed flask equipped with a reflux condenser was added 20 ml ethanol (95%) followed by “tetrazarin” 31 (500 mg, 1.72 mmol) which was stirred at room temperature while slow addition of sodium borohydride (257 mg, 6.8 mmol) was carried out over 5-10 minutes. The mixture was brought to reflux and stirred continuously for 45 minutes before quenching (carefully) with cold water (10 ml). The brown precipitate was collected by vacuum filtration and washed with water and cold methanol and dried to give 28 without further purification (249 mg, 65% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.89 (s, 2H), 8.73 (s, 2H), 8.16-8.12 (m, 2H), 7.69-7.65 (m, 2H), 7.16 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 184.67, 140.86, 133.89, 131.50, 130.91, 130.51, 128.90, 127.90.
Naphthalene-2,3-dicarboxylic acid (30). To a 100 ml round-bottomed flask was added 65 ml N,N-dimethylformamide followed by α,α',α'-tetrabromo-o-xylene (6.4 g, 15.2 mmol), maleic anhydride (3.2 g, 32.6 mmol) and powdered sodium iodide (18 g, 120 mmol). The mixture was heated to 70 °C and stirred continuously for 18 hours. The reaction mixture was poured into a saturated aqueous sodium bisulfite solution (500 ml) and the yellow precipitate collected by vacuum filtration and washed with water (500 ml). The product 30 was dried under vacuum and could be used without further purification (1.8 g, 79% yield). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ (ppm): 12.6-13.4 (br s, 2H), 8.29 (s, 2H), 8.06-8.09 (m, 2H), 7.64-7.67 (m, 2H). \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) δ (ppm): 169.39, 133.46, 130.54, 129.75, 129.20, 129.09.

1,4-Dihydroxytetracene-5,12-quinone (31). To a flame-dried 500 ml 3-neck round-bottomed flask equipped with mechanical stirrer, condenser and a sand bath was added a mixture of aluminum trichloride (17 g, 127.5 mmol) and sodium chloride (3 g, 51.3 mmol) which was carefully heated to a melt (220 °C) and stirred. To the melt was then added a pulvarized mixture of naphthalene-2,3-dicarboxylic anhydride (30, 3.27 g, 16.5 mmol) and hydroquinone (2.27 g, 20.6 mmol) and the mixture stirred for 30 min. Upon cooling to 0 °C the mixture solidified and was digested by slow addition of 300 ml 50% HCl and allowed to stir overnight. The aqueous mixture was filtered, washed with 200 ml water and dried in a 90 °C oven. The dried cake was pulvarized and extracted continuously by a Soxhlet apparatus into hot xylenes. Upon concentration of xylenes, the bright orange precipitate was collected by filtration, washed with hexanes and dried.
under vacuum to cleanly obtain the product 31 as orange amorphous solids (2.25 g, 7.8 mmol, 47% yield). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 13.08 (s, 2H), 8.91 (s, 2H), 8.15-8.12 (m, 2H), 7.76-7.73 (m, 2H), 7.33 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 187.16, 157.89, 135.26, 130.30, 130.00, 129.71, 129.37, 129.19, 113.75.

1,4-Dihydroxy-6,11-diphenyltetracene-5,12-quinone (32). To a 100 ml round-bottomed flask was added 50 ml benzene followed by 1,3-diphenylisobenzofuran (711 mg, 2.63 mmol) and naphthazarin (500 mg, 2.63 mmol) and the mixture was brought to reflux for 3.5 hours at which time pTsOH monohydrate was added and the resulting mixture allowed to reflux for an additional 20 hours. The crude reaction mixture was concentrated to an oil and the crude product precipitated with cold methanol. The precipitate was collected by filtration and washed with additional methanol successively followed by saturated aqueous sodium bicarbonate, water, methanol and hexanes. Tetracenequinone derivative 32 was isolated as a bright orange amorphous solid by silica gel chromatography with dichloromethane as eluent (850 mg, 73%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 12.56 (s, 2H), 7.60-7.50 (m, 10H), 7.31-7.28 (m, 4H), 7.20 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 188.2, 156.6, 145.0, 140.3, 135.9, 129.3, 129.0, 128.5, 128.4, 128.2, 127.1, 126.8, 114.3.

1,4-Dihydroxy-6,13-diphenylpentacene-5,14-quinone (35). To a 50 ml round-bottomed flask was added 10 ml benzene followed by p-toluenesulfonic acid monohydrate (pTsOH, 200 mg, 1.05 mmol) which was brought to reflux in the presence
of a Dean-Stark trap for 30 min to azeotropically remove water. To this warm mixture was added the pentacene endoxide derivative 69 and the solution was allowed to reflux with stirring for 12 hours in the presence of a Dean-Stark trap. The crude reaction mixture was washed in a separatory funnel sequentially with saturated sodium bicarbonate, water and brine then dried over calcium chloride pellets. The organic layer was filtered and concentrated under reduced pressure and dried under vacuum. The crude product was washed with hexane and a small amount of cold acetone to give clean 35 as a red amorphous solid. M.P.: 388-390 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 12.63 (s, 2H), 8.12 (s, 2H), 7.85-7.82 (m, 2H), 7.66-7.59 (m, 6H), 7.52-7.48 (m, 2H), 7.38-7.36 (m, 4H), 7.21 (s, 2H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 188.1, 156.5, 146.3, 140.5, 133.0, 132.9, 129.8, 128.8, 128.6, 128.5, 128.0, 127.7, 127.2, 125.4, 114.7.

**9,10-Diphenylanthracene-1,4-quinone (36).** To a 50 ml round-bottomed flask was added 8 ml THF, 1 ml water and 5 drops concentrated sulfuric acid. To the stirring solution was then added 1,4-dimethoxy-9,10-diphenylanthracene 39 (39.0 mg, 0.1 mmol) followed by N-bromosuccinimide (NBS) (30 mg, 0.169 mmol). And the reaction allowed to proceed at room temperature for 5 minutes. The reaction mixture was quenched with aqueous sodium bicarbonate and extracted with ethyl acetate. The combined extracts were washed with water and brine, the organic layer separated and dried over calcium chloride, filtered and evaporated under reduced pressure to cleanly give 36 (30 mg, 0.083 mmol, 83% yield). \(^1\)H NMR (500 MHz, benzene-\(d_6\)) \(\delta\) (ppm): 7.65-7.58 (m, 2H), 7.40-7.34 (m, 4H), 7.33-7.28 (m, 2H), 7.21-7.14 (m, 4H), 7.02-6.95 (m, 2H), 6.20 (s, 2H).
13C NMR (125 MHz, benzene-\textit{d}_6) \delta (ppm): 185.32, 143.77, 140.34, 139.66, 136.07, 129.58, 129.42, 129.23, 128.98, 127.66.

\textbf{1,4-Dimethoxyanthracene-9,10-quinone (37).} To a 500 ml 3-neck flask equipped with mechanical stirring and reflux condenser was added 250 ml acetone followed by quinizarin (10 g, 41.6 mmol). The solution was stirred and then to it was added potassium carbonate (23.01 g, 167 mmol) and then stirred again for 5 min. Subsequently dimethyl sulfate (11.84 ml, 125 mmol) was added drop-wise over 2 min. The mixture was stirred and brought to reflux for 20 hrs. The crude mixture was taken up in 300 ml water and then filtered. The crude product was washed with 200 ml cold acetone and dried to give yellow crystalline 37 (9.1 g, 33.9 mmol, 81% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta (ppm): 8.19-8.13 (m, 2H), 7.74-7.68 (m, 2H), 7.35 (s, 2H), 4.00 (s, 2H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \delta (ppm): 183.41, 154.12, 134.21, 133.29, 126.40, 123.00, 120.22, 57.01.

\textbf{9,10-Dihydroxy-1,4-dimethoxy-9,10-diphenylanthracene (38).} To a flame-dried 3 neck round-bottomed flask charged with 50 ml dry toluene and equipped with nitrogen purge and reflux condenser was added phenylmagnesiumbromide (28.9 ml, 87 mmol) by flame-dried glass syringe. The mixture was slowly heated and stirred while a suspension of 1,4-dimethoxyanthracene-9,10-quinone 37 (3.87 g, 14.43 mmol) in 200 ml dry toluene was added over 30 min by a self-equalizing addition funnel. During the addition the temperature was continuously raised to reflux and the mixture was allowed to stir under nitrogen flow at reflux for 4 hours. The reaction was cooled and quenched with \textasciitilde{}20 ml
saturated aqueous ammonium chloride and then extracted into ethyl ether and dichloromethane. The organic extract was washed thrice with water, separated and dried over calcium chloride pellets. The organic solvents were evaporated under reduced pressure and the crude was triturated with hexanes, filtered and washed with ~60 ml hexanes and dried under vacuum. The crude product 38 (4.8 g, 11.31 mmol, 78 % yield) was obtained as a yellow powder. The product was recrystallized from methanol giving 3.1 g (50% yield overall). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.62-7.57 (m, 2H), 7.54-7.49 (m, 4H), 7.25-7.21 (m, 4H), 7.20-7.17 (m, 2H), 7.17-7.11 (m, 2H), 6.89 (s, 2H), 5.09 (s, 2H), 3.49 (s, 6H).

1,4-Dimethoxy-9,10-dipheny lanthracene (39). To a 100 ml round-bottomed flask was added 72 ml glacial acetic acid followed by 9,10-dihydroxy-9,10-diphenyl-1,4-dimethoxy anthracene (1 g, 2.356 mmol) and potassium iodide (2.66 g, 16.02 mmol, 6.8 equiv.). The mixture was heated to reflux and left stirring for 2.5 hours. The mixture was then cooled and added to 200 ml aqueous sodium bisulfite. The precipitate was collected by filtration and washed with 100 ml water to give clean 39 (0.85 g, 92%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.54-7.50 (m, 2H), 7.48-7.44 (m, 4H), 7.42-7.38 (m, 2H), 7.36-7.32 (m, 4H), 7.28-7.24 (m, 2H), 6.59 (s, 2H), 3.35 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 151.4, 143.8, 135.6, 131.1, 129.5, 127.1, 127.0, 125.7, 125.0, 124.2, 104.8, 56.2.

9,10-Di(p-tert-butylphenyl)-1,4-anthracenequinone (40). To a 50 ml round-bottomed flask was added 10 ml THF, 1 ml water and 5 drops concentrated sulfuric acid. The mixture was stirred at room temperature and 9,10-di-p-tert-butylphenyl-1,4-
dimethoxyanthracene (186 mg, 0.370 mmol) was added followed by N-bromosuccinimide (72 mg, 0.407 mmol) and the reaction was left to proceed at room temperature for 15 min. The reaction was then quenched with water and extracted into dichloromethane. The organic layer was washed sequentially with aqueous sodium bisulfite, water and brine, dried over calcium chloride and filtered. The solvent was removed under reduced pressure and the crude product dried under vacuum. 9,10-Di-p-tert-butylphenyl-1,4-anthraquinone 40 (170 mg, 0.360 mmol, 97 % yield) was obtained as a yellow green powder. The product was purified by silica gel column chromatography using DCM as eluent. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.61-7.58 (m, 2H), 7.58-7.54 (m, 4H), 7.52-7.49 (m, 2H), 7.20-7.17 (m, 4H), 6.8 (s, 2H), 1.44 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 186.2, 150.2, 143.9, 139.9, 136.4, 135.8, 129.2, 129.1, 128.5, 125.5, 34.9, 31.7.

**Benzo[1,2-c:3,4-c':5,6-c'']trithiophene, 1,3,4,6,7,9-hexahydro-, 2,2,5,5,8,8-hexaoxide (42).** To a 50 ml round-bottomed flask was added 25 ml 32% by weight peracetic acid (AcOOH) in acetic acid. Hexamethylbenzene trisulfide (45) (808 mg, 3.2 mmol) was added in portions at room temperature over 3 min. The mixture was left to stir at room temperature for 24 hours. After addition of 20 mL water, the white mixture was vacuum filtered and washed with 20 mL water, 10 mL ethanol and 30 mL hexanes and then dried under vacuum. Hexamethylbenzene trisulfone (42) (1.11 g, 3.2 mmol, 100 % yield) was obtained clean as a white powder and could be used without further purification. $^1$H NMR (500 MHz, DMSO-d6) $\delta$ (ppm): 4.62 (s). $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ (ppm): 129.88, 55.44.
Hexakis(bromomethyl)benzene (43). To a 2-neck 250 ml round-bottomed flask equipped with stirring and condenser was added ethylene bromide (95 ml) and 1,3,5-tris(chloromethyl)-2,4,6-trimethylbenzene (44, 2 g, 7.5 mmol) which was heated with stirring to a gentle reflux. To the solution was added a solution of bromine (l) (3 ml, 9.3 g, 58.3 mmol) in ethylene bromide (20 ml) dropwise via self-equalizing addition funnel over 30 min. The reaction was continued at reflux for 3 days. The crude reaction mixture was cooled to room temperature and the precipitate filtered, washed with 200 ml hexanes and dried under vacuum to give the product 43 as tan crystals (3.6 g, 5.8 mmol, 78% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 4.70 (s, 12H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 138.52, 24.58.

1,3,5-tris(chloromethyl)-2,4,6-trimethylbenzene (44). To a 250 ml round-bottomed flask equipped with mechanical stirring and reflux condenser was added 75 ml of concentrated hydrochloric acid, sodium chloride (3 g, 51 mmol), zinc chloride (6g, 44 mmol), paraformaldehyde (18.9 g, 630 mmol) and finally mesitylene (5 g, 42 mmol). The mixture was stirred under reflux for 40 hours, cooled to room temperature, vacuum filtered through a Buchner funnel and washed with 300 ml water. The crude solid was taken up in 300 ml methylene chloride and washed twice with 250 ml portions of water in a separatory funnel. The organic layer was separated, dried over magnesium sulfate, filtered and the solvent evaporated under reduced pressure. The resulting powder was dried under vacuum which produced 44 (10.5 g, 93%). No further purification was needed. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 4.68 (s, 2H), 2.50 (s, 3H). \(^{13}\)C NMR (125
Benzo[1,2-c:3,4-c':5,6-c'""]]trithiophene, 1,3,4,6,7,9-hexahydrate (45). A 250 ml round-bottomed flask equipped with reflux condenser and mechanical stirrer was charged with 95% ethanol (74 ml), tetrahydrofuran (38 ml), and water (5 ml). To the solvent mixture was then added freshly crushed sodium sulfide nonahydrate (1.5 g, 6.25 mmol) and hexakis(bromomethyl)benzene 43 (500 mg, 0.8 mmol) and the mixture was stirred and brought to reflux for 2 days. The crude reaction mixture was reduced to a 10 ml volume, filtered and washed with 200 ml water followed by small volumes of cold methanol, ethanol, and hexanes. The product was dried under vacuum and obtained as an off-white amorphous solid 45 (198 mg, 98%) and could be used without further purification. $^1$H NMR (500 MHz, DMSO-d$_6$) δ (ppm): 4.18 (s). $^{13}$C NMR (125 MHz, DMSO-d$_6$) δ (ppm): 135.54, 36.01.

Benzo[1,2-c:3,4-c':5,6-c'""]]triphthalic anhydride-1,4,5,8,9,12-hexahydrate (48). To a 25 mL round-bottomed flask was added diphenyl ether (7 ml) followed by maleic anhydride (66 mg, 0.67 mmol) and hexamethylbenzene trisulfone 42 (30 mg, 0.86 mmol). Oxygen was removed by nitrogen flow through the mixture which was then brought to reflux under a nitrogen blanket for 22 hrs. The mixture was sonicated with about 10 mL hexanes, filtered, washed with hexanes and dried to give the crude product hexahydrotetraphenylene trisanhydride 48 (32.8 mg, 0.72 mmol, 85 % yield) as tan solids. No further purification was needed. $^1$H NMR (400 MHz, DMSO-d$_6$) δ (ppm): 3.69-3.66 (br m, 1H), 3.61-3.54 (m, 1H), 3.51-3.44 (m, 1H), 3.30-3.24 (br m, 1H), 3.16-3.04 (m,
$^{2}$H), 2.92-2.84 (m, 1H), 2.80-2.73 (m, 1H), 2.71-2.64 (br m, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm): 175.67, 175.50, 174.98, 132.40, 132.17, 131.81, 25.31, 25.21, 25.10.

5,10,15,20,25,30-Hexa($p$-t-butylphenyl)[4.4.4]tridecastarphene-6,9,16,19,26,29-triquinone (49). To a 50 ml rbf was added 10 ml diphenylether followed by 9,10-di-$t$-butylphenyl-1,4-anthraquinone (270 mg, 571 µmol) and hexamethylbenzene trisulfone (60.3 mg, 173 µmol). The mixture was degassed with nitrogen for 10 min and then heated to reflux for 16 hours under nitrogen flow. The crude reaction mixture was cooled and crude product precipitated from 150 ml cold methanol, filtered through sintered glass and washed with 60 ml cold methanol to give $t$-butylphenyl-starphene-triquinone (131 mg, 84 µmol, 48.4 % yield) crude as a brown solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 9.40 (s, 6H), 7.69-7.58 (m, 18H), 7.55-7.49 (m, 6H), 7.29-7.21 (m, 6H), 1.53 (s, 54H).

5,10,15,20,25,30-Hexa($p$-t-butylphenyl)-6,9,16,19,26,29-hexahydro[4.4.4]tridecastarphene (50). To a 8 ml sealed-tube was added 5 ml glacial acetic acid, 1 ml hydriodic acid (50-55%) and triquinone 49 (75 mg, 0.048 mmol) and the mixture was purged with nitrogen gas for 5 minutes with stirring. The reaction vessel was then heated to 140 °C for 2 hours in a CEM microwave reactor. The crude reaction mixture was added to an aqueous solution of sodium bisulfite (25 ml) and extracted into methylene chloride. The solvent was removed under reduced pressure and the film dried under vacuum to give the product 50 as a yellow powder (55 mg, 0.035 mmol, 73%
yield). $^1$H NMR (500 MHz, CDCl₃) δ (ppm): 8.32 (s, 6H), 7.64-7.61 (m, 12H), 7.46-7.40 (m, 6H), 7.38-7.33 (m, 12H), 7.31-7.23 (m, 6H), 4.16 (s, 12H), 1.53 (s, 54H). $^{13}$C NMR (125 MHz, CDCl₃) δ (ppm): 149.94, 136.64, 136.48, 135.79, 132.59, 131.83, 130.13, 128.16, 126.46, 125.45, 124.85, 121.51, 34.80, 31.79.

**Syn, syn-tris[60]fullerene-5,10,15,20,25,30-hexa(p-t-butylphenyl)**

[4.4.4]tridecastarphene (52a) and **Syn, anti-tris[60]fullerene-5,10,15,20,25,30-hexa(p-t-butylphenyl)** [4.4.4]tridecastarphene (52b). To a 50 ml rbf was added 20 ml o-dichlorobenzene followed by [60]fullerene (100 mg, 0.14 mmol, 6 eq.) which was stirred until dissolved. To the vibrant purple solution was then added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (32 mg, 0.14 mmol, 6 eq) and hexahydro-[4.4.4]starphene 50 (36 mg, 0.024 mmol) and the mixture was heated to reflux and stirred for 24 hours. Upon cooling, the solvent was evaporated under reduced pressure and the crude product was subjected to silica gel chromatography with carbon disulfide as a mobile phase to remove excess fullerene. A partial separation was achieved with the first fraction giving [60]fullerene, the second fraction giving **syn,anti-trisadduct 52b**, and the third fraction giving **syn,syn-trisadduct 52a** as the dominant diastereomer in addition to about 10% 52b.

Mass spectrometry (LDI-MS) of the mixture predominantly showed [60]fullerene (m/z = 720) and 5,10,15,20,25,30-hexa(p-t-butylphenyl)-[4.4.4]tridecastarphene 51 (m/z = 1472) with no peaks higher than 1472. **Syn,syn-trisadduct 52a** $^1$H NMR (500 MHz, CS₂) δ (ppm): 9.00 (s, 2H), 8.99 (s, 2H), 8.98 (s, 2H), 7.72-7.22 (m, 36H), 7.08-7.03 (m, 6H), 6.29 (s, 2H), 6.28 (s, 2H), 6.25 (s, 2H), 1.48 (s, 18H), 1.41 (s, 18H), 1.40 (s, 18H).
*Synt,syn-trisadduct 52b* $^1$H NMR (500 MHz, CS$_2$) $\delta$ (ppm): 8.93 (s, 6H), 7.74-7.62 (m, 12H), 7.52-7.45 (m, 12H), 7.41-7.33 (m, 12H), 7.20-7.16 (m, 6H), 7.10-7.05 (m, 12H), 6.21 (s, 6H), 1.50 (s, 54H).

9,10-Dihydroxy-1,4-dimethoxy-9,10-di(p-t-butylphenyl)anthracene (66). To a flame-dried 250 ml 3-neck round-bottomed flask was added $p$-$t$-butylphenylmagnesium bromide (15 ml, 30.0 mmol) (2M in diethyl ether) followed by 50 ml dry toluene and the system purged with nitrogen. A 100 ml solution of 1,4-dimethoxy-9,10-diphenylanthracene 37 (1 g, 3.73 mmol) in dry toluene was added slowly over 15 min by addition funnel while the mixture was heated to reflux. After addition was complete, the reaction mixture was allowed to reflux with stirring for 3 hours under nitrogen flow. The reaction was cooled and quenched with ~20 ml saturated aqueous ammonium chloride and then extracted into ethyl ether and dichloromethane. The organic extract was washed thrice with water, separated and dried over calcium chloride pellets. The organic solvents were evaporated under reduced pressure and the crude was triturated with hexanes, filtered and washed with ~60 ml hexanes and dried under vacuum. The product 67 was obtained cleanly as a yellow powder (1.2 g, 2.26 mmol, 60% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.68-7.64 (m, 2H), 7.39-7.34 (m, 4H), 7.22-7.18 (m, 6H), 5.22 (s, 2H), 3.50 (s, 6H), 1.26 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 151.96, 149.11, 146.51, 137.80, 131.29, 127.98, 127.59, 125.69, 124.63, 113.24, 73.81, 56.71, 34.51, 31.57.
**1,4-Dimethoxy-9,10-di(p-t-butylphenyl)anthracene (67).** To a 100 ml round-bottomed flask was added 75 ml acetic acid followed by potassium iodide (1.4 g, 8.43 mmol) and then compound 67 (.9 g, 1.677 mmol). The reaction was brought to reflux for 1.5 hours before cooling and quenching with 50 ml saturated aqueous sodium bisulfite. The precipitate was collected by filtration through sintered glass, washed with 3 x 100 ml water and dried to give pure 68 (0.8 g, 1.591 mmol, 95 % yield) as a light green amorphous solid. $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.61-7.58 (m, 2H), 7.48-7.45 (m, 4H), 7.28-7.24 (m, 6H), 6.57 (s, 2H), 3.31 (s, 6H), 1.45 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 151.55, 148.42, 140.67, 135.62, 131.24, 129.10, 127.25, 124.86, 124.55, 123.74, 105.07, 56.48, 34.63, 31.63.

**1,4-Dihydroxy-6,13-diphenyl-6,13-endoxypentacene-5,14-dione (68).** To a 50 ml round-bottomed flask was added 15 ml benzene followed by freshly prepared 1,3-diphenylisonaphthofuran (173 mg, 0.54 mmol) and naphthazarin (105 mg, 0.55 mmol). The mixture was brought to reflux for 1 hour during which time the deep red solution became pale yellow. The reaction mixture was concentrated to dryness in vacuo and the crude white solid product was obtained (220 mg, 80%), dried under vacuum and used without further purification.
3.1 Introduction

3.1.1 CH - π Interactions

A CH - π interaction by convention is defined as an interaction between a slightly acidic CH hydrogen and a π base. First suggested in 1952 to explain the interaction between benzene and chloroform, CH - π interactions are regarded as the weakest of all hydrogen bonds with an estimated enthalpy of approximately 1 kcal/mol. Gas-phase studies report the interaction energy of benzene-methane to be 1.03-1.13 kcal/mol. Examples include the benzene dimer which adopts a T-shaped conformation in the solid state and the benzene-chloroform complex in which the relatively acidic hydrogen on chloroform associates with the benzene π-system.

Figure 26: Schematic representations of CH - π interactions between benzene - benzene (left) and benzene - chloroform (right). Only one p-orbital is shown for clarity.
NMR studies of the methyl hydrogens in a number of substituted toluene derivatives in both CC14 and benzene solvent reveal chemical shift differences (i.e., greater shielding in benzene solvent than in CC14) as a function of the acidity of the methyl groups. Nakagawa and Fujiwara suggest this is evidence for CH-π interactions between the methyl hydrogens and benzene. In this and other traditional CH-π interactions, the interacting orbitals are presumably a σ* of the H- donor and a π orbital of the H- acceptor.\(^{140}\)

Recently, Nishio and coworkers made a compelling case that fullerenes routinely participate in CH – π interactions. They surveyed the Cambridge Crystallographic Database and found numerous examples in which the fullerene π system is located within 3 Å of a CH donor. Often, a CH – fullerene distance was observed at or below 2.9 Å, as low as 2.5 Å.\(^{135}\) For example, Olmstead, and coworkers found that ethyl substituents in porphyrin-[60]fullerene complexes preferentially orient in the crystal structure such that they lie within the van der Waals' distance of the [60]fullerene cage.\(^{141}\)

3.1.2 [60]Fullerene [4+2] o-Quinodimethane Chemistry

Shortly after the discovery\(^{142}\) and preparative scale-up\(^{143}\) of [60]fullerene a number of derivatives were synthesized, including Diels-Alder [4+2] cycloadducts. Most of these have been carefully reviewed elsewhere\(^{144,145}\) and will not be covered in further detail in this work. Among the Diels-Alder derivatives, one of the earliest was one prepared by Mullen and coworkers in which o-quinodimethane (QDM) was generated in-situ and reacted with [60]fullerene to form adduct 53 (Scheme 16).\(^{146}\) Mullen identified
17 unique carbon resonances from the $^{13}$C- NMR spectrum of this compound which indicates a $C_{2v}$ symmetric structure consistent with a [6:6] addend engaging in dynamic ring-inversion about the methylenes. Further demonstration of dynamic ring-inversion is apparent in the $^1$H- NMR spectrum which shows a broadened AB spin-system centered around 5.03 ppm, indicating that "the ring inversion of the cyclohexene ring is slow on the NMR time scale at room temperature."\textsuperscript{146}


Since the reported work of Mullen and coworkers in 1993, numerous QDM analogs have been reacted with [60]fullerene in a similar fashion to give a variety of derivatives.\textsuperscript{13-18} In most cases, a dynamically broadened AB multiplet is reported for the methylenes attached to the sp\textsuperscript{3} hybridized carbons on the fullerene at the site of addition. Several reports include variable temperature $^1$H NMR experiments to further study this dynamic phenomenon. Rubin and coworkers carried out synthesis of a 3,6-dimethyl-4,5-diphenyl QDM derivative 54 (\textbf{Figure 27}) which shows coalescence of the AB multiplet at 35 °C. Low temperature experiments were conducted to obtain an NMR spectrum of the slow-exchange region which showed a clear AB quartet below -20 °C ($\Delta\nu = 94.8$ Hz, $J = 13.8$ Hz) indicating a free energy of activation of 14.6 kcal/mol.\textsuperscript{147} Rubin and others\textsuperscript{148} suggest that the relatively high barrier to inversion of the cyclohexene ring is
due to the rigidity of the fullerene cage which forces a planar transition-state.

Nishimura and coworkers have synthesized several benzocyclobutene homologs which were reacted with [60]fullerene to generate derivatives that all demonstrate dynamically broadened AB multiplets. Two such compounds (55 and 56) are shown in Figure 27. Variable temperature NMR (VT-NMR) experiments reveal activation barriers for 54, 55 and 56 of 14.6, 13.1 and 13.2 kcal/mol respectively. In a follow-up study, Nishimura and coworkers additionally examined compounds 57 and 58 (Figure 28). VT-NMR experiments gave free energies of activation of 13.6 and 16.6 kcal/mol for these compounds respectively.

\[ \text{Figure 27: [60]Fullerene-QDM adduct analogs showing dynamic exchange of hydrogens from methylenes attached to the fullerene.} \]

\[ \text{Figure 28: [60]Fullerene-QDM adduct analogs showing dynamic exchange of hydrogens from methylenes attached to the fullerene.} \]
A unique benzoquinone derivative 59 synthesized by Martin and coworkers shows a significantly reduced barrier to inversion of the cyclohexene ring which was measured at 11.3 kcal/mol. Martin finds an interesting correlation between the $\Delta G^\dagger$ of compounds 53, 55, 57-59 and the bond-distance between the sp$^2$-hybridized carbons (C62-C63) attached to the methylene carbons as shown in Figure 29.$^{151}$

![Figure 29: Fullerene adducts 53, 55, 57-59 showing a correlation between bond-length C62-C36 and the barrier to inversion of the cyclohexene ring colored blue.](image)

The interest in pyrimidine rings for inclusion in target pharmaceuticals prompted Martin and coworkers to design several unique substituted pyrimidine-fullerene derivatives 60-61 as shown in Figure 30.$^{152}$ From VT-NMR experiments conducted on these systems, there is a clear substituent effect related to the barrier to inversion. Notably, the presence of aryl groups seems to add approximately 2 kcal/mol to the barrier. Martin suggests the effect “could be due to high torsional and angular constraints
of these structures because of the rigidity of the [fullerene] cage, which is reinforced by the presence of the aryl groups on the pyrimidine ring.\textsuperscript{152} It is unclear exactly how the presence of the aryl groups might reinforce the rigidity of the fullerene cage. Nevertheless, these aryl substituted derivatives exhibited the highest free energy of activation to date.

![Figure 30](image.png)

**Figure 30**: [60]Fullerene-pyrimidine adduct derivatives showing a correlation between aryl substitution and the barrier to inversion of the cyclohexene ring.

### 3.2 Results and Discussion

#### 3.2.1 Novel diphenyl substituted \(\alpha\)-quinodimethane [60]fullerene adduct conformationally “locked” on NMR time-scale

Synthesis of [60]fullerene-QDM derivative 62 was carried out for the purposes of designing novel fullerene self-assembled monolayers in the labs of Glen Miller as described in Scheme 17.\textsuperscript{153,154} Unexpectedly, the \(^1\)H NMR spectrum for this compound at 25 °C showed the “slow-exchange limit” (a sharp AB multiplet for the methylene hydrogens). This anomalous find prompted further study of the dynamic behavior of the system.
Variable temperature studies revealed a coalescence temperature for the exchangeable hydrogens to be over 100 °C in toluene and a coalescence spectrum was obtained in o-dichlorobenzene-$d_4$ at 80.5 °C as measured by an ethylene glycol chemical shift thermometer. This gives a free energy of activation of 16.6 kcal/mol at 80.5 °C according to Equation 4 where $\Delta G^\ddagger_c$ is the Gibbs free energy of activation at the coalescence temperature, $T_c$ is the coalescence temperature in Kelvin, $\Delta v_{AB}$ is the chemical shift difference for the A and B nuclei in Hz, $J_{AB}$ is the coupling constant in Hz and $c$ is a constant dependent on the nature of the exchange, here equal to 9.97.$^{155}$

$$\Delta G^\ddagger_c = 4.57 T_c [c + \log \left( \frac{T_c}{\sqrt{\Delta v_{AB}^2 + 6J_{AB}^2}} \right) ] \quad \text{Eq. 4}$$

This effect was again observed in derivative 63 and coalescence was achieved at 87.3 °C giving a $\Delta G^\ddagger_c$ equal to 17.2 kcal/mol. A side-by-side set of stacked variable temperature plots for compounds 62 and 63 are shown in Figure 31.
3.2.2 Design and synthesis of phenyl substituted QDM-[60]fullerene adducts to probe CH – π effects using VT-NMR studies

A force-field calculation (Ghemical, following steepest descent algorithm, ΔE 10^4 kJ/mol tolerance) of the ground-state “boat” conformer for compound 62 shows the ortho hydrogen from the phenyl substituent placed 2.814 Å from the nearest fullerene carbon suggesting a CH – π interaction with the π surface of the fullerene as shown in Figure 32. It is conceivable that this electrostatic interaction is a major contributing factor to the relative increase in activation energy for the boat-to-boat inversion with respect to the unsubstituted QDM-fullerene adduct. Given this, two other phenyl substituted analogs of
compound 62 were synthesized to more directly study this CH – π interaction.

Compounds 64 and 65 are shown in Figure 33.

![Figure 32: Several views of compound 62 depicting the proximity (2.814 Å) of the phenyl hydrogens (green) to the nearest fullerene carbons (blue).](image)

![Figure 33: QDM-fullerene series 62, 64 & 65 for the variable temperature (VT) study of a CH – π interaction between phenyl ortho hydrogens and the π surface of the fullerene.](image)

The syntheses and purification of compounds 62 and 64 were carried out by Jon Briggs (Schemes 17 and 18), while synthesis and purification of compound 65 was carried out by Dr. Mikaël Jazdzyk (Scheme 19) in the research labs of Dr. Glen Miller. It was hypothesized that since the phenyl substitution pattern of compounds 62 and 64 is the only significant difference between these constitutional isomers, any difference that they may show in their activation energies for the boat-to-boat inversion should closely approximate the strength of the two CH – π interactions present in compound 62.
Scheme 18: Synthesis of [60]fullerene-QDM derivative 64 carried out by Jon Briggs.

Variable temperature $^1$H NMR (VT-NMR) was conducted for compounds 62, 64, and 65 at the approximate temperatures of 25, 40, 55, and 70 °C in o-dichlorobenzene-$d_4$. A low temperature spectrum was collected for compound 64 on the same instrument at -15 °C to obtain values from the slow-exchange limit. Exact temperatures of the probe were measured using an ethylene glycol chemical shift thermometer and are reported in Table 17. All dynamically broadened spectra were simulated using Reich’s WinDNMR software with all input parameters taken from the slow-exchange or near slow-exchange limit spectra. Adjustment of spectral amplitude and rate constant ($k$) was carried out iteratively until the line-shapes matched. Following this, $\Delta \nu$ was iterated until the simulated line-shape overlay the spectrum. Subsequent iteration on $k$ and spectral amplitude was carried out if needed until a best fit was achieved.
Figure 34: Line-shape analyses (simulations above spectra in each case) for dynamically broadened methylenes on fullerene adducts 62, 64, and 65.

Table 17: Summary of VT-NMR results for compounds 62, 64 and 65. Entries in bold indicate simulations closest to the coalescence temperature and therefore represent the most accurate values.
Simulations for 62, 64, and 65 at 70, 55 and 70 °C respectively are shown in Figure 34. The activation energy for boat-to-boat inversion (ΔG\textsuperscript{‡}) was obtained from the Eyring equation (Equation 5) where \( R \) is the gas constant, \( T \) is temperature in Kelvin, \( k \) is the rate-constant obtained from the simulation, \( K \) is the transmission coefficient (equal to 1 in a first order transition), \( k_B \) is Boltzmann's constant and \( h \) is Planck's constant. The results of the study are summarized in Table 17.

\[
\Delta G^\ddagger = RT \left[ \ln\left(\frac{T}{k}\right) + \ln\left(\frac{K k_B}{h}\right) \right] \quad \text{Eq. 5}
\]

In order to use the information collected from Table 17 to approximate the strength of the CH – π interaction in compounds 62 and 65, a few assumptions must be made. First, it is assumed that the steric bulk of the QDM phenyl substituents is approximately the same so that the effects of solvent reorganization may be ignored in the analysis. Second, activation energies are best approximated from line-shape analysis done at or near the coalescence temperature and are confined to reflect the ΔG\textsuperscript{‡} at the temperature simulated. However, compounds 62 and 65 coalesce at temperatures approximately 16 °C higher than compound 64, and we assume that this discrepancy minimally impacts the comparison of ΔG\textsuperscript{‡} values. With appropriate assumptions in place, the best ΔG\textsuperscript{‡} values for boat to boat inversions of 62, 64 and 65 are 17.0, 15.1, and 16.7 kcal/mol, respectively. As predicted, the ΔG\textsuperscript{‡} values are largest for 62 and 65 consistent with the inclusion of stabilizing CH – π interactions in these derivatives. The difference in ΔG\textsuperscript{‡} values determined for 62 and 64, 1.9 kcal/mol, is taken as the total strength of two CH – π interactions in 62 suggesting that each CH – π interaction accounts for
approximately 0.95 kcal/mol of stabilization. This value is in agreement with previously measured values for CH – π interactions in CH₃Cl / benzene and benzene / methane systems.²,³

Although the measured ΔΔG° values for 62 and 65 are just larger than the error associated with the measurements, we believe the difference (≈0.3 kcal/mol) to be real and to represent additional conformational restrictions associated with 65. As illustrated in Figure 35, the calculated equilibrium geometry (Gchemical force-field) shows a “pin-wheel” bias in the rotation of the phenyl substituents due to the additional steric bulk from phenyls at the 4,5- carbons of the QDM moiety. This enables only one stabilizing CH – π interaction for this set of conformational enatiomers. However, the interaction may be slightly strengthened due to the shorter non-bonded distance (2.78 Å) relative to that of compound 62.

![Figure 35: Several views of compound 65 (calculated ground state equilibrium geometry, Gchemical force-field) depicting the proximity (2.78 Å) of a phenyl hydrogen (green) to the nearest fullerene carbon (blue).](image)

3.3 Conclusions

o-Quinodimethane – [60]fullerene cycloadducts show dynamic exchange between the hydrogens of the methylene attached to the fullerene cage. The literature suggests
that the rigidity of the fullerene cage is responsible for the relatively large barrier for boat to boat inversions. Derivatives with properly positioned phenyl substituents appear to be conformationally slow on the NMR time-scale at room temperature suggesting an even larger barrier to inversion. We have demonstrated the dependence on positional location of the phenyl substituents through the synthesis and study of compounds 62, 64 and 65. The difference in activation energies (ΔG°) for boat to boat inversion of compounds 62 and 64 suggest a stabilizing CH – π interaction energy of 0.95 kcal/mol in 62.

3.4 **Experimental**

3.4.1 **'H VT-NMR Spectroscopy**

Variable temperature 'H NMR spectra were collected from a Varian INOVA 500 FT-NMR operating at 499.763 MHz. Chemical shift values were reported in parts per million (ppm) relative to (CH₃)₃Si (TMS, external). The solvent used in all cases was o-dichlorobenzene-d₄. Low temperature spectra were obtained with the use of a FTS cooling system.

3.4.2 **NMR Line-shape Analysis**

Dynamically broadened NMR spectra were simulated using WinDNMR (Reich). All parameters except the rate-constant (k) were taken from the slow-exchange spectra or near the slow-exchange limit which was iterated on until the line-shapes matched. Subsequently, Δυ was iterated until the simulated line-shape overlay the spectrum. Iteration on k and spectral amplitude was carried out until a best fit was achieved.
REFERENCES


37. Tyutyulkov, N. and Polansky, O., Naturwissenschaften A. 1975, 30, 1308.
42. Lonsdale, K., Nature 1928, 122, 810.


APPENDIX

NMR SPECTRA
$^1$H-NMR (400 MHz)
$^{13}$C-NMR (400 MHz)
**H-NMR (400 MHz) 23**

![NMR Spectrum Image]

Chemical Shifts:
- 7.9
- 8.2
- 8.5

Solvent: CDCl₃
$^{13}$C-NMR (400 MHz)
\[^{1}H-\text{NMR (500 MHz)}\] 28

\[\text{CDCl}_3\]

\[8.3 \text{ ppm} \]

\[8.0 \text{ ppm} \]

\[7.7 \text{ ppm} \]

\[\text{H}_2\text{O} \]

\[
\begin{array}{c}
\text{9.5} \\
\text{9.0} \\
\text{8.5} \\
\text{8.0} \\
\text{7.5} \\
\text{7.0} \\
\text{6.5} \\
\text{6.0} \\
\text{5.5} \\
\text{5.0} \\
\text{4.5} \\
\text{4.0} \\
\text{3.5} \\
\text{3.0} \\
\text{2.5} \\
\text{2.0} \\
\text{1.5} \\
\text{1.0} \\
\text{0.5} \\
\text{0.0}
\end{array}
\]
$^{13}$C-NMR (400 MHz)
$^{1}H$-NMR (500 MHz) 29
$^1$H-NMR (500 MHz) 30
$^{13}$C-NMR (500 MHz)
$^1$H-NMR (500 MHz)
\[ ^1H-NMR (500 MHz) \]
$^{13}$C-NMR (500 MHz)
$^1$H-NMR (500 MHz) 35

[Diagram of a spectroscopy graph with chemical shifts and peaks labeled]
$^{13}\text{C-NMR (500 MHz)}$
$^3$CDCl$_3$
$^{13}$C-NMR (500 MHz) 37
$^1$H-NMR (500 MHz)
$^{13}$C-NMR (500 MHz)
$^1$H-NMR (500 MHz)
$^{13}$C-NMR (500 MHz)
$^1$H-NMR (500 MHz) 42
$^1$H-NMR (400 MHz)
$^{13}$C-NMR (400 MHz)
$^{13}$C-NMR (500 MHz)
$^{13}$C-NMR (400 MHz)
$^1$H-NMR (500 MHz)
$^1$H-NMR (500 MHz) 50

![Chemical Structure Diagram]
$^{13}$C-NMR (500 MHz) 50

\[
\text{CDCl}_3
\]
syn,anti-tris[60] adduct (minor) in C8

syn,syn-tris[60] adduct (major) in C8

\[ ^1H \text{ NMR (500 MHz) 52(a)} \]
$^1$H-NMR (500 MHz) 52b

syn,anti-tris[C$_{80}$] adduct in CS$_2$
\( ^1H\text{-NMR (500 MHz)} \) 52(a)

- **major** in benzene-\( d^6 \)
- **minor** in benzene-\( d^6 \)

- **syn', syn'-ths[\( C^9 \)] adduct**
- **syn, syn'-ths[\( C^9 \)] adduct**
$^1$H-NMR (500 MHz) 52b

syn,anti-tris[C₆] adduct in benzene-d₆
\( ^{1}\text{H-NMR (500 MHz)} \)
$^{13}$C-NMR (400 MHz) 66
$^{13}$C-NMR (500 MHz) 67