Fullerene-acene chemistry: Part I Studies on the regioselective reduction of acenes and acene quinones; Part II Progress toward the synthesis of large acenes and their Diels-Alder chemistry with $[60]$ fullerene

Andreas John Athans

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Fullerene-acene chemistry: Part I Studies on the regioselective reduction of acenes and acene quinones; Part II Progress toward the synthesis of large acenes and their Diels-Alder chemistry with [60]fullerene

Abstract
The regioselective reduction of acenes and acene quinones has been studied. Using hydriodic acid (HI) in acetic acid (HOAc) as reductant, it was found that acenes smaller than five rings reduce in a regioselective fashion. It was also found that phenyl substituted acenes with as many as seven rings will reduce regioselectively to leave the internal terphenyl moieties intact. In the cases of 6,13-diphenylpentacene and 5,7,12,14-tetraphenylheptacene quinone, reduction occurs at alternating rings such that the end rings and the internal terphenyl moieties were left intact. When large unsubstituted acenes are reduced, the reduction occurs with no selectivity resulting in complex mixtures of variously hydrogenated isomers. In all cases, the reduced acenes or acene quinones were more stable and more soluble than either the acenes or acene quinones themselves. These hydrogenated species could be stored and handled under ambient conditions and readily dehydrogenated to the desired acenes on demand.

In addition to the reduction of acenes and acene quinones, the syntheses of various large acenes and their Diels-Alder chemistries with [60]fullerene were studied. These studies were focused toward preparing multiple [60]fullerene adducts as precursors to cyclacenes. The synthesis of nine- and eleven-ring acenes was undertaken and was found to be quite difficult. Concurrently, the synthesis of end-functionalized acenes was undertaken in order to prepare cyclacenes via a complimentary supramolecular approach. Three methyl substituted pentacenes were prepared, along with their [60]fullerene adducts. Additionally, work toward preparing pentacenes with different end functionalities was undertaken.

Finally, a flexible [60]fullerene bisadduct was prepared via reaction of tetrakis(bromomethyl) terphenyl and [60]fullerene in the presence of iodide. This bisadduct maps directly onto the previously prepared bis[60]fullerene adduct of 6,13-diphenylpentacene. While this adduct would in theory have conformational flexibility, it was found to exist solely in the cis conformation on the NMR time scale, suggesting that internal pi-pi stacking between [60]fullerenes locks the molecule into the cis conformation.

Keywords
Chemistry, Organic
FULLERENE-ACENE CHEMISTRY: PART I: STUDIES ON THE
REGIOSELECTIVE REDUCTION OF ACENES AND ACENE QUINONES; PART II:
PROGRESS TOWARD THE SYNTHESIS OF LARGE ACENES AND THEIR DIELS-
ALDER CHEMISTRY WITH [60]FULLERENE

VOLUME I

CHAPTERS 1-5

BY

ANDREAS JOHN ATHANS

B.S. University of New Hampshire, 2001

DISSERTATION

Submitted to the University of New Hampshire
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the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

May, 2007
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January 3, 2007
Date
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ABSTRACT

FULLERENE-ACENE CHEMISTRY: PART I: STUDIES ON THE REGIOSELECTIVE REDUCTION OF ACENES AND ACENE QUINONES; PART II: PROGRESS TOWARD THE SYNTHESIS OF LARGE ACENES AND THEIR DIELS-ALDER CHEMISTRY WITH [60]FULLERENE

by

Andreas John Athans
University of New Hampshire, May 2007

The regioselective reduction of acenes and acene quinones has been studied. Using hydriodic acid (HI) in acetic acid (HOAc) as reductant, it was found that acenes smaller than five rings reduce in a regioselective fashion. It was also found that phenyl substituted acenes with as many as seven rings will reduce regioselectively to leave the internal terphenyl moieties intact. In the cases of 6,13-diphenylpentacene and 5,7,12,14-tetraphenylheptacene quinone, reduction occurs at alternating rings such that the end rings and the internal terphenyl moieties were left intact. When large unsubstituted acenes are reduced, the reduction occurs with no selectivity resulting in complex mixtures of variously hydrogenated isomers. In all cases, the reduced acenes or acene quinones were more stable and more soluble than either the acenes or acene quinones themselves. These hydrogenated species could be stored and handled under ambient conditions and readily dehydrogenated to the desired acenes on demand.

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Finally, a flexible [60]fullerene bisadduct was prepared via reaction of tetrakis(bromomethyl) terphenyl and [60]fullerene in the presence of iodide. This bisadduct maps directly onto the previously prepared bis[60]fullerene adduct of 6,13-diphenylpentacene. While this adduct would in theory have conformational flexibility, it was found to exist solely in the cis conformation on the NMR time scale, suggesting that internal π-π stacking between [60]fullerenes locks the molecule into the cis conformation.
CHAPTER 1

INTRODUCTION

1.1 Discovery of the Fullerenes

In 1984, the first spectroscopic evidence for a third allotrope of carbon, the fullerenes (Figure 1), was observed.¹

Figure 1. Buckminsterfullerene.

Rohlfing, Cox, and Kaldor published¹ the first mass spectrometric evidence for [60]fullerene. Originally thought to consist of linear carbyne fragments, they observed a maximum intensity at m/z = 720. Although they published their result, there was no special significance attached to this or any other C_{2n} (n≥10) clusters. In part, this was because this group, working at Exxon, was interested in studying the formation of numerous carbon clusters, some of which were postulated to exist in deep space. In 1985, Kroto and Smalley reproduced the Exxon group's findings. One of their research students, Heath, was able to find conditions whereupon [60]fullerene was formed with great selectivity.

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It was shown to be stable upon standing for prolonged periods of time under ambient conditions. The group proposed a cage-like structure for [60]fullerene. In a *Nature* paper dated 12 Sept. 1985, the formation of [60]fullerene, as well as Heath's formation of the first endohedral metalofullerene (incorporating lanthanum inside the cage) was published.² Kroto and Smalley named the molecule buckminsterfullerene, after R. Buckminster Fuller, the designer credited (albeit incorrectly) with the geodesic dome. Kroto, Smalley, and Curl were awarded the Nobel Prize in chemistry in 1996 for this landmark accomplishment.

In a *Nature* paper dated 7 Aug. 1990, Krätschmer and Huffman reported their attempts to replicate the formation of carbon grains in outer space via vaporization of graphite. In these experiments, they produced benzene-soluble material that was found, upon crystallization and mass spectral studies, to be [60]fullerene.³ Higher fullerenes, most notably [70]fullerene, were also extracted out of the Krätschmer-Huffman soot, isolated pure, and characterized. Further developments included Iijima's 1990 discovery of carbon nanotubes,⁴ which can be seen as elongated fullerenes (or alternatively graphene tubes with hemi-fullerene endcaps). Although carbon nanotubes have attracted considerable attention from scientists, their poor solubility makes them difficult species to manipulate in either a chemical or physical sense. Conversely, the relatively high solubility of [60]fullerene has led to an explosion of chemistries since its discovery.
1.2 Chemistry

1.2.1 [60] Fullerene

Buckminsterfullerene undergoes many chemistries, including hydrogenation, redox chemistry (both chemically and electrochemically), nucleophilic addition, electrophilic addition, radical reactions, and cycloadditions. Of these chemistries, by far the most studied and utilized is undoubtedly cycloaddition chemistry. Buckminsterfullerene undergoes the following cycloaddition chemistries: [1+2], [2+2], [3+2], [4+2], [6+2], and [8+2] cycloadditions. The cycloadditions that have garnered the most attention are the Prato, Bingel, and Diels-Alder (or [4+2]) cycloadditions. However, in recent times the chemistry of [60]fullerene has been greatly expanded in both scope and application. For instance, in recent years, [60]fullerene chemistry has been expanded to include the separation of multiple adducts of fullerenes, photochemistry with amines, peptide and cyclodextrin chemistries with [60]fullerene for uses in aqueous biological systems, and using [60]fullerene in the construction of new materials. This will be discussed in the following sections.

1.2.1.1 Recent Advances in the Photochemistry of [60] Fullerene

Nakamura, Nishimura, and coworkers published a report on photochemical reactions between [60]fullerene and various aromatic tertiary amines. They found that the resulting adducts, based on previously reported tetrahedrally symmetric

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hexapyrrolidine (THP) adducts, exhibited strong fluorescence. Their interest in these compounds lay in their potential applications in organic light emitting diodes. They improved upon the Prato-reaction route, which is typically used to produce molecules of this type and which tends to use rather harsh reaction conditions. In particular, they increased the variety of pyrrolidine moieties that could be formed to include aromatic functionalities, which normally cannot be prepared in a typical Prato reaction. This expansion of functionality was focused mainly on developing the photochemistry using tertiary aromatic amines. They found that these photoreactions resulted primarily in the desired pyrrolidine adducts 1 (Figure 2), with side products also formed.

1. Figure 2. Nakamura's tertiary pyrrolidino [60]fullerene adduct 1 (see reference 5).

1.2.1.2 Biological Applications of [60]Fullerene

One area of fullerene chemistry that has seen growth in recent years involves incorporating [60]fullerene into biological systems. Tome's group reported the synthesis of multiple α-amino acid substituted [60]fullerene adducts 2 (Figure 3), which could be useful in the preparation of [60]fullerene containing pharmaceuticals. Indeed,
there has been much interest in recent years as to the potential pharmacological properties and applications of [60]fullerene and its derivatives, as will be discussed.

![Figure 3](image)

**Figure 3.** An example of Tome's amino acid substituted [60]fullerene (see reference 6).

In 2002, Toniolo described the synthesis\(^7\) of a helical peptide receptor with a hydrophobic, electron-rich cavity large enough for [60]fullerene to bind, thus creating an artificial "fullerene enzyme." An artificial enzyme such as this could potentially have use in preparing new artificial enzymes with properties similar to those of naturally occurring enzymes. These could then be used to interact specifically with [60]fullerene-containing drug compounds which may be prepared in the future.

Prato and Tossi reported\(^8\) the synthesis of protected [60]fullerene-containing amino acid 3 that was subsequently used in solid phase peptide syntheses to prepare polypeptides with [60]fullerene at one terminus (Figure 4).
These compounds prepared by Prato and Tossi could be incorporated into new pharmaceuticals or artificial enzymes containing [60]fullerene.

Geckeler and Murthy reported the first instance of [60]fullerene being included into β-cyclodextrin.\(^9\) The resulting 2:1 (β-cyclodextrin:[60]fullerene) inclusion complex was water soluble (Figure 5).

This result is important for a variety of reasons. The only previous cycloextrin-[60]fullerene inclusion complexes\(^{10}\) utilized γ-cyclodextrin, which is four times as expensive as β-cyclodextrin. Also, water-soluble [60]fullerene compounds have been shown recently to have anti-HIV activity, so an entry into these compounds in a cheaper fashion would be beneficial. Numerous other studies on the complexation of...
[60]fullerene with calixarenes and calixnaphthalenes\textsuperscript{11} have been reported as well, all with potential applications in the treatment of HIV, cancer, and other diseases.

\subsection*{1.2.1.3 Studies Concerning the Regioselectivity of [60]Fullerene Chemistry}

Nishimura and coworkers reported the first isolation and characterization of eight regioisomers of [60]fullerene-benzyne bisadducts 4 (Figure 6) via HPLC separation.\textsuperscript{12} This was significant as the second addition of benzyne proceeds with a relative lack of regioselectivity, thus making separations necessary to isolate specific regioisomers. In fact, benzyne bisadducts of [60]fullerene had not been previously reported in the literature prior to this paper.

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{figure6.png}
\caption{Bisbenzyne adducts 4 of [60]fullerene (see reference 12).}
\end{figure}

In this same vein, Nishimura also published a paper in 2003 detailing the systematic separation of [60]fullerene derivatives that had chiral addition patterns.\textsuperscript{13, 14}
In this case, the addends were bis-Bingel additions, bis-benzyne additions, or bis-Prato additions.

Hirsch recently published two papers on the regioselectivity of reactions with [60]fullerene.\(^{15,16}\) The first report\(^ {15}\) concerned the regioselective synthesis of an \(e,e,e\) tris-adduct which was followed by selective deprotections to expose desired faces of the fullerene cage. The second report\(^ {16}\) detailed regioselective and stereoselective syntheses of enantiomerically pure tris-adducts with chiral \(e,e,e\) addition patterns. This was achieved using chiral cyclomalonate tethers which underwent triple Bingel reactions with [60]fullerene in the equatorial positions. Hirsch has also published papers describing the preparations of some hexakis adducts of [60]fullerene.\(^{17,18}\)

The work of both Nishimura and Hirsch demonstrate advances in the regioselective chemistry of [60]fullerene, as well as the ability to separate regioisomers produced by this chemistry. Diederich was a pioneer in this field and utilized a tether-directed approach in order to prepare many regioselective adducts of [60]fullerene.\(^ {19}\) This is important, as there are few regioselective reactions that can be run on [60]fullerene, and separations have always proven difficult for mixtures of isomers. The recent developments in this area should prove to be most beneficial to chemists trying to prepare specific regioisomers of [60]fullerene.

1.2.1.4 Materials Applications of [60]Fullerene Chemistry

Perhaps the most active area of recent fullerene research has been in the applications of fullerenic compounds in new materials. For example, Zhu's group
prepared fullerene compounds 5 bearing 2,6-bis(acylamino) pyridine substituents.\textsuperscript{20} These addends were designed to undergo intramolecular hydrogen bonding in order to take advantage of this non-covalent interaction. They subsequently formed self-assembled nanoparticles. These nanoparticles consisted of functionalized [60]fullerene dimers held together by quadruple hydrogen bonds (Figure 7).

![Figure 7. Zhu's dimer for nanoparticle preparation (see reference 20).](image)

Taillemite and Fichou synthesized the first tetracene-[60]fullerene dyad (Figure 8).\textsuperscript{21} They were interested in preparing an acene-fullerene compound that was not assembled via Diels-Alder reaction between the acene and the fullerene, which occurs readily and is well known in the literature.\textsuperscript{22}
In this case, they wanted to use the tetracene as a donor in the dyad system. They were able to achieve the synthesis of this dyad by preparing a mono-tetracene, mono-3,5-bis(dodecyloxy)benzoyl malonate substrate that then underwent a Bingel reaction to give the [60]fullerene dyad structure. Most intriguing is that the resulting dyad structure remains intact; no Diels-Alder chemistry between the tetracene moiety and the [60]fullerene moiety is observed, although the tetracene $\pi$-stacks over the surface of the fullerene.

Fullerene epoxides of the form $\text{C}_{60}\text{O}_n$ have been used as starting points for preparing fullerene-based nanostructures. They have also been utilized in biological systems.

Tajima and his group reported an efficient acetylation of the epoxy rings on [60]fullerene via the action of substituted benzaldehydes in the presence of a pyridinium salt. In this way they were able to prepare 1,3-dioxolane and bis(1,3-dioxolane) substituted [60]fullerenes (Figure 9).
Also in the area of epoxyfullerenes, Wang's group reported in 2006 a novel cycloaddition reaction of [60]fullerene with a unique carbonyl ylide generated from epoxides. In his report, substituted trans-epoxides thermally formed the carbonyl ylides, which afforded the cis-substituted furano[60]fullerenes as the major product. This was an unprecedented way to prepare carbonyl ylides and could prove to have more utility in future epoxidation chemistry of [60]fullerene.

Bhattacharya et al reported a π-electronic charge-transfer between [60]fullerene and tetrahexylporphyrin in a supramolecular complex between the two. This was achieved by taking advantage of the tendency of [60]fullerene’s surface to be attracted to the center of either a porphyrin or metalloporphyrin.

The design and synthesis of “molecular machines” has been a burgeoning field recently, and Takata’s group reported in 2005 the synthesis of rotaxanes incorporating [60]fullerene. In the systems prepared, [60]fullerene is either present at the end of an “axle” or as a moiety on the “loop” threaded onto the axle (Figure 10).
While rotaxanes can be prepared in a host of ways,\textsuperscript{27} the simplest method, used by Takata, was the threading-capping approach, where the “loop” is threaded onto an “axle” which has one end blocked off. After the threading, the open end is capped to prevent the “loop” from dethreading. Takata’s group utilized two irreversible Diels-Alder reactions to incorporate the [60]fullerenes. One approach involved reaction between a 1,3-butadiene (prepared thermally from a 3-sulfolene) and [60]fullerene; the other approach involved an o-quinodimethane (prepared thermally from a sultine) reacting with [60]fullerene. Further studies on these molecular machines are underway, including an investigation of the work that they may be able to perform.

Hudhomme, Gorgues, and coworkers published in 2001 a report\textsuperscript{28} on [60]fullerene-tetrathiafulvalene (TTF)-cyclohexene fused polyadducts (Figure 11).

\textbf{Figure 10.} Rotaxane with [60]fullerene either on the loop (left) or on the axle (right) (see reference 26).
In particular, tri- and tetra-Diels-Alder adducts of the variously substituted dimethylidene[2H]tetrathiafulvalenes with [60]fullerene were studied. This was done to produce dyads with the TTF acting as the $\pi$-electron donor and the [60]fullerene as the $\pi$-electron acceptor. The resulting radical cation/radical anion pair would possess a charge-separated species that was predicted to be greatly stabilized. The synthesis of these poly-TTF adducts was achieved by preparing TTF-fused 1,4-butadienes which then underwent Diels-Alder reaction with [60]fullerene. Upon electrochemical analysis, it was shown that the multiple TTF addends could donate either one or two electrons each to the [60]fullerene cage reversibly.

Miller’s group reported\textsuperscript{29} in 2005 the scalable regioselective synthesis of C$_{60}$H$_{18}$ using the relatively mild conditions of refluxing in neat polyamines. This reaction produces C$_{3v}$ C$_{60}$H$_{18}$ as the sole product in good purity. This reaction is a great improvement on the previous hydrogenation methods, which tended to be much harsher and produced complex mixtures of hydrogenated fullerenes with no apparent selectivity. Hydrogenated fullerenes and nanotubes could prove useful in fuel cell devices (H$_2$ storage) and as radiation shields.

An amphiphilic hexasubstituted [60]fullerene compound with 10 steroidal units and a bis-carboxylic acid polar head group was found to form Langmuir-Blodgett films in
a 2005 paper by Flesch. Buckminsterfullerene was incorporated into poly(phenylacetylene) polymers as a pendant group. The resulting helical polymer was shown to be optically active. The [60]fullerene pendants themselves formed one-handed helical arrays with a predominant screw sense along the polymer backbone.

1.2.1.5 Cycloaddition Chemistry of [60]Fullerene

The three cycloaddition reactions that have received the most attention from chemists working with [60]fullerene are the Prato, Bingel, and Diels-Alder reactions. The Bingel reaction involves formation of an α-carbanion enolate formed via deprotonation of α-bromomalonates, which adds to the [60]fullerene. The resulting [60]fullerene anion displaces the bromine to give methanofullerenes. The Prato reaction involves a [3+2] cycloaddition of an azomethine ylide with [60]fullerene to give pyrrolidinofullerenes. Troshin and coworkers were able to get around the limitations of the Prato reaction, namely the substitution on the resulting pyrrolidine rings. In particular, the authors prepared 2',5'-disubstituted and 1',2',5'-trisubstituted pyrrolidinofullerenes (Figure 12).

![Figure 12](image_url)

**Figure 12.** An example of Troshin’s pyridyl-appended fullerene ligands (see reference 34).
This was done by preparing a series of pyridine-substituted adducts via reaction of [60]fullerene with picolylamine and various substituted aldehydes via a [2+3] cycloaddition. Most striking was the high diastereoselectivity, which the authors could not explain.

Wang and coworkers prepared [60]fullerene adducts of 9-substituted anthracenes in the solid state. The solid state reaction was undertaken to avoid the well-known retro-Diels-Alder reaction, which occurs readily in solution phase. Using a mechanochemical milling technique, they were able to prepare Diels-Alder adducts of [60]fullerene and 9-substituted anthracenes (Figure 13), including an intriguing tethered bis[60]fullerene species.

Figure 13. An example of Diels-Alder product between 9-substituted anthracenes and [60]fullerene (see reference 35).

These reactions were also run in solution phase for comparison. The solution phase reactions gave lower yields, needed longer reaction times, and resulted in complex oligomeric mixtures, owing to the readiness of the retro-Diels-Alder reaction.

Murata tackled the problem of retaining the 60 π-electron system of the fullerene while functionalizing the surface. This was done by preparing fulleroid and
bis(fulleroid) structures. While fulleroids tend to isomerize readily to give methano[60]fullerenes, bisfulleroids do not. They were able to prepare hydrophilic [60]fullerene carboxylic acid derivatives via cyclohexadiene reaction on the fullerenes, which isomerized thermally to give a bisfulleroid (Figure 14).

\[
\begin{align*}
\text{Bu}^\text{O}_2\text{C} & \quad \text{CO}_2\text{Bu} \\
\text{Bu}^\text{O}_2\text{C} & \quad -\quad \text{C} \quad -\quad \text{C}^\text{Bu}
\end{align*}
\]

**Figure 14.** Murata's bisfulleroid (see reference 36).

Another paper by Murata\(^{37}\) detailed the results of his studies on this cyclohexadiene rearrangement to give bisfulleroids. A tetra-\(t\)-butyl ester was prepared in this way,\(^ {36}\) as illustrated in Figure 14. This molecule was subjected to a variety of chemistries to give bisanhydrides, monoanhydride-bisacids, and tetracarboxylic acids, all of which exhibited greatly improved solubility in water while retaining the 60 \(\pi\)-electron system of the fullerene cage.

### 1.2.2 Carbon Nanotubes

Carbon nanotubes can be placed into two categories: single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). SWNTs are single tubes, whereas
MWNTs are concentric tubes nested inside one another. SWNTs have attracted the most interest due to their electrical, physical, and chemical properties, although they are harder to produce and thus more expensive and less readily available. They exist in three fundamental forms: zig-zag, armchair, and chiral (Figures 15 and 16). There have been improvements in the preparation and purification of SWNTs in recent years. SWNTs usually contain defect sites and other abnormalities that render them more difficult to manipulate as compared to [60]fullerene. SWNTs also have a tendency to bundle, which further complicates their manipulation. Additionally, SWNTs are insoluble. Despite these problems, many groups have found ways to utilize SWNTs in order to prepare novel materials and derivatives based on SWNTs.

Figure 15. Armchair (top), zig-zag (center), and chiral (bottom) carbon nanotubes.
http://pages.unibas.ch/Phys-meso/Education/Teaching/Nanotubes.gif (accessed 10/23/06)
1.2.2.1 Advances in Preparation of SWNTs

In the area of preparing SWNTs, Ajayan and coworkers\textsuperscript{38,39} were able to directly prepare long SWNT ropes via reaction of \textit{n}-hexane, thiophene, and hydrogen under an optimized temperature and flow rate of H\textsubscript{2}. These nanoropes are approximately 10-20 cm in length, clearly on the macroscopic scale. They have a diameter on the order of 0.3 to 0.5 mm. The nanoropes have electrical behavior ranging from conducting to resistive depending upon the temperature. These ropes have tensile strength five times the Young’s modulus for SWNT fibers and fifty times that of bucky paper, which is a thin film of tangled SWNTs that can be peeled off into sheets. They are also remarkably flexible, and can be tied into knots or manipulated with no apparent damage.

Terranova reported\textsuperscript{40} the preparation of helically wound SWNTs, which can be described as “braided”, with nanotubes wrapped around a central tube at a 20 degree angle. Sato’s group studied the electrical properties of radial SWNTs bundles, which
were synthesized and shown to be composed of semi-conducting and metallic individual
SWNTs.

On the question of the true electronic nature of SWNTs, Lieber’s group studied
zig-zag and armchair SWNTs via STM. They found the “metallic” SWNTs to have
small band gaps whereas the “metallic” armchair tubes did not. However, even in the
case of “metallic” armchair SWNTs, their bundling behavior produces small energy gaps
(pseudogaps) that disrupt electron flow along the nanotubes. Lieber concluded that while
the SWNTs may have excellent conducting properties, they are not, in fact “true metals”.

1.2.2.2 Advances in Solubilizing and Functionalizing SWNTs

In a review on covalent surface chemistry of SWNTs, Wong discussed a range
of chemistries demonstrating the recent advances in covalent SWNT chemistry, from
endcap and defect site chemistry to addition of molecular moieties, doping with quantum
dots, biologically inspired functionalization, and coordination chemistry. Additionally,
sidewall functionalization, including fluorination, ozonolysis, organic functionalization
via cycloaddition or other addition chemistries, osmylation, and azomethine ylide
addition were discussed.

Dieckmann and coworkers were able to selectively solubilize SWNTs via peptide
cyclization. In this paper, synthesized peptides with thiol terminating groups were able
to cyclize into rings that could accommodate SWNTs in a diameter-selective fashion via
host-guest interactions. In this way, the SWNTs can then be solubilized into water or
polar organic media without the usual SWNT bundling that is so common under standard conditions.

SWNTs have also been shown to interact in non-covalent, π-stacking interactions with polycyclic aromatic hydrocarbons (PAHs). In a report from 2006 by Hedderman and coworkers, SWNTs were solubilized in the presence of p-terphenyl and anthracene. Remarkably, this solubilization phenomenon was found to purify SWNTs. The p-terphenyl selectively interacts with semiconducting SWNTs, whereas anthracene maps directly onto metallic SWNTs. The resulting “complexes” unbundle the SWNTs and selectively suspend the corresponding SWNTs in solution, which is stable for up to 48 months.

A 2006 paper by Prato, Guldi, Maggini, and Paolucci reported on supramolecular hybrid molecules incorporating [60]fullerene and SWNTs together in the same system. In this paper, [60]fullerene was functionalized via a Bingel reaction to incorporate a tether and a pyrene moiety at the end. They found that the [60]fullerene/pyrene tether compound π-stacked onto the sidewall surface of the SWNT via the pyrene moiety. The π-stacking interaction was also found to solubilize the SWNTs and form stable, well-dispersed suspensions of SWNTs.

1.2.2.3 Materials Applications

By far, the most interest in SWNTs lies in their potential applications in new materials. This is due to the range of electrical and mechanical properties they can possess, both of which can be utilized for a large number of different applications.
Dai's group grew aligned SWNTs on solid SiO$_2$/Si substrates using electric-field-directed CVD growth. In this way they were able to grow aligned SWNTs on the solid surface. When the electric field was not applied, or when it was shut off, the tubes were found to form a random array on the surface.

Liu et al were able to assemble SWNTs in a perpendicular orientation to the solid surface by functionalizing the SWNTs to have carboxylic acids as terminal groups where the endcaps had been. Self-assembled monolayers consisting of long hydrocarbon chains with thiol groups on one end and amino groups on the other end were prepared. When an electric field was applied, the electrostatic interaction between the negatively charged carboxyl groups and the positively charged amino groups non-covalently linked the tubes to the surface in a perpendicular fashion, while the electric field caused the tubes to align parallel to each other.

Ellison's group reported in 2004 the adsorption of NH$_3$ and NO$_2$ onto SWNTs. This study was undertaken because a previous study by Kong's group showed that exposure to these gases dramatically altered the conductivity of SWNTs. In Ellison's study, SWNTs were exposed to NH$_3$, NO$_2$, and NMe$_3$ and the adsorption studied. They found that NH$_3$ and NO$_2$ did adsorb onto SWNTs, while NMe$_3$ did not. This was due to the fact that NH$_3$ and NO$_2$ were adsorbed via an interaction involving their lone pair, while NMe$_3$ was too hindered for effective interaction with the surface of the SWNTs. Yates and Kondratyuk similarly reported on the adsorption and desorption of $n$-nonane and CCl$_4$ on SWNTs.

Applications for SWNTs have been developed incorporating oxidized SWNTs into polybutylene terephthalate (PBT) nanocomposites. SWNTs generally increase the
tensile strength and conductivity of polymers they are incorporated into. They found that a tiny amount of oxidized SWNTs incorporated into the polymers made a large difference in the thermo-mechanical properties. In fact, the SWNT-incorporated polymer had better tensile strength and a higher fracture strain than neat PBT.

1.3 Acenes

1.3.1 Properties of the Acenes

The acenes are members of a class of organic molecules known as polycyclic aromatic hydrocarbons (PAHs). Specifically, they are a class of PAHs which are alternant cata-annelated benzenoid ring systems. The acenes, which are fused linear ribbons of benzene rings (Figure 17), were synthesized, studied, and explained in the most detail by Eric Clar. While a cursory look at the acene series would lead one to believe that they are simply linear, aromatic molecules, this is not the case. Benzene, which can be considered the simplest acene (although it is not technically considered an acene, as it consists solely of one ring), is an aromatic compound and as such, contains all of the inherent stability and the unique properties that are associated with aromatics. It contains 6 π-electrons in its aromatic sextet. As one investigates the larger acenes, however, it becomes clear that only one ring in each acene can possess a sextet of electrons.
Thus, naphthalene, anthracene, tetracene, and larger acenes can each be drawn in several resonance forms, but only one aromatic sextet can be present in any of those forms (Figure 18).

Clar's aromatic sextet rule\textsuperscript{52} dictates that as the acenes get larger and larger, they should become more and more reactive as only one aromatic sextet is shared by increasingly larger numbers of rings. Indeed, this is what is observed experimentally. For example, naphthalene is not as stable as benzene and will undergo reactions such as sulfonation at room temperature. It does not undergo Diels-Alder reaction unless a very active dienophile is utilized. Anthracene is even more reactive. It can be chemically oxidized to 9,10-anthraquinone with relative ease and it undergoes facile Diels-Alder chemistry. Upon reaching tetracene, the acenes become highly colored, in this case orange. Tetracene will readily photooxidize under ambient conditions. This reactivity becomes even more pronounced with pentacene (violet colored) and hexacene (green colored), which must be handled under inert atmospheres and in the dark in order to prevent
photooxidation. Hexacene is the largest acene that has been prepared, isolated pure, and characterized. Heptacene, which is a dark green solid, has never been isolated pure due to its high reactivity and poor solubility. In this case, there is only one aromatic sextet available in the seven ring framework. Indeed, as described by Clar, “with an infinite number of rings, the system becomes a cyclic polyene in which one sextet is not enough to give some degree of stability.” Clar concluded that “it is obvious that higher acenes finally lose all aromatic character and become cyclic polyenes.”

Clar postulated that the central ring of any acene containing three or more rings would be the “least aromatic” ring and thus the most reactive, while the terminal rings tend to be the “most aromatic”, “most benzene-like”, and thus least reactive rings. While Clar’s hypothesis seems reasonable, it is an older idea not rooted in MO theory. More recent studies, especially those based on NICS, suggest that Clar was nearly but not completely correct. The center rings of large acenes are the most reactive, but they are also indeed the most aromatic. This is explained through the NICS (nuclear independent chemical shift) calculations, which postulate a higher diamagnetic ring current in the center rings than in the end rings. Clar’s aromatic sextet rule predicts that since only one ring in the acene can contain a full aromatic sextet, aromaticity will decrease as the number of nonsextet rings increases. However, Schleyer and coworkers have utilized NICS calculations to demonstrate that there is no significant decrease in aromatic stabilization as one moves to larger acenes. Instead, they argue that the increased reactivity for the larger acenes is a result of product-driven equilibrium. Reactions at the central ring of large acenes leads to more stable products. For example, addition of a dienophile across the central ring of anthracene results in the formation of two benzene
moieties, whereas addition at one of the end rings would result in the formation of a naphthalene moiety. NICS calculations do not necessarily solve the question of acene aromaticity and the debate will likely continue for some time to come.

1.3.2 Preparation of the Acenes

The syntheses of acenes typically involve classic chemistry techniques in order to prepare them, although some acenes are derived from natural sources. The synthetic approaches tend to involve either Diels-Alder chemistry, aldol condensation chemistry, or Friedel-Crafts chemistry. These techniques have been used to prepare a host of PAHs in addition to acenes. Naphthalene and anthracene are still obtained in bulk from natural sources, most commonly from the pyro-condensations of coal-tar. The fractions containing these molecules are collected at high temperatures as oils, which are allowed to cool down, crystallizing out the acenes. As such, it is unnecessary to describe any synthetic approaches to these molecules. While there have been numerous approaches to acene syntheses, the following description aims to be a brief but inclusive overview.

Tetracene has been isolated from natural sources, but much more work has been done to prepare both unsubstituted tetracene and several substituted derivatives. Clar’s classic synthesis\(^5\) of tetracene involved reaction between phthalic anhydride and tetralin in the presence of AlCl\(_3\) to give the keto-acid, which was reduced with Zn\(^0\)/NaOH and then reacted in a Zn\(^0\)/NaCl melt to give the dihydrotetracene. The dihydrotetracene was subsequently aromatized via either copper or chloranil (Scheme 1). Additional syntheses
utilized benzyne-type intermediates or benzocyclobutane chemistry to generate tetracene.\textsuperscript{56}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [above] {\textbf{Scheme 1.} Clar’s classic tetracene synthesis (see reference 55).};
\end{tikzpicture}
\end{center}

Pentacene has been synthesized numerous times, usually passing through 6,13-pentacenequinone. However, a classic synthesis of pentacene passes instead through the 6,13-dihydro intermediate.\textsuperscript{57} A Friedel-Crafts reaction between $m$-xylene and benzoyl chloride gives bis-benzoyl-$m$-xylene, which is cyclized via the Elbs pyrolysis to give 6,13-dihydropentacene. This is finally aromatized by heating in nitrobenzene in the presence of 9,10-phenanthrenequinone (Scheme 2).
Scheme 2. Classic synthesis of pentacene that does not pass through quinone intermediate (see reference 57).

More commonly, however, the synthesis of pentacene involves 6,13-pentacenequinone, as this can be easily prepared on large scales. Reid and Anthöfer showed that aldol condensation, followed by dehydrative aromatization affords 6,13-pentacenequinone quite easily (Scheme 3). Thus, o-phthalaldehyde and 1,4-cyclohexanedicarboxylic acid were reacted in ethanol with a small amount of aqueous KOH to initiate condensation.

Scheme 3. Reid and Anthöfer's aldol approach to 6,13-pentacenequinone (see reference 58).
In a complimentary reaction, Cava showed\textsuperscript{59} that α,α,α',α'-tetrabromo-o-xylene was an o-quinodimethane precursor that could react with benzoquinone followed by spontaneous elimination of HBr to give 6,13-pentacenequinone as well (Scheme 4). Cava initially was attempting to prepare 1,4-anthraquinone and obtained 6,13-pentacenequinone as a byproduct. Upon adjusting the equivalents of the reactants used, 6,13-pentacenequinone was obtained as the sole product.\textsuperscript{60}

![Scheme 4. Cava's o-quinodimethane approach to 6,13-pentacenequinone (see references 59 and 60).]

Additional preparations of the quinone have also been achieved utilizing isobenzofuran and benzoquinone Diels-Alder reactions, followed by dehydrative aromatization.\textsuperscript{61} Numerous other syntheses of pentacene exist.\textsuperscript{62,63,64,65,66}

Hexacene is the largest acene that has been prepared, isolated pure, and characterized. Clar's classic syntheses involve Friedel-Crafts chemistry at their heart (Scheme 5). In the first synthesis,\textsuperscript{67} phthalic anhydride and 1,5-dihydroxynaphthalene were reacted in a NaCl/AlCl\textsubscript{3} melt to give a dihydroxyhexacene diquinone. This was then heated in a NaCl/AlCl\textsubscript{3}/Zn\textsuperscript{6} dust melt to give a mixture of dihydrohexacenes, which were aromatized in a stream of CO\textsubscript{2} over copper to give hexacene.
Scheme 5. Clar’s first synthesis of hexacene (see reference 67).

The second synthesis\textsuperscript{68} begins by reacting phthalic anhydride with \textit{o}-xylene in the presence of \textit{AlCl}_3 (Scheme 6). This is followed by \textit{KMnO}_4 oxidation and dehydration to give the anhydride-keto-acid. This is reacted in another Friedel-Crafts reaction with tetralin and \textit{AlCl}_3 to give the bis-keto-acid, which is then reduced with \textit{Zn}^0/\textit{NaOH} to give the diacid, subjected to a \textit{NaCl}/\textit{ZnCl}_2/\textit{Zn}^0 melt to give dihydrohexacene, and finally aromatized in a stream of \textit{CO}_2 over copper to give hexacene. There have also been other approaches to hexacene utilizing aldol and Diels-Alder chemistries.\textsuperscript{69,70}
Scheme 6. Clar’s second synthesis of hexacene (see references 69 and 70).

The classic synthesis of heptacene\textsuperscript{71} by Clar (Scheme 7) began by reacting pyromellitic anhydride and tetralin in a Friedel-Crafts reaction using AlCl\textsubscript{3} to give the bis-keto-acid, which was reduced to the diacid using Zn\textsuperscript{0}/CuSO\textsubscript{4}, cyclized via a ZnCl\textsubscript{2}/NaCl melt reaction, and aromatized in a stream of CO\textsubscript{2} over copper.
Scheme 7. Clar's classic synthesis of heptacene (see reference 71).

A simultaneous preparation of heptacene was undertaken by Bailey using a Diels-Alder approach (Scheme 8). However, upon studying both preparations, Clar came to the conclusion that neither he nor Bailey ever prepared pure heptacene, stating that he was "unable to obtain pure heptacene by dehydrogenation of its hydro-compounds: the deep green crude heptacene always contained hydro-derivatives which could not be removed...the very sensitive heptacene became less pure during these operations, until the green color disappeared completely." Thus, although there have also been numerous other approaches to the heptacene backbone, no one has ever prepared, isolated pure, and characterized heptacene. Recently, however, a substituted heptacene was prepared and isolated by Anthony.72
Thus, Anthony and coworkers reported\textsuperscript{72} separate syntheses of a hexacene and a heptacene that they were able to prepare, isolate pure, and characterize. Their approach utilized steric blocking groups which need to have a diameter that is 35-50% of the length of the acene. In this way they were able to prepare hexacenes and heptacenes protected by bulky silyl acetylene groups (Figure 19).

Figure 19. Anthony’s blocking-group protected hexacenes and heptacenes (see reference 72).

Clar described two quinone derivatives of octacene prepared by Marschalk, but the parent acene is not known. This is not surprising given the highly reactive nature of
heptacene and the difficulties encountered in its preparation. Marschalk’s synthesis of a tetrahydroxyoctacene quinone (Scheme 9)\textsuperscript{73} involved reacting anthracene-dicarboxylic anhydride with \textit{leuco}-napthoquinizarin.

\begin{center}
\begin{tikzpicture}
  \node (1) at (0,0) {\includegraphics[width=0.5\textwidth]{scheme9.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 9}. Synthesis of tetrahydroxyoctacene quinone (see reference 73).

A tetrahydroxyoctacene diquinone was prepared by reacting 9,10-anthraquinone-2,3-dicarboxylic anhydride with \textit{leuco}-napthoquinizarin to give the resulting product (Scheme 10).\textsuperscript{74} Neither of these derivatives exhibited good solubility and neither was converted into octacene.

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Scheme 10. Synthesis of a tetrahydroxyoctacene diquinone (see reference 74).

A derivative of nonacene was prepared by Marschalk\textsuperscript{75} via the reaction of pyromellitic anhydride and \textit{leuco}-quinizarin, followed by oxidation to give the hexaquinone (Scheme 11).

Scheme 11. Synthesis of a nonacene hexaquinone (see reference 75).
Marschalk also reported the preparation of three derivatives of undecacene. A double condensation of 9,10-dihydroanthracene-tetracarboxylic dianhydride with leucoquinizarin gave an octahydroxyundecacene diquinone (Scheme 12).

Scheme 12. Synthesis of an octahydroxyundecacene diquinone (see reference 75).

Reaction of pyromellitic anhydride and leuco-naphthoquinizarin gave an octahydroxyundecacene diquinone (Scheme 13).
Scheme 13. Synthesis of an octahydroxyundecacene diquinone (see reference 75).

And finally, reaction of 9,10-dihydroanthracene-tetracarboxylic dianhydride and hydroquinone, followed by reaction with phthalaldehyde acid and cyclization in the presence of chlorosulfonic acid gave rise to a tetrahydroxydiketoundecacene diquinone (Scheme 14).
Scheme 14. Synthesis of a tetrahydroxydiketoundecacene diquinone (see reference 75).

When looking at these larger acenes, it may be tempting to theorize that the increasing length will result in such a degree of instability that the higher acenes will never be prepared and isolated. However, the increase in reactivity is not linear. Biermann and Schmidt studied the reactivity of acenes via Diels-Alder reactions with excess maleic anhydride.\textsuperscript{76,77} There is a twenty fold increase in reactivity from anthracene to tetracene, and a thirty-six fold increase upon moving from tetracene to pentacene, but only a twofold increase when going from pentacene to hexacene (Table 1).
**Acene** | **Relative Reactivity**
---|---
Naphthalene | NA
Anthracene | 1
Tetracene | 20
Pentacene | 720
Hexacene | 1450
Heptacene | not available

**Table 1.** Relative Diels-Alder reactivity of acenes.\textsuperscript{76,77}

This suggests a limit to the reactivity of the higher acenes. Indeed, it has also been postulated that nonacene itself represents an electronic threshold. Nonacene and larger acenes are predicted to exist as either ground-state triplets\textsuperscript{78} or singlets.\textsuperscript{79} This is due to the fact that as the acenes increase in size, the HOMO-LUMO gap (or band gap if a crystal or other material is considered) decreases. Initial studies by Houk\textsuperscript{78} and coworkers concluded that as the acenes increase in size, the HOMO-LUMO gap “vanishes” and, upon reaching nonacene, a triplet ground state is reached. Using B3LYP/6-31G* calculations, they determined that the orbitals are located on the “ribbons” of the acenes, that is the top and bottom edges of the molecules, while the bonds connecting the two edges are elongated. However, in a later study, Houk’s\textsuperscript{79} group found that by studying large acenes using unrestricted broken symmetry B3LYP (UB3LYP) calculations, large acenes are predicted to exist in a singlet state with a large amount of diradical character. Again, these calculations showed the SOMOs of the acenes located on the “ribbons” of the acenes. While both of these theoretical results are intriguing, the true electronic nature of acenes larger than hexacene will never be fully known until they can actually be prepared and isolated for study.
1.4 Reactions of [60]Fullerene with Acenes

Diels-Alder reactions between acenes and [60]fullerene are known in the literature. Anthracene is the smallest acene that will react with [60]fullerene in a Diels-Alder fashion, and as such, it was the earliest studied and is among the most studied. It was reported\(^8\) that when anthracene and [60]fullerene were refluxed for 3 days in toluene, a monoadduct was formed (Figure 20).

\[\text{Figure 20. [60]Fullerene-anthracene monoadduct (see reference 80).}\]

This monoadduct is thermally labile and must be stored at low temperatures. If the monoadduct is heated above 60 °C in solution, the retro-Diels-Alder reaction occurs and regenerates the starting materials. However, if a crystal of the monoadduct is heated to 180 °C, a 1:1 mixture of the antipodal trans-1 bisadduct and [60]fullerene is formed.\(^8\) This is due to the fact that in the crystal lattice, the fullerene moiety is “nested” inside the cleft of an adjacent anthracene. Heating induces a retro-Diels-Alder reaction to occur,
with the freed anthracene in the correct location to add to the antipodal site of an adjacent [60]fullerene.

Mechanochemical chemistry has been utilized by Komatsu, among others, to generate [60]fullerene Diels-Alder adducts with various dienes. This is done using high-speed vibrational milling (HSVM), which involves placing the solid reactants and a steel ball-bearing in a stainless-steel canister followed by shaking at high speeds. Using this mechanochemical approach, Komatsu improved the synthesis of the [60]fullerene-anthracene monoadduct, increasing the yield to 55% versus the typical yields of 10-20% in the solution phase reaction. Komatsu also reported the reaction of larger acenes with [60]fullerene using HSVM. Tetracene and [60]fullerene were reacted to give the mono[60]fullerene adduct of tetracene in 61% yield (Scheme 15).

\[
\text{HSVM}
\]

\[\text{Scheme 15. Komatsu's HSVM synthesis of a tetracene-[60]fullerene monoadduct (see reference 82).}\]

When Komatsu reacted pentacene and [60]fullerene using HSVM, he obtained the \(C_{2v}\) monoadduct in 19% yield and a compound he labeled a bis[60]fullerene adduct in 11% yield. In contrast, Miller and Mack reported the exclusive formation of the \(C_{2v}\) monoadduct of pentacene in refluxing toluene in 54% yield (Figure 21).
No other products were observed, even though the authors were looking for the formation of bis[60]fullerene adducts via cycloaddition to the reactive sites flanking the center ring.

In 2000, Miller and Mack achieved the synthesis of a bis[60]fullerene adduct (6) of 6,13-diphenylpentacene. The phenyl groups were introduced to impart solubility, stability, and more importantly, to block the center ring of the acene from reacting with [60]fullerene. While both cis- and trans- bisadducts were expected, only the cis-bisadduct was formed, in 85% isolated yield (Figure 22). This was attributed to the π-stacking interactions between the fullerenes, which are within the preferred van der Waals distance (3.20 Å) of each other. Indeed, the π-stacking interactions between [60]fullerenes can be more accurately described as an induced dipole-induced dipole interaction. Evidence for this favorable interaction includes a computational study, as well as an X-ray crystal structure which shows the [60]fullerenes 3.20 Å apart, well within the distance expected for such an interaction.
Furthermore, Miller and Briggs reported the formation of a cis-,cis-tris[60]fullerene adduct of tetraphenyleptacene (7) in 20% isolated yield (Figure 23). The remarkable regioselectivity and syn-diastereoselectivity associated with these reactions prompted further studies within the Miller group concerning the reactivity between large acenes and [60]fullerene.

Figure 22. cis-Bis[60]Fullerene adduct of 6,13-diphenylpentacene (6) prepared by Miller and Mack (see reference 84).

Figure 23. cis,cis-Tris[60]Fullerene adduct (7) of tetraphenyleptacene prepared by Miller and Briggs (see reference 86).
In all of these cases, the adducts are reported to be all cis as demonstrated by NMR spectroscopy\textsuperscript{84} as well as X-ray crystalography.\textsuperscript{85} This remarkable result has been described as being due to relatively strong \( \pi-\pi \) stacking between the adjacent fullerenes. Not only does this explain the \( \text{cis} \)-diastereoselectivity, but also explains the stabilization afforded to the resulting adducts.

We are interested in exploiting this diastereoselectivity in order to prepare cyclacenes, and ultimately, uniform single-walled nanotubular compounds (SWNCs).\textsuperscript{87} As seen in Figures 22 and 23, the acene backbone is “kinked” at the site of Diels-Alder reaction with [60]fullerene. If a large enough acene could be prepared, the ends of the results [60]fullerene adduct would be close enough to tie together to form a cyclacene precursor. If these cyclacenes could then be iteratively coupled, nanotubular compounds could be formed. This approach is attractive for a variety of reasons. First, the SWNCs would be single walled. Second, the diameter of the SWNCs could be directly tuned by controlling the length of the acene used in the [60]fullerene Diels-Alder reaction, thus custom tailoring the electronic properties of the SWNCs. And third, the length of the SWNCs could be controlled by the number of iterative couplings undertaken (Figure 24).
Figure 24. (a) Proposed synthesis of a cyclacene via closure of a pentakis[60]fullerene adduct; (b) iterative coupling of cyclacenes to give SWNCs (see reference 87).

The promise of preparing SWNCs leads us to pursue the synthesis of large acenes. Since large acenes are known to be unstable species, we have also undertaken studies to prepare hydrogenated or “hydrogen-protected” acenes which are stable, soluble precursors to acenes. Both of these studies will be discussed in the following chapters.
CHAPTER 2

STUDIES OF THE REDUCTION OF ACENES AND ACENE QUINONES BY
ACTION OF HI AND ACETIC ACID

2.1 Background

One of the main drawbacks in working with and preparing acenes is the generally poor solubility of the corresponding quinone intermediates. Acene quinones tend to be readily accessible intermediates that are generally robust and convenient to handle. As such, most acene syntheses pass through an acene quinone intermediate. Perhaps the most direct result of the poor solubility is the difficulty in reducing the quinone functionalities in order to access the desired acene. One way to get around this problem is to use a reductant consisting of hydriodic acid (HI) and acetic acid (HOAc). Hydriodic acid-acetic acid reductions of polycyclic aromatic hydrocarbons (PAHs) were first reported by Liebermann in the late 1800s. Further work demonstrating the utility of this method was achieved by Ronald Harvey in the 1970s. Since then, there has been little attention paid to HI-HOAc reductions and no systematic studies of acene and acene quinone reductions using HI-HOAc have been reported. In our group, we were interested in using this chemistry to reduce heptacene quinone 8 to either the dihydro species 9 or the heptacene 10 itself (Scheme 16).
Instead, Briggs and Miller found\textsuperscript{86} that not only was the quinone reduced, but two additional, alternating rings were also reduced. With the end rings and the terphenyl moieties intact, hexahydro heptacene 11 was formed in highly regioselective fashion and 100% yield (Figure 25).

**Scheme 16.** Proposed conversion of 8 to either 9 or 10.
Unlike tetrphenylheptacene 10, hexahydroheptacene 11 is stable indefinitely to air and light. Additionally, 11 is soluble in a variety of organic solvents and it can be easily converted to heptacene 10 in situ using an oxidant like DDQ (dichloro dicyanohydroquinone), which can in turn be reacted with [60]fullerene to give 7. With this unexpected result, we decided to apply the HI-HOAc chemistry to other acene quinones to see if they too could be reduced in regioselective fashion and then oxidized to the corresponding acenes on demand. In this way, we would be utilizing hydrogen as an acene protecting group.

2.2 Results and Discussion

In order to study this chemistry, it was decided to produce a variety of acenes and acene quinones, both with or without phenyl substituents. Some of these acenes, such as anthracene (12), 9,10-anthracene quinone (13), 9,10-diphenylanthracene (14), tetracene (15), tetracene quinone (16), and pentacene (17), are commercially available (Figure 26).
Other larger or differently substituted acenes and acene quinones are not readily available and need to be prepared.

Likewise, 1,4,5,8-tetraphenylanthracene quinone 18 was prepared according to Bergmann, Bergmann, and Haskelberg's report in the literature. Commercially available \textit{trans,trans}-1,4-diphenylbutadiene was refluxed with benzoquinone in nitrobenzene, resulting in tandem Diels-Alder-aromatization chemistries to give 18 in one step (Scheme 17).

**Figure 26.** Commercially available acenes used in study.
Pentacene-6,13-quinone 19 was prepared according to the literature in two separate fashions: (1) by reacting commercially available o-phthalaldehyde with 1,4-cyclohexanedione in ethanol with catalytic base in a tandem aldol-dehydration reaction;\(^{58}\) (2) by preparing an o-quinodimethane \textit{in situ} via debromination of \(\alpha,\alpha,\alpha',\alpha'\)-tetrabromo-o-xylene and reacting this with benzoquinone (Scheme 18).\(^{60}\)

\begin{equation}
\begin{aligned}
\text{CHO} + \text{CHO} \overset{\text{EtOH, aq. KOH}}{\longrightarrow} \text{O} \\
\text{O} + \text{Br} + \text{Br} + \text{Br} + \text{O} \overset{\text{DMF, NaI}}{\longrightarrow} \text{O} \\
\end{aligned}
\end{equation}

\textbf{Scheme 18. Two syntheses of 19 (see references 58 and 60).}
Pentacene diquinone 20 was prepared according to Mills and Mills' procedure (Scheme 19). Friedel-Crafts acylation of pyromellitic anhydride with benzene, followed by acidic ring closure afforded 20 in overall 48% yield.

Highly soluble 6,13-diphenylpentacene 23 was prepared in 85% overall yield (2 steps from 19) according to Allen and Bell's procedure. Compound 19 was phenylated with phenyl lithium, followed by aromatization in refluxing acetic acid in the presence of KI (Scheme 20).
Scheme 20. Allen and Bell's Synthesis of 23 (see references 60 and 94).

Symmetric 5,7,12,14-tetraphenylpentacene-6,13-quinone 25 was prepared in 45% overall yield according to the literature via Diels-Alder addition of commercially available diphenylisobenzofuran and benzoquinone, followed by p-TsOH mediated dehydrative aromatization (Scheme 21).
Likewise, 6,8,15,17-tetraphenylheptacene-7,16-quinone 8 was prepared in 65% overall yield according to Miller's procedure by reacting 1,3-diphenyl naphtho[2,3-c]furan 27 with benzoquinone followed by \( p\-\text{TsOH} \) mediated dehydrative aromatization (Scheme 22).\(^9\)
Insoluble 7,16-heptacene quinone 29 was prepared according to a literature procedure\textsuperscript{97} that is similar to the previously described synthesis of 6,13-pentacenequinone.\textsuperscript{58}

Likewise, 7,9,18,20-nonacene diquinone 30 was prepared by the author (Scheme 23) using a procedure that is similar to the previously described alternative synthesis of 6,13-pentacenequinone.\textsuperscript{60}
Scheme 23. Synthesis of 29 and 30 (see references 58, 60, and 97).

Additionally, the author also prepared 8,19-nonacene quinone\textsuperscript{98} 34 and 9,22-undecacene quinone 35 using the Aldol route. These latter two reactions involve condensation of large aromatic $o$-dialdehydes, prepared according to the literature (Scheme 24).\textsuperscript{99}
Scheme 24. Synthesis of 34 and 35 (see references 98 and 99).

For this study, standard HI/HOAc reduction conditions involved refluxing 0.11 g of the substrate in a mixture of 25.0 g of 47% HI and 150 mL of glacial acetic acid in the dark under N₂ for 5 days. Work-up involved quenching excess iodide with aqueous sodium bisulfite, at which point the product may precipitate from solution. If the product precipitated, the product was simply vacuum filtered, washed with water, and dried. If the product did not precipitate out, the mixture was extracted with CH₂Cl₂, washed with water, dried, and the solvent removed to afford the product. In every case, the
hydrogenated product was a light yellow powder. The hydrogenated products all showed better solubility in organic solvents than the starting compounds. As shown in Table 2, all but the last two entries show considerable regioselectivity in their reduction reactions. In particular, when phenyl substituents are present, the reductions are directed at alternating rings along the acene backbone that are unsubstituted, preserving the internal terphenyl moieties. The terminal rings are never reduced, which is consistent with Clar's hypothesis that the end rings of acenes are the least reactive. Most importantly, the reductions occur in excellent yields in most cases.
Table 2. Results of HI/HOAc reduction studies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactant</th>
<th>Product</th>
<th>% Yield (ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td></td>
<td><img src="image1" alt="Structure" /></td>
<td>99</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td><img src="image2" alt="Structure" /></td>
<td>99</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td><img src="image3" alt="Structure" /></td>
<td>99, (2:1)*</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td><img src="image4" alt="Structure" /></td>
<td>99</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td><img src="image5" alt="Structure" /></td>
<td>99</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td><img src="image6" alt="Structure" /></td>
<td>98</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td><img src="image7" alt="Structure" /></td>
<td>98, (1:2)</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td><img src="image8" alt="Structure" /></td>
<td>99, (1:7)</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td><img src="image9" alt="Structure" /></td>
<td>79, (2:1)</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td><img src="image10" alt="Structure" /></td>
<td>98</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td><img src="image11" alt="Structure" /></td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td><img src="image12" alt="Structure" /></td>
<td>99</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>Complex mixture of hydrogenated heptacenes</td>
<td>49</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>Complex mixture of hydrogenated nonacenes</td>
<td>83</td>
</tr>
</tbody>
</table>
For the smaller unsubstituted acenes such as 12, 13, 15, 16, 17, 19, and 20 considerable selectivity is observed. Smaller acenes like 12 and 13 are only reduced at one site, in this case the central ring. Tetracene 15 can be reduced at one of two rings, the central two, which are equivalent sites. Pentacene and pentacene quinone compounds are reduced within the central rings but never simultaneously on adjacent rings. In the case of pentacene 17, reduction occurs mostly on the rings flanking the center ring, with some reduction also occurring at the central ring, in a 2:1 ratio. More intriguing are the results arising from the reductions of quinones 19 and 20. In the case of 19, two products are observed in a 1:7 ratio, respectively, where reduction occurs at either the central ring or at both rings flanking the center ring. In the case of 20, the same two products form but in a 2:1 ratio, respectively. It is interesting that in both cases, the major product arises from reduction at the non-quinone rings. Previous work by Harvey suggested that the reductions of PAH quinones pass through the PAH and then proceed to the over-reduced hydrogenated structures. Given the very different product ratios formed in the reductions of 17, 19, and 20, a common intermediate does not seem likely.

Reduction of phenyl substituted pentacene 23 occurs solely at the rings flanking the central ring of the acene backbone, thereby preserving the internal terphenyl moiety, an apparent driving force in this process. Likewise, when tetraphenylquinone 25 was reacted, reduction occurs at the central ring, once again leaving the terphenyl moieties intact. This was observed to greater effect in the case of heptacene 8, where alternating rings are reduced, leaving both internal terphenyl moieties and the terminal rings intact.
When heptacene quinone 29 and nonacene diquinone 30 are reacted, a collection of hydrogenated isomers are obtained. Thus, it appears that regioselectivity is lost for large acenes that do not bear phenyl substituents.

In summary, the HI/HOAc reduction of acenes and acene quinones that are shorter than five rings takes place in one of the equivalent central rings. For acenes and acene quinones with five or more rings, reduction occurs at any of the internal rings, never a terminal ring, and never on adjacent rings. For phenyl substituted acenes and acene quinones, reduction generally occurs at the rings that are unsubstituted, thereby preserving the internal terphenyl moieties. The one example studied that seemingly contradicts this pattern is the case of 9,10-diphenylanthracene, 14, which actually reduces on the central ring at the carbons bearing the phenyl substituents (Scheme 25).

![Scheme 25](image)

In this manner, a mixture of the cis- and trans- dihydro isomers, 38 and 39, are produced in quantitative yield. One of the isomers is preferred by a 2:1 ratio but it is not known which as no separation was attempted. However, this result shows that preservation of the terminal rings along the acene backbone is more important than the preservation of...
internal terphenyl moieties. Clar's hypothesis that the terminal rings of the acene are the least reactive is borne out by these experiments.

The most important application of this HI/HOAc reduction chemistry is the fact that it allows for long term storage of acene precursors. All of the hydrogenated products appear to be stable indefinitely upon storage in a vial at ambient temperature in the presence of light. Each product is more stable than the corresponding starting material and, most conveniently, the hydrogenated products are, in nearly every case, readily converted to the desired acene under standard dehydrogenation conditions. Typically, aromatization can be effected by action of either DDQ or 10% Pd/C in refluxing organic solvents over 80 °C (typically aromatic solvents such as benzene, toluene, xylene, or o-dichlorobenzene). When possible, the acene itself can be isolated. This is typically the case for pentacenes or smaller acenes. For the larger acenes, we have found that aromatization reactions run in the presence of [60]fullerene (which is soluble in the solvents mentioned above) directly afford the [60]fullerene adduct.

By systematically studying the HI/HOAc reduction of acenes and acene quinones, chemistry, we have found a convenient way to prepare “protected” acenes which are both stable and soluble. The acenes themselves are readily accessible via standard organic chemistry and can be either isolated or prepared in situ in the presence of a dienophile. As of this writing, the HI/HOAc reduction technique has worked for every acene or acene quinone tested, save one. This exception will be discussed in the upcoming chapter.
CHAPTER 3

STUDIES OF ACENES AND ACENE/[60]FULLERENE CHEMISTRY

3.1 Toward Preparation of Hexaphenyl Nonacene and its Tetrakis[60]Fullerene Adduct

As discussed previously, [60]fullerene undergoes Diels-Alder cycloadditions with various acenes. The smallest acene that will cyclodadd to [60]fullerene is anthracene. However, the resulting adduct is thermally unstable and readily undergoes a retro-Diels-Alder addition at temperatures over 60 °C. Buckminsterfullerene has been reported to undergo a solution phase Diels-Alder reaction with tetracene, and Komatsu has reported the synthesis of this adduct in the solid state using HSVM.\(^{82}\) If one considers the structures of anthracene and tetracene in light of Clar's aromatic sextet rule, the terminal rings should be the least reactive and the center rings most reactive. Indeed, [60]fullerene cycloaddition occurs across the central rings of anthracene and tetracene. Furthermore, anthracene only has one ring available for cycloaddition, while tetracene has two equivalent rings for cycloaddition. Pentacene, on the other hand, has two non-equivalent rings present in the center of the molecule: the center ring and the two equivalent rings flanking the center. Thus, non-equivalent [60]fullerene adducts of pentacene could be formed, at least in theory, and these would include two bis[60]fullerene adducts. Miller and Mack attempted to prepare the bis[60]fullerene adducts of pentacene, \(C_{2v} 41\) and \(C_{2h} 42\). However, when pentacene was refluxed in CS\(_2\)
with excess [60]fullerene, the sole product formed was the $C_{2v}$ mono[60]fullerene adduct 40 (Scheme 26).  

Scheme 26. Reaction of pentacene and [60]fullerene (see reference 83).

In this case, reaction is most likely occurring at the rings flanking the center, but the products are labile and the cycloaddition is highly reversible. The $C_{2v}$ monoadduct 40
can be seen as the thermodynamic product of the reaction with pentacene. In 1999, Komatsu reported a solid state (HSVM) synthesis of what he claimed to be the trans-bis[60]fullerene adduct 42 of pentacene. However, the yield was very low (11%) and he was not able to fully characterize the product. He assigned a structure corresponding to trans-bisadduct 42 based upon an apparent steric problem with the cis-structure, 41 (Figure 27). This assumption is likely in error (vide infra).

Figure 27. Possible bis[60]fullerene adducts of pentacene and [60]fullerene (see reference 82).

However, in 2000, Miller and Mack showed that the bis[60]fullerene adduct of 6,13-diphenylpentacene, 6, is formed diastereoselectively owing to the favorable \( \pi \)-stacking interactions between the fullerene moieties (Scheme 27).
Scheme 27. Miller and Mack's synthesis of 6 (see reference 84).

Additional related studies in the Miller group included a systematic attempt to prepare multiple [60]fullerene adducts of increasingly large phenyl substituted acenes. In 2003, Miller and Briggs reported the formation of a cis,cis-tris[60]fullerene adduct 7 (Scheme 28) of tetraphenylheptacene. As before, the reaction proceeds with high syn-diastereoselectivity.
As can be seen in Scheme 28, tris[60]fullerene adduct 7 was prepared not from reaction of [60]fullerene with the parent acene but rather with a hydrogenated precursor of the acene. The acene was prepared *in situ* via dehydrogenation with DDQ and reacted instantly with [60]fullerene. Hydrogenated heptacene 11 is essentially a stable, protected acene that may be deprotected (i.e. dehydrogenated) on demand. Discussions concerning preparation of protected (hydrogenated) acenes using hydriodic acid-acetic acid mixtures are described in the previous chapter of this dissertation.

We are interested in utilizing the *syn*-diastereoselectivity associated with [60]fullerene cycloadditions across acenes as a means to prepare cyclacenes. Thus utilizing an acene of appropriate length, multiple [60]fullerene cycloadditions across the same face of the acene would effectively "kink" the acene backbone in such a way that...
the two ends of the acene would be brought close together. Indeed, molecular modeling has shown that adding four [60]fullerenes to a nonacene brings the ends to within 3.06 Å (Scheme 29). Likewise, adding five [60]fullerenes to an undecacene brings the ends of the acene to within 2.95 Å (Scheme 30). Assuming that reactive functionalities can be placed at appropriate positions on the starting acene (or acene precursor), the opposite ends could be “tied” together to produce a cyclacene precursor and then ultimately a cyclacene (Scheme 31). Thus, besides the synthetic challenge that the synthesis of these molecules poses, we are interested in exploiting this chemistry in order to potentially prepare cyclacene molecules, an interesting class of aromatic compounds. As such, we first sought to prepare tetrakis and pentakis [60]fullerene adducts (43 and 44, respectively).
Scheme 29. Compound 43 arising from acene 44.
Scheme 30. Compound 45 arising from acene 46.
Scheme 31. Proposed formation of a cyclacene using syn-diastereoselective [60]fullerene addition chemistries.
In order to prepare these adducts, the corresponding acenes must be synthesized. Indeed, the bulk of the work in this area centers on the preparation and manipulation of acene precursors, all required in order to achieve synthesis of structures like 43 and 45. Likewise, our first synthetic target molecule was 6,8,10,17,19,21-hexaphenylnonacene 44.

Our initial attempt at synthesizing nonacene 44 was based on the synthesis of a centerpiece molecule, 9,10-diphenylnanthracene-1,4,5,8-diquinone 47 (Figure 28). Retrosynthetic analysis showed that if this molecule could be made, it could be converted to a nonacene precursor via the double addition of an isonaphthofuran.

![Figure 28. Centerpiece molecule 47.](image)

Initial attempts to prepare 47 included the oxidation of commercially available 9,10-diphenylnanthracene, but the desired product was not formed in this manner.

We next attempted to synthesize the centerpiece molecule via dimethoxydiphenylisobenzofuran 48. This synthesis of 48 had been reported in the literature in papers by Lepage (Scheme 32)\textsuperscript{100} and Miller (Scheme 33).\textsuperscript{101} Miller’s approach involves a double Friedel-Crafts acylation of 2,5-diphenylfuran using succinoyl dichloride and AlCl\textsubscript{3}. Repeated attempts at effecting this transformation were unsuccessful, possible due to the low reactivity of 2,5-diphenylfuran. Consequently,
Lepage’s synthesis was undertaken. Commercially available 2,3-dicyano-1,4-dimethoxybenzene was methylated using Krapcho’s conditions\textsuperscript{102} via reaction with dimethylsulfate in 2-butanone in the presence of potassium carbonate to give the dimethylated product 49 in 94% yield. The product was then dissolved in concentrated H\textsubscript{2}SO\textsubscript{4} and heated in a boiling water bath for 1 hour to give the anhydride 50 in 99% yield as described by Krapcho. Subsequent reduction of one of the carbonyl groups by reaction with either Zn/HOAc (97% yield) or NaBH\textsubscript{4} in ethanol (99% yield) gave 51.\textsuperscript{103} The final step in the Lepage synthesis\textsuperscript{100} requires reaction of the lactone with NBS in refluxing CCl\textsubscript{4} to give a reactive $\alpha$-bromo compound which is isolated crude and reacted immediately with phenylmagnesium bromide in a “Grignard coupling” reaction to give the desired isobenzofuran 48. However, every attempt at this reaction failed. Indeed, the intermediate bromide was never observed and presumably never formed. Since the bromolactone was reported to be unstable, it probably decomposed during workup, which is why it was never isolated.
Scheme 32. Attempted synthesis of isobenzofuran 48 (see reference 100).

Scheme 33. Miller’s synthesis of isobenzofuran 48 (see reference 101).
Given these unsatisfactory results, it was decided to attempt the synthesis of the centerpiece using a different stepwise approach.

The centerpiece was retrosynthetically divided into two parts: dimethoxybutadiene 52 and the dihydroxydiphenyl naphthalene derivative 53 (Figure 29).

![Figure 29. Compounds 52 and 53 for the construction of 47.](image)

In order to prepare 53, the Diels-Alder reaction between diphenylbutadiene and benzoquinone was attempted in refluxing xylene but gave only starting materials. In fact, despite a literature report to the contrary, the reaction did not work. However, Lepage reported a different synthesis of 54 that required the two reactants to sit in glacial acetic acid for three weeks at room temperature (Scheme 34). When this was attempted, large yellow prisms of product 54 were formed. The crystals were removed from the mixture with tweezers, rinsed with acetone, and dried to give 54 in 33% yield. This Diels-Alder adduct was then aromatized to give hydroquinone derivative 53 by dissolving it in boiling ethanolic HCl and stirring for 10 minutes. This afforded 53 in 90% yield.
With 53 in hand, dimethoxybutadiene was synthesized according to the literature (Scheme 35).\textsuperscript{106} Thus, 1,4-dihydroxy-2-butyne was dissolved in water and to it was added alternate portions of crushed solid NaOH and dimethyl sulfate with stirring. The temperature of the reaction was kept below 40 °C by means of an ice bath. After complete addition, the mixture was heated at 90 °C for 3 hours to give 55. Reaction with potassium tert-butoxide in DMSO at 60 °C for 3 hours gave dimethoxybutadiene as a mixture of cis,cis, cis,trans and trans,trans isomers (Scheme 35) in 49% overall yield (2 steps).

The NMR of the mixture was identical to that reported in the literature. According to the literature, all three isomers of 52 are Diels-Alder reactive, but to differing extents. The
decision was made to react the mixture with dienophile 53. However, every attempt yielded a complex product mixture that could not be separated or characterized. The literature\textsuperscript{106} reported that the butadiene had a tendency to decompose under the heating required for reaction with dienophile 53. Additionally, 52 was reported to have a tendency to lose methanol upon cycloaddition, aromatizing the resulting molecule, which would further complicate the reaction mixture.

Since these step-wise approaches toward formation of the anthracene framework were unsuccessful, it was decided to commence a new approach with the anthracene backbone already assembled. The first attempt was made starting from inexpensive, commercially available 1,8-dihydroxyanthracene quinone. It is well known in the literature that phenols can be converted to p-quinones by the action of Fremy's Salt (Figure 30).\textsuperscript{107}

![Figure 30. Fremy's Salt.](image)

Additional evidence suggests that this transformation can be applied to polycyclic systems as well. As such, it was postulated that if 9,10-diphenyl-1,8-dihydroxyanthracene could be prepared, Fremy’s Salt oxidation would give centerpiece molecule 47. The synthesis was started by deprotonating the hydroxyl groups with NaH in dry THF, followed by methylation with dimethyl sulfate to give 56 in 68% yield after recrystallization.\textsuperscript{108} This was followed by addition of phenyl lithium in dry toluene at -78
°C to give the diphenyl diol 57 in 64% crude yield. Aromatization with KI in refluxing acetic acid gave the anthracene 58 in 87% yield (Scheme 36).

\[
\begin{align*}
\text{57} & \xrightleftharpoons{\text{NaH, Me}_2\text{SO}_4, 68\%} \xrightarrow{\text{PhLi, 64\%}} \text{56} \\
\text{57} & \xrightarrow{\text{KI, HOAc, 87\%}} \text{58}
\end{align*}
\]


This is where the synthesis stalled, however, as demethylation of 58 was not achieved. A variety of conditions and reagents were tried, including TMSI, HBr/HOAc, HI/HOAc, BBr₃, and BBr₃·Me₂S. While it appeared by NMR that a small amount of the desired product was formed during the reaction with HBr/HOAc, the amount was so small that this path was abandoned.

We next decided to try this system with a different protecting group that would be easier to remove at the end of the synthesis. To this end, it was decided that the benzyl group would be ideal. The commercially available 1,8-dihydroxyanthracene quinone was reacted with benzyl bromide and potassium carbonate in refluxing acetone to give the dibenzylated 59 in 95% yield. This was then subjected to phenyl lithium addition in dry...

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toluene at -78 °C to give the diphenyl diol 60 in 76% yield. This was aromatized with Zn°/HOAc to give the anthracene 61 in 80% yield (Scheme 37).

The next step involved hydrogenolysis to remove the benzyl groups. Surprisingly, this was unsuccessful, as only complex product mixtures (which included some starting material) were obtained. It is possible that this failure was due to the bulk of the phenyl groups adjacent to the benzylic-protected alcohols, which could hinder adsorption onto the catalyst surface, thus preventing hydrogenation.

Concurrent with this effort, a second approach starting from a 1,4,5,8-tetrasubstituted anthracene framework was also attempted. Numerous groups in the literature have reported the preparation of $p$-quinones from 1,4-dimethoxy benzenes via
oxidative demethylation\(^{114}\). Thus, it was decided to utilize 1,4,5,8-tetrahydroxyanthracene quinone 62 as a starting material (Figure 31).

Compound 62, however, is not commercially available. Thus, it needed to be prepared in sufficient quantity that would support a multi-step synthesis. A procedure reported by Larry Miller's group\(^{115}\) started with 1,4,5,8-tetraaminoanthracene quinone 63, which is commercially available as the dye Disperse Blue 1. This dye is sold adsorbed on a polymer with anywhere from 30% to 70% dye content by weight. A Soxhlet extraction with acetone as solvent affords free 63. This was then reacted in hot 1 M aqueous NaOH with sodium dithionite at 90 °C to give a mixture of leuco-quinone 64 and the desired 1,4,5,8-tetrahydroxyanthracene quinone 62. This mixture was refluxed in nitrobenzene containing a small amount of pyridine to give 62 in 63% yield (Scheme 38).
Even though 62 was prepared, this synthesis was not ideal, as Disperse Blue 1 is expensive and its isolation is time intensive. Thus, a chemical synthesis of 62 was undertaken.

It is reported in the literature\textsuperscript{116} that 62 can be prepared from 1,8-dihydroxy-4,5-diaminoanthracene quinone 65. Thus, 1,8-dihydroxyanthracene quinone was reacted with HNO\textsubscript{3} in oleum in the presence of boric acid, and then boiled in a mixture of ethanol, benzene, and DMF to give 1,8-dihydroxy-4,5-dinitroanthracene quinone 66 and minor isomers in 54\% overall yield. This mixture was added to concentrated H\textsubscript{2}SO\textsubscript{4} and heated to 60 °C. To it was added iron and the mixture was then heated to 90 °C with stirring until the color became dark green. After workup and filtration, crude 65 was obtained (Scheme 39).

It was discovered after this synthesis was completed that 65 is also commercially available in relatively large quantities. Thus, 65 was henceforth purchased from commercial sources. Compound 65 was reacted with sodium dithionite in 10% aqueous NaOH and n-butanol at 60 °C to give leuco-quinone 64 in 81% yield. Refluxing this in a mixture of nitrobenzene and pyridine as previously mentioned afforded 62 as before. Compound 62 was methylated in 2-butanone with dimethyl sulfate and potassium carbonate to give the tetramethyl derivative 67 in 53% yield. This was phenylated with phenyl lithium in dry THF at -78 °C to give diphenyl diol 68 in 68% yield. Aromatization with Zn°/HOAc gave the desired anthracene 69 in 90% yield (Scheme 40).
The next step in the synthesis was to be the oxidative demethylation to yield the diquinone. According to the literature, this is most commonly achieved using ceric ammonium nitrate (CAN) in a 1:1 solution of water and acetonitrile. However, all attempts at this reaction were unsuccessful, resulting in crude products that appeared by NMR to contain a small amount of product within a complex product mixture. Varying temperature and concentration did not affect these results. Other reports suggested that ceric ammonium sulfate (CAS) and nitric acid impregnated MnO₂ could also be utilized as oxidants. Unfortunately, these too failed. One last oxidant was prepared and reacted, a mixture of CAN and the addition of pyridine-2,6-dicarboxylic acid-N-oxide. Pyridine-2,6-dicarboxylic acid was suspended in a solution of 30% H₂O₂ and Na₂WO₄·2H₂O and heated to 100 °C. Additional 30% H₂O₂ was added until dissolution was complete. Following work-up, the N-oxide was obtained in 28% yield. While this yield is much lower than that reported in the literature, the reaction was carried out on a
large scale using inexpensive starting materials, so sufficient quantities were generated. It is claimed\textsuperscript{120} that addition of the $N$-oxide during CAN oxidations of dimethoxy benzenes increases the reactivity of CAN and the rate of product formation. However, when this approach was attempted, the same complex crude product was obtained as in previous attempts. One possible reason all of these oxidative demethylation attempts failed is the presence of the phenyl groups. The phenyl groups, if coplanar with the anthracene backbone, would be electron withdrawing via resonance, which would enhance the reactivity of the anthracene backbone toward one electron oxidation, which is the first step in the CAN reactions. However, if the rings are orthogonal to the anthracene backbone, which is the likely actual orientation of the molecule, these rings would only be inductively withdrawing, which is a much weaker effect and thus would not enhance the reactivity of the anthracene backbone toward one electron oxidation. This is supported by the fact that the parent molecule, which is missing the phenyl groups, readily undergoes CAN oxidative demethylation at room temperature.

While our attempts to form 47 were unsuccessful, it is interesting to note that the parent system, anthracene-1,4,5,8-tetraone 70, is known in the literature.\textsuperscript{114} Compound 70 is easily prepared by a CAN oxidation of 1,4,5,8-tetramethoxyanthracene. It appears that the phenyl groups sandwiched between the ether functions of 58, 61, and 69 adversely effect their respective deprotection reactions.

Other approaches to hexaphenylnonacene 44 that were explored include reaction between a terphenyl bisbenzyne equivalent (71 or 72) and furan according to Scheme 41. The bisbenzyne molecule depicted, however, most likely would not exist. Instead, what is more likely is a stepwise reaction, where benzyne would form on one side of the
molecule, react, and then this would be repeated on the other side. The bisbenzyne shown is depicted simply for ease of representation. This holds true for every example in this dissertation when bisbenzyne is depicted.

![Scheme 41. Alternative synthesis of hexaphenynonacene 44.](image)

This approach utilizes a bisisobenzofuran as the centerpiece molecule. The first bisbenzyne precursor whose synthesis was attempted was 71, based on work by Wudl\textsuperscript{121} on an analogous system that will be discussed later. The reactive benzyne site is formed by TBAF-induced loss of TMS, which in turn induces loss of triflate, one of the best leaving groups known.
Commercially available 2,5-diphenyl-\textit{p}-benzoquinone was reduced by Zn\textsuperscript{0}/HOAc to give the hydroquinone 73 in 92\% yield.\textsuperscript{122} This was brominated using bromine in chloroform, followed by re-reduction in ethanol with SnCl\textsubscript{2} to give the hexasubstituted benzene 74 in 98\% yield. The hydroxyl groups were protected using TMSCl to give 75 in 90\% yield. The next step was to replace the bromines with TMS groups. Compound 75 was heated to boiling in dry toluene in the presence of sodium metal. To this solution was added TMSCl and the heating continued overnight. These conditions were identical to those reported by Wudl\textsuperscript{121} for the parent system without phenyl substituents. However, the reaction of phenyl substituted 75 is sluggish and these conditions did not produce the desired 76, but rather the compound where only one TMS group added to the ring in 82\% yield. Presumably the sluggish nature of the reactions is due to the increased steric hindrance created by the adjacent phenyl groups. The reaction was rerun and allowed to reflux for two days. Under these conditions, the desired 76 was formed in 89\% yield. Deprotectios of the alcohols also proved problematic. Wudl's conditions\textsuperscript{121} for the parent system called for simple stirring of the TMS-protected compound in dioxane at room temperature in the presence of 6M HNO\textsubscript{3}. However, treating TMS-protected 76 in this manner did not produce the desired hydroquinone 71, but rather the quinone. Clean deprotection was eventually achieved by heating 76 in 20\% aqueous methanol, the reaction progress monitored by TLC. The reaction typically took 4 days and yielded, very cleanly, the desired hydroquinone 71 (Scheme 42).
The final step in the synthesis of the bisbenzyne precursor was the installation of triflate groups adjacent to the TMS groups. In Wudl's synthesis of the parent compound, this was achieved by reacting the hydroquinone in pyridine with triflic anhydride at 50 °C. However, these conditions failed for diphenyl substituted 71. Additionally, attempts at using the more reactive triflic chloride also failed. Apparently, the hydroxyl groups of 71 are simply too hindered, being flanked by a large TMS group on one side and a phenyl group on the other side. As such, it was decided to attempt a synthesis of a different bisbenzyne precursor, namely tetrabromoterphenyl 78 via hexahalobenzene 77 (Scheme 43). This approach is potentially attractive because 1,2,4,5-tetramethoxy-3,6-diphenylbenzene 78 is reported in the literature as having been made in two steps from commercially available 1,2,4,5-tetrabromobenzene.123

Scheme 42. Synthesis of 71 (see references 121 and 122).
Tetrabromobenzene was diiodinated in concentrated H$_2$SO$_4$ in the presence of I$_2$ and KIO$_3$ for 5 days to give 1,2,4,5-tetrabromo-3,6-diiodobenzene 77 in 89% yield. The next step in the reported synthesis involves an Ullmann coupling by heating 77 in a Pyrex tube at 230 °C in the presence of copper powder and iodobenzene for 15 minutes followed by immediate quenching with toluene (Scheme 43).$^{123}$

![Scheme 43. Synthesis of 78 to potentially lead to 72 (see reference 123).](image)

While the desired product 78 was formed and observed in the crude NMR spectrum, TLC analysis showed a mixture of products that eluted so close to 70 that a separation was nearly impossible. Furthermore, judging from the relative size of the signals in the $^1$H NMR spectrum, the yield of 78 was actually quite low.
Since all attempts to form nonacene 44 using a three-ring centerpiece molecule failed, it was decided to try an alternative approach involving a one-ring centerpiece, p-benzoquinone, as illustrated in Scheme 44.

Scheme 44. Alternative synthesis of hexaphenynonacene 44 via diphenylisoanthrafuran 79.

This approach, which utilizes 4,11-diphenylisoanthrafuran 79, seemed promising given the extensive work done in our group on isobenzo- and isonaphthofurans, both of which are discussed in detail below. Thus, a synthesis of 79 (Figure 32) was undertaken.
Precedents in the literature for isofuran systems larger than naphthalene-based ones are rare, but it was reported that the parent compound, isoanthrofuran, was indeed prepared and reacted with dieneophiles in situ.\textsuperscript{124} In our case, a diphenyl analog needed to be prepared. The synthesis started by reacting maleic anhydride and 1,3-diphenyl naphtho[2,3-c]furan \textsuperscript{27} in benzene at room temperature. Compound \textsuperscript{27} is a molecule utilized in our group quite often and as such, we have developed an optimized synthesis of \textsuperscript{27} based upon an original synthesis reported by Cava and VanMeter.\textsuperscript{96,125} The aforementioned Diels-Alder reaction produces adduct \textsuperscript{80} in 89\% yield. Compound \textsuperscript{80} was dehydratively aromatized to the anthracene anhydride \textsuperscript{81} via reaction with \textit{p}-toluenesulfonic acid (tosic acid) in refluxing benzene using a Dean-Stark trap for azeotropic removal of water. This was achieved in 84\% yield. The next step called for reduction of one of the carbonyl groups. Utilizing the same reaction conditions used in the synthesis of \textsuperscript{51} (dimethoxyphthalic anhydride)\textsuperscript{103} produces a complex product mixture that appears to contain small amounts of the desired product \textsuperscript{82}. However, when reduction is carried out using NaBH\textsubscript{4} as reductant, the desired lactone \textsuperscript{82} is formed in fair yield. Simple purification via flash silica column chromatography gave \textsuperscript{82} in 66\% yield. Reduction of the lactone with DIBAL-H in dry CH\textsubscript{2}Cl\textsubscript{2} at -78 °C gave lactol \textsuperscript{83} in 72\% yield (Scheme 45).
Interestingly, no ring-opened tautomer was observed in the proton NMR spectrum of 83. The parent compound is reported\textsuperscript{124} in the literature as existing as an 85:15 mixture of ring opened and ring closed species. Here it seems the phenyl groups affect this equilibrium such that the lactol dominates.

In the literature procedure to form the parent isoanthrofuran,\textsuperscript{124} an acid catalyzed conversion of the corresponding methyl acetal is utilized. Lactol 83 was reacted multiple times in the presence of benzoquinone using several different acids including tosic acid, trichloroacetic acid, and acetic acid. Each acid was tested in various solvents and at various temperatures for varying lengths of time. Unfortunately, there was no evidence for the formation of the isoanthrofuran for subsequent reaction with benzoquinone.
Nearly all of the NMR spectra showed complex product mixtures containing unidentifiable species in addition to some unreacted benzoquinone. The authors that prepared the parent isoanthrofuran\textsuperscript{124} discussed the speed of formation of the isofuran species. The smallest furan, isobenzofuran, forms much faster than both isonaphthofuran and isoanthrofuran presumably because of a greater disruption of the aromaticity in the latter two cases. However, once formed, the reactivity of the larger isofurans is expected to be much greater than that of the smaller ones. Isoanthrofuran is reportedly more reactive than isonaphthofuran, which is in turn more reactive than isobenzofuran. However, there appears to be something else affecting the formation and reactivity of 79 from 83. As observed in other examples noted above, the addition of phenyl substituents retards the reactivity on an adjacent ring. In this case, the phenyl groups seem to slow the dehydration of 83, at least relative to hydrolysis decomposition. In an attempt to enhance the formation of 79, 83 was reacted with PBr\textsubscript{3} in pyridine at 0 °C. We had hoped that the corresponding bromide could be isolated and dehydrobrominated in a subsequent step to give 79. Indeed, the bromide was isolated but was quick to decompose upon standing. When the freshly prepared bromide was immediately refluxed in pyridine in the presence of benzoquinone, once again a complex product mixture was obtained.

It was decided to try another method for preparing nonacene 44, one that did not involve formation of a large isoanthrofuran like 79 nor a 3-ring diquinone hub like 47. A search of the literature revealed that Larry Miller reported\textsuperscript{126} the synthesis of a tetraaryl nonacene triquinone in 1986. This triquinone was prepared utilizing the novel bisisobenzofuran 84 (Figure 33).
Miller used \textit{p-tert-}butylphenyl groups as the aryl substituents in order to impart greater solubility and because the \textit{tert-}butyl groups appear as a simple singlet in the $^1$H NMR spectrum and are upfield of any peaks of interest in the aromatic region. It was decided to attempt to prepare an analogous system using phenyl groups as the aryl substituents using Miller's synthetic approach. In the synthesis of large acenes, our group has noted that phenyl groups alone impart substantial solubility to these species. The key intermediate in the preparation of bisisobenzofuran 84 is 2,5-diphenylfuran-3,4-dicarboxaldehyde 85 (Figure 34).

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{figure33.png}
\caption{Larry Miller's bisisobenzofuran 84 (see reference 126).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{figure34.png}
\caption{Key intermediate 85.}
\end{figure}
The synthesis of 85 began with commercially available diphenylfuran, which was dibrominated to give the 3,4-dibromo compound using two different methods. The first, reported in the literature specifically for the synthesis of 86, involved stirring diphenylfuran at room temperature for 3 days with NBS in benzene to give 86 in 98% yield (Scheme 45). The second was adapted from Miller’s synthesis. Diphenylfuran was reacted with bromine in CHCl₃ at 0 °C for 15 minutes and then stirred at room temperature for 15 minutes to give 86 in 92% yield. This second method is advantageous in that it does not involve an excess of NBS, does not use carcinogenic benzene, and requires only 30 minutes to complete. Cyanation was effected utilizing the Rosenmund-Von Braun reaction. Refluxing 86 in NMP with CuCN gave a mixture of di- and mono-cyano products. These could be separated easily via recrystallization from heptane. The yields varied seemingly with no reason, although 58% yield for the dicyano 87 was the best obtained. This was then hydrolyzed to diacid 88 by refluxing it in ethylene glycol with a small amount of 3M NaOH. The reaction was monitored by holding a wet piece of pH paper over the top of the condenser and letting the mixture reflux until the evolution of ammonia ceased and the pH paper was neutral. This took anywhere from 3 to 7 days depending on the scale of the reaction. When run on a 700 mg scale, the reaction took 5 days and gave diacid 88 in 84% yield. This was then reduced with BH₃·THF complex in dry THF to give diol 89 in 38% isolated yield. This yield should have been much higher. Indeed, in Miller’s synthesis this reduction proceeds in quantitative yield. However, the lowered yield is most likely due to diacid 88 not being thoroughly dried. Still, diol 89 was subsequently oxidized to 85 via a Swern oxidation, which proceeded in 95% yield (Scheme 46).
While this synthesis provided 85, it was not ideal for a variety of reasons. First, it was long, six steps in total, including one that could take upwards of a week to complete. Second, it used stoichiometric amounts of CuCN, which is dangerous and must be disposed of separately from other chemical waste. And third, it was not easily scalable; a substantial amount of material was lost throughout the course of the synthesis due to the relatively low yields, number of steps, and the fact that 87 was formed in a mixture and had to be separated from its mono-cyano isomer. Thus, it was decided to devise a better synthesis that would be shorter, higher yielding, and would be scalable so that a large amount of 85 could be prepared.

As an easily accessible route to 85, it was decided to attempt the synthesis of 2,5-diphenylfuran-3,4-diesters. These esters should be easy to prepare, soluble, and would be
easily converted to 85. A report published\textsuperscript{128} by Pohmakotr and coworkers on the synthesis of 2,5-diphenylfuran-3,4-diethylester 90 utilized the closing of an alcohol adjacent to a ketone, as shown in Scheme 47. His synthesis involved forming the dianion of 91 and reaction of this dianion with benzaldehyde to give 92, followed by acid catalyzed cyclization to give dihydrofurans 93 and 94. Oxidation with DDQ would then afford 90.

Compound 91 was synthesized according to the literature: ethyl benzoyl acetate and ethyl bromoacetate were heated, neat, with KI and K\textsubscript{2}CO\textsubscript{3} at 65 °C with stirring for 2 hours.\textsuperscript{129} Crude 91 was obtained in 99% yield. This was then subjected to Pohmakotr’s conditions, which involved formation of the dianion at -78 °C using LDA as base, followed by addition of benzaldehyde. Quenching with acetic acid at -78 °C afforded the crude aldol product, which was immediately refluxed in toluene with p-TsOH through a Dean-Stark trap for azeotropic removal of water as per Pohmakotr’s protocol (Scheme 47).
The desired cis- and trans-furans 93 and 94, which were to be oxidized to 90 in the next step, were formed in very low yields and were hard to purify. Two separate attempts at this reaction yielded the same results. It was decided to try a different approach.

The dimethylester analogue, 95, was reported in the literature as having been prepared from alkene 96 in quantitative yield via reaction with PPh₃ at room temperature (Scheme 48).¹³⁰

---

**Scheme 47.** Pohmakotr's synthesis of 90 (see references 128 and 129).

**Scheme 48.** Reported synthesis of 95.
A recent report in the literature for the synthesis of 96 was reported by Nair and coworkers\textsuperscript{131} involving a novel rearrangement during the reaction of benzil and DMAD in DME with catalytic pyridine at -10 °C (Scheme 49).

\[
\begin{align*}
\text{CO}_2\text{Me} &\quad \text{Ph} \\
\text{CO}_2\text{Me} &\quad \text{Ph} \\
\text{DME} &\quad \text{cat. pyr} \\
11\% &\quad 96
\end{align*}
\]

Scheme 49. Nair's synthesis of 96 (see reference 131).

Although Nair and coworkers report 96 forming in 68% isolated yield, the reaction was tried three times and in each case afforded 96 in only 11% yield. The reason for this lowered yield is unknown. Thus, it was decided to pursue a more classic approach to 90.

Papers published by Perkin and Schlosser in 1888\textsuperscript{132} and 1890\textsuperscript{133} reported the synthesis of 90 using an acid-catalyzed cyclization of succinate 97. Succinate 97 was synthesized according to Perkin and a modification of his procedure published by Pan and coworkers in 1997.\textsuperscript{134} Sodium ethoxide was prepared by dissolving freshly cut sodium metal in absolute ethanol at room temperature. Commercially available ethyl benzoylacetic acid was added and the sodium salt of ethyl benzoylacetic acid was isolated. This was suspended in dry ether and to it was added a solution of iodine in dry THF, dropwise. After workup of the resulting brown solution, dibenzoyl succinate 97 was isolated in 38% yield. Although this yield is low, the reaction is run using inexpensive, readily available starting materials and can be run on a large scale. For instance, 20 grams of ethyl benzoylacetic acid affords approximately 8 grams of 97. Compound 97 was dehydratively...
cyclized to furan 90 by dissolving it in concentrated H\textsubscript{2}SO\textsubscript{4} and stirring at room temperature for 16 hours. This afforded furan 90 in 93\% yield. Compound 90 was then reduced to the diol via LAH reduction in ether at room temperature in 95\% yield. Diol 89 was oxidized as before using the Swern oxidation to give dialdehyde 85 in 98\% yield (Scheme 50).

\begin{center}
\includegraphics[width=\textwidth]{scheme50.png}
\end{center}

**Scheme 50.** The best synthesis of 85 (see references 132, 133, and 134).

Using this revised synthesis, dialdehyde 85 can be synthesized in gram quantities in fewer steps and with higher yields (compare Schemes 46 and 50). Additionally, purifications are unnecessary, as the crude products are virtually pure.

Adapting once again the conditions set forth by Miller, dialdehyde 85 was reacted with commercially available cyclohexane-1,4-dione in ethanol with a small amount of aqueous KOH.\textsuperscript{126} After three hours, the mixture was extracted with CHCl\textsubscript{3} and the solvent evaporated to give bisisobenzofuran 98. Unlike Miller's bisisobenzofuran, which he claimed was quite soluble owing to the \textit{p-}\textit{tert}-butyl groups on the phenyl substituents,
98 was sparingly soluble, and extractions gave only 35% yield of the solids, whereas Miller’s reported yield was quantitative. Thus, an alternate workup was devised where the reaction mixture was diluted with a large amount of water and the solids filtered, dried, and dried further under vacuum. In this way, 98 was isolated in 75% yield (Scheme 51). Compound 98 is a deep red/purple solid, sparingly soluble in organic solvents, and unstable in solution in the presence of light. In the presence of light, solutions of 98 quickly bleach and become light yellow solutions.

\[
\begin{align*}
\text{OHC} & \quad \text{CHO} \\
\text{Ph} & \quad \text{Ph} \\
85
\end{align*}
\]

\[
\begin{align*}
\text{KOH} & \quad \text{75\%} \\
\text{EtOH} & \\
98
\end{align*}
\]

\textbf{Scheme 51. Synthesis of 98.}

Compound 98 appears, however, to be stable to air and heat in the absence of light.

Compound 98 was dissolved in CHCl₃ with naphthoquinone and to this mixture was added, in one portion, TMSOTf. The resulting mixture was stirred for 24 hours in the dark under an N₂ atmosphere. Miller explained in a series of papers\textsuperscript{135} that 84 is quite
reactive at room temperature with dienophiles such as maleic anhydride and \( N \)-phenylmaleimide. Upon reacting 98 with naphthoquinone, however, we saw no reaction, even at elevated temperatures. However, the addition of TMSOTf appeared to catalyze the Diels-Alder reaction. Additionally, the TMSOTf subsequently aromatizes the resulting endoxide, as the product isolated is the fully aromatic nonacene triquinone 99. Attempts made by Miller and coworkers to isolate their corresponding endoxide intermediate were unsuccessful. Apparently, the dehydrative aromatization occurs immediately after Diels-Alder reaction. Triquinone 99 is a sparingly soluble yellow solid (Scheme 52).

While remarkably soluble for a triquinone of its size, 99 still does not possess great solubility. Additionally, the formation of 99 was not as clean as the formation of the analogous triquinone that Miller reported.\textsuperscript{126} Even after preparative TLC purification of 99, there was an impurity present that co-eluted and could not be removed. In the \( ^1H \)
NMR spectrum of impure 99, the signals corresponding to 99 can be clearly seen. The integrations are quite accurate, and the signals and their positions correspond nicely to those reported by Miller for his system. However, the identity of the stubborn impurity is puzzling. Impure 99 was subjected to an HI/HOAc reduction as elaborated in Chapter 2. It was hoped that reduction of 99 would occur on every other ring, giving a stable, soluble derivative of the target nonacene. Additionally, it was hoped that the reduced species could be separated from the stubborn impurity. Reduction of 99 in this manner gave a light brown powder that appeared, in the 'H NMR spectrum, to be a mixture of hydrogenated species. This material was subjected to oxidation via DDQ in the presence of [60]fullerene. However, no adduct was observed to form.

Concurrent with the synthesis of 99, it was decided to repeat Miller’s synthesis of the p-tert-butylphenyl substituted nonacene triquinone. Once again, key in this synthesis was the corresponding furan dialdehyde, this time furan 100 (Figure 35).

![Figure 35. Key intermediate 100.](image)

The synthesis of 100 began with the Friedel-Crafts acylation of fumaryl chloride and tert-butylbenzene with AlCl₃ in TCE to give unsaturated diketone 101 in 39% isolated yield (Scheme 53). The double bond was reduced via reaction with SnCl₂ in HCl and HOAc to give the saturated diketone 102 in 87% isolated yield. This was then dehydratively cyclized to give furan 103 via dissolution in BF₃·OEt₂ and stirring for 42 hours at room
temperature. Furan 103 was isolated in 90% yield. This was dibrominated with Br₂ in CHCl₃ to give the dibromide 104 in 82% yield. The Rosenmund-Von Braun reaction was utilized once again by refluxing 104 in NMP with CuCN to give, as before, a mixture of the dicyano and monocyano furans in roughly a 92:8 ratio as determined by ¹H NMR integration. Upon fractional recrystallization from hot heptane, separation was effected giving the dicyano furan 105 in 83% yield. This was hydrolyzed by refluxing in ethylene glycol and 3 M NaOH yielding diacid 106. The reaction was monitored by holding a wet piece of pH paper over the top of the condenser until the evolution of ammonia ceased. After aqueous acidic workup, diacid 106 was obtained in 96% yield. This diacid was reduced to the diol in THF using BH₃·THF to give 107 in 80% yield. A Swern oxidation of 107 gave the desired diformylfuran 100 in 95% yield (Scheme 53).
Scheme 53. Synthesis of 100.

With dialdehyde 100 in hand, preparation of bisisobenzofuran 84 could be undertaken (Figure 33).
Miller's approach involved suspending 100 and 1,4-cyclohexanedione in ethanol and adding a small amount of aqueous KOH to induce the double aldol condensation/dehydration. Following the conditions set forth by Miller exactly, 84 was prepared in quantitative yield (Scheme 54).

Scheme 54. Synthesis of 84.

Compound 84 is a deep purple solid that gives deep purple solutions in CHCl₃ and deep reddish/purple solutions in toluene. It is quite soluble, and readily subjected to both TLC and NMR analyses. It is light sensitive, and solutions, when exposed to light, bleach to give light orange/yellow solutions within hours. However, when kept in the dark, it appears to be quite stable to both heat and air. Miller reports quantitative conversion of 100 to 84. However, in our hands, formation of 84 was not complete, with amounts of 100 always present in the ¹H NMR spectrum. It was thought that perhaps the poor solubility of 100 in ethanol was responsible for the initially low yields obtained for 84. Dialdehyde 100 and 1,4-cyclohexanedione are both suspended in the ethanol prior to the addition of the aqueous KOH. Even though the suspension immediately becomes a dark purple mixture when the base is added, the dialdehyde did not completely dissolve. Even letting the reaction stir overnight (as opposed to the 3 hours set forth by Miller) had no
effect on the conversion. However, sonication of the solids in the ethanol to finely dispersed them led to a nearly quantitative conversion of 100 to 84.

Compound 84 was subsequently reacted with excess 1,4-naphthoquinone (freshly sublimed) in dry CHCl₃ in the presence of TMSOTf to form nonacene triquinone 108 as a soluble yellow solid in 26% isolated yield (Scheme 55).

\[
\begin{array}{cccc}
84 & + & \text{\text{tBu}} & \text{\text{tBu}} \\
\text{TMSOTf} & \text{CHCl₃, rt} & \text{26\%} \\
\end{array}
\]

Scheme 55. Synthesis of 108.

The formation of 108 is quite interesting in that TMSOTf acts as both a Lewis-Acid catalyst for the Diels-Alder reaction and the dehydrating agent to aromatize the resulting endoxides. Indeed, the Diels-Alder adduct is never isolated. Miller reports that the reaction in the absence of TMSOTf does not occur, even in refluxing toluene for prolonged periods of time. Miller claimed the reaction to be clean, giving only 108 after workup. However, in this study the formation of 108 was always accompanied by the formation of what appeared by ¹H NMR analysis to be a mono-addition product. Also
observed was the formation of a product which looked like the hydrolyzed bisisobenzofuran. The compounds co-eluted on silica gel and could not be separated. However, when the crude solids were rinsed with copious amounts of acetone until the washings were clear, nearly pure 108 was left behind. Final purification was achieved by running the acetone-washed material through a silica column with CHCl₃ as eluant and collecting the bright yellow band that ran with the solvent front to give pure 108 in 26% isolated yield. While this yield is lower than the 45% yield reported by Miller, it is still an acceptable method for obtaining the nonacene triquinone.

The next step in the synthesis of a \(p^-t\)-butylphenyl substituted nonacene involved reduction of the quinone functionalities of 108 to give the hydrogenated nonacenes, including isomer 109 as Scheme 56. To effect reduction of 108, the HI/HOAc conditions as elaborated in Chapter 2 of this thesis were utilized.

\[108 \xrightarrow{\text{HI/HOAc}} 109\]

Scheme 56. Anticipated reduction of 108 to give 109.

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However, this reaction did not proceed as expected. When 108 was subjected to refluxing HI and HOAc for 5 days under nitrogen in the dark, our standard conditions, the resulting product mixture contained roughly an equal amount of unreacted starting material and multiple hydrogenated isomers of 108. Upon changing reaction times and conditions, 108 was not cleanly reduced to any hydrogenated species. Variables that were examined in this reaction included time, quality of HI reagent, and additives. Reacting 108 for longer periods of time did not appreciably increase the amount of desired product. Adding fresh portions of HI each day actually reduced the yield as pure starting material was recovered. Trying the reaction with older bottles of HI, as well as fresh HI, seemed to have no effect. Stabilized HI and unstabilized HI were both tried, with no difference in the end result. Additives were also investigated, chiefly red phosphorous, which had been used in the original HI literature dating back to the late 1800s, as well as in much of Ronald Harvey’s work on the reduction of polycyclic aromatic hydrocarbon quinones with HI. However, the addition of red phosphorous did not improve the reaction. The end result of this work was that no selective or complete reduction of 108 was achieved.

Other reductions of 108 were also attempted, but they all met with the same result, to varying degrees. A Wolff-Kishner reduction, which consisted of refluxing 108 in ethylene glycol with hydrazine and NaOH, gave, after 2 weeks a minimal amount of reduced product. Various attempts at reducing with NaBH₄, KBH₄, or LiAlH₄ gave complex mixtures which did not appear to be related to the desired product, as well as unreacted starting material.
At this point, we do not have a practical method for the conversion of 108 to an hydrogenated nonacene(s) for subsequent reaction with [60]fullerene. Future work in the group should involve attempting to devise a method to cleanly and perhaps selectively reduce 108 (or 99) to an hydrogenated nonacene(s) that can be aromatized in the presence of [60]fullerene to produce a tetrakis[60]fullerene adduct of a nonacene as in Scheme 29. This could perhaps be done in the solid state using HSVM techniques to achieve this goal.

3.2 Toward the Preparation of an Octaphenyl Undecacene and its Pentakis[60]Fullerene Adduct

Preparation of the pentakis[60]fullerene adduct of 6,8,10,12,19,21,23,25-octaphenylundecacene, 45, was also undertaken simultaneous to the work undertaken to form 43 and 44 as described above. As with nonacene 44, the synthesis of undecacene 46 was approached by dividing the acene into smaller parts and attempting to synthesize these “building blocks” before bringing them together to form the acene. The first approach to this end utilizes bisbenzyne chemistry, similar to the approach taken in the attempted synthesis of 72. Hart had published\textsuperscript{137} the synthesis of bisfuran precursor 110, prepared from the reaction between bisbenzyne and diphenylfuran (Scheme 57).

\[
\begin{align*}
\text{Scheme 57. Synthesis of bisfuran precursor 110.}
\end{align*}
\]
Using chemistry analogous to that reported in the literature\textsuperscript{138} and utilized previously by our group, it was expected that 110 could be reacted with di(2-pyridyl)tetrazine to give a tetraphenylbisisobenzofuran, which could then add in a Diels-Alder fashion to a host of dienophiles. In particular, we were interested in preparing pentacenediquinone 111 via reaction between the bisisobenzofuran and \(p\)-benzoquinone (Scheme 58).

![Scheme 58. Proposed synthesis of 111.](image)

Thus, the synthesis of 110 was undertaken. The most obvious and straightforward approach involves preparation of bisbenzyne via reaction of 1,2,4,5-tetrabromobenzene and \(n\)-BuLi at -78 °C in THF, followed by subsequent reaction with 2,5-diphenylfuran.\textsuperscript{137} However, repeated attempts at this reaction failed, with unreacted diphenylfuran recovered in full. As noted earlier, we have repeatedly found 2,5-diphenylfuran to be unreactive in a variety of reactions, and that can perhaps explain this result. An alternative bisbenzyne synthesis was sought. Harold Hart reported the synthesis of a bisbenzyne precursor in the form of diaminobenzobistriazole 112 (DABT) that would form bisbenzyne irreversibly.\textsuperscript{139} The 1,5- and 1,7-DABT isomers, when oxidized with
lead tetraacetate (LTA), lose four molecules of N₂ gas and form bisbenzyne in a completely irreversible fashion. Thus, the synthesis of DABT was undertaken (Figure 36).

![Figure 36. 1,7-DABT 112.](image)

1,3-Dichlorobenzene was nitrated with KNO₃ in concentrated H₂SO₄ at 125 °C to give the dinitrobenzene 113 in 63% yield (Scheme 59). This material was made on a large scale (50.0 g) so the yield was satisfactory. However, care must be taken during this reaction as product 113 is a severe skin blistering agent. Hand protection should be worn when working with this material. The dinitro compound was then aminated in hot ethylene glycol by bubbling ammonia gas into the mixture until solids began to precipitate out of the solution. The gas was bubbled in a little longer and then stopped. The mixture was cooled and the solids filtered and washed with water to give the nucleophilic aromatic substitution product 114 in 80% yield. The amino nitrogens were acylated by refluxing in acetic anhydride with two drops of H₂SO₄ for 5 minutes. This afforded 115 in 89% yield. Next, in a two step process, 115 was converted to the bis(N-acetyl) benzobistriazole. This was achieved by first reducing bis(N-acetyl)dinitrobenzene 115 to bis(N-acetyl)diaminobenzene 116 via H₂ reduction with 10% Pd/C in absolute ethanol. Upon complete reduction to the diamine, the crude reaction mixture was filtered to remove the catalyst, HCl was added, and the mixture cooled in an ice bath. To this
was added a solution of NaNO₂ in water, upon which a white solid instantly precipitated out of solution. In this way, 117 was obtained in 53\% yield. This yield was reproducibly less than that reported by Hart.¹³⁹ Deacetylation was achieved in 93\% yield by refluxing 117 in a 1:1 mixture of water and ethanol with a small amount of H₂SO₄ added for 1 hour to give 118. This material was then doubly N-aminated by dissolving 118 in aqueous KOH, heating to 60 °C, and adding dry hydroxylamine-O-sulfonic acid in portions over one hour.¹⁴⁰ The alkaline solution was continuously extracted for one week using a liquid-liquid extractor with ether as the extraction solvent to give a mixture of 1,5-(119), 1,7-(112), and 1,4-(120)-DABT as tan solids in 26\% total yield (Scheme 59).
The yield of DABT was markedly lower than that reported by Hart. Of the three DABT isomers, only 112 and 119 will give bisbenzyne upon reaction with LTA. Thus, as per Hart’s procedure, the mixture was recrystallized from ethanol to give 112 and 119 as tan solids. With these compounds in hand, the preparation of bisbenzyne and subsequent double Diels-Alder reactions with 2,5-diphenylfuran were attempted. Using Hart’s method, DABT and the furan were dissolved in THF and a suspension of LTA in THF
was added dropwise. Evolution of nitrogen gas from the reaction was evident almost immediately. However, contrary to Hart's report of more than 75% yield for this reaction, only trace amounts of 110 were formed, with the vast majority of material recovered being unreacted diphenylfuran.

An alternative approach to bisbenzyne and diendoxide 110 is Wudl's precursor, 121 (Figure 37).121

![Figure 37. Wudl's bisbenzyne precursor 121 (see reference 121).](image)

Compound 121 can form bisbenzyne via TBAF initiated desilylation, followed by elimination of the triflate leaving group. Thus, 121 was synthesized as illustrated in Scheme 60. Hydroquinone was brominated in glacial acetic acid via addition of bromine to give the dibromo compound 122 in 26% yield.142 Since the starting materials were very inexpensive and the reaction was run on a large scale, this yield was satisfactory. Compound 122 was O-protected with trimethylsilyl (TMS) groups via refluxing in dry toluene and pyridine and adding TMSCl. Compound 123 was obtained in 92% yield. The bromines were replaced with TMS groups by refluxing 123 in dry toluene in the presence of sodium metal and dripping in TMSCl. Compound 124 was obtained in this way in 90% yield. Removal of the TMS groups on the oxygens by stirring 124 in 1,4-dioxane with a small amount of 6 M HNO3 at room temperature gave hydroquinone 125

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in 66% isolated yield. Finally, putting triflate groups onto the oxygens via action of triflic anhydride (Tf₂O) in dry pyridine gave 121 in 81% yield (Scheme 60).\textsuperscript{121}

![Scheme 60. Synthesis of 121 (see references 121 and 142).]

With 121 in hand, the preparation of 110 was once again attempted via bisbenzyne addition to diphenylfuran. Using Wudl's conditions, 121 and diphenylfuran were dissolved in dry CH₂Cl₂ and to this solution was added, under N₂, anhydrous TBAF (1M solution in THF). However, it was once again found that only negligible amounts of 110 were formed and the vast majority of the material recovered was unreacted diphenylfuran. A variety of reaction conditions were altered, including varying the solvent, the amount of solvent, the reaction time, using molten diphenylfuran as solvent, and the amount of TBAF. None of these changes improved the yield or conversion. A recent paper reports the formation of completely anhydrous TBAF prepared \textit{in situ} via...
reaction of KF and Bu₄NCN. This method has not been tried by this author but should be attempted in the future.

In the preparation of trisadduct 7, heptacene precursor 8 was prepared via synthesis and reaction of 27 with benzoquinone (Scheme 61).

![Scheme 61. Synthesis of 8 (see references 86 and 95).](image)

Additionally, other isobenzofurans have been synthesized in our laboratory. It was decided that an approach to undecacene 46 analogous to that illustrated in Scheme 61 would be worth exploring. A synthesis analogous to that developed by Cava and modified by our group could be used to prepare a key intermediate, pentacene diquinone 111. We have long desired to prepare this molecule as it would be a valuable intermediate in a variety syntheses. Pyromellitic anhydride was doubly acylated with benzene in the presence of AlCl₃ to give a mixture of 126 and 127 bisketo acids in 98% total yield. This mixture was then reductively cyclized to a mixture of the 128 and 129 bislactones in quantitative yield via action of NaBH₄ in 10% aqueous NaOH at room
temperature. The bislactones were converted to a mixture of 130 and 131 bislactols via addition of phenylmagnesium bromide in dry THF at 0 °C. The resulting mixture was obtained in 88% crude yield (Scheme 62).


Reaction of bislactols 130 and 131 in acetic acid in the presence of benzoquinone, however, did not lead to desired product 111. Reaction in benzene with excess p-TsOH with azeotropic removal of water was also unsuccessful.

A second attempt at preparing 111 involved adapting chemistry reported by Lepage in the 1970s. Lepage reported that when o-bisbenzoyl aromatics were reacted with hydroquinones in the presence of p-TsOH, they underwent acid-catalyzed aldol additions followed by dehydrations to give the aromatized quinones (Scheme 63).
Scheme 63. Lepage's synthesis via aldol reactions of benzoylated aromatics.

A retrosynthetic analysis of 111 showed that it could conceivably be constructed from hydroquinone and 1,2,4,5-tetrabenzoylbenzene 132 (Scheme 64). A synthesis of 132 was undertaken. While there are several reports in the literature that discuss the synthesis of 132, the most direct approach utilizes 85, already synthesized as previously discussed during the preparation of bisisobenzofuran 98.
Scheme 64. Retrosynthetic analysis of 111 using 132 as per Lepage’s protocol (see reference 144).

The double aldol condensation/dehydration of furan dialdehyde 85 and 1,2-dibenzoylethane to give isobenzofuran 133 has been described by Lepage.\textsuperscript{145} His synthesis involves heating the reactants in refluxing piperidine with a small amount of tetramethylammonium hydroxide added. It proved challenging to obtain 133 using this approach, despite the report by Lepage. Using an adaptation of chemistry reported by Kreher and Vogt,\textsuperscript{146} the two reactants were added simultaneously to an ethanolic KOH solution and refluxed for two hours. The resulting bright orange solids were collected by filtration to give isobenzofuran 133 in 77\% yield. This isobenzofuran was then oxidized to give 132 using Lepage’s conditions.\textsuperscript{145} A 1:1 mixture (by volume) of HNO\textsubscript{3} and HOAc was stirred at room temperature and to this solution was added 133 in one portion. Bright orange 133 instantly turned white upon contact with the solution, and the resulting
white solids were stirred at room temperature for 10 minutes. Pouring the crude acidic mixture into a large amount of water, filtering the solids, and drying them gives 132 in 96% yield. This synthesis was scaled up to give multi-gram quantities of 132 (Scheme 65).

With 132 in hand, the synthesis of diquinone 111 using Lepage's conditions was attempted. Compound 132 was boiled in CHCl₃ with an excess of hydroquinone in the presence of freshly dried p-TsOH. A Dean-Stark trap was added for azeotropic removal of water. Upon completion of the reaction, a tan/brown solid was obtained that showed only one spot upon TLC analysis. This spot did not match with either of the starting materials. Additionally, a ¹H NMR spectrum showed signals consistent with the product, including the presence of a singlet at approximately 6.80 ppm. The ¹³C NMR spectrum also showed evidence for the corresponding quinone carbonyl. Neither signal corresponded to those of p-benzoquinone. Puzzling, however, was that 132 was apparently present, at least according to ¹H NMR and ¹³C NMR spectra. The remainder

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of the signals in the NMR spectra were identical to those in the NMR spectra of 132. Without any definitive proof that desired 111 was formed, this approach was suspended.

3.3 Preparation of End-Functionalized Pentacenes and Their [60]Fullerene Adducts

While attempting to prepare acene precursors whose fullerene adducts could be converted into cyclacenes, we also considered a complimentary approach involving an assembly of smaller [60]fullerene-acene adducts. In order to advance this approach, acenes with functionality on the ends would need to be prepared. Dialdehyde functionalities, for example, would allow for an assembly using cyclohexanedione as illustrated in Scheme 66.
Scheme 66. Potential assembly of a cyclacene precursor
Cyclacene structures?

Scheme 66 (continued). Potential assembly of a cyclacene precursor.

Other examples of functional groups on the termini of acenes that could prove useful include acids, esters, aldehydes, anhydrides, and halogenated methyl groups. It
was decided initially to prepare pentacenes, as they are small enough to be prepared and isolated without substantial decomposition, assuming proper handling. Additionally, pentacene derivatives are often sufficiently soluble that they may be fully characterized by $^1$H and $^{13}$C NMR spectroscopies. We chose tetramethylpentacene 134, diphenyltetramethylpentacene 135, and tetramethyltetraphenylpentacene 136 as targets (Figure 38).

Figure 38. Methylated pentacenes to be prepared.

Of these compounds, only 134 was known in the literature.\textsuperscript{147} The preparation of 135 and 136 would thus also give us an opportunity to develop new methods for constructing pentacenes.

The first pentacene to be prepared was tetramethylpentacene 134.\textsuperscript{147} It was decided to synthesize this pentacene via the 6,13-quinone, and to prepare the quinone via the double aldol-dehydration chemistry used in our group to prepare a variety of other acene quinones. Thus, a suitable o-dialdehyde was first prepared. Commercially

122
available starting materials dimethylacetylene dicarboxylate (DMAD) and
dimethylbutadiene were boiled in benzene to afford Diels-Alder adduct 137 in 67% yield
(Scheme 67). Although DDQ aromatization was reported in the literature, this proved to
be a very messy and low-yielding method in our hands.\textsuperscript{148} However, refluxing the adduct
in o-dichlorobenzene with excess 10% Pd/C gave the aromatized product 138 cleanly in
92% yield. This was reduced to diol 139 in 76% yield using LAH in dry THF. Finally, a
Swern oxidation gave dialdehyde 140 in 66% isolated yield. This synthesis was scalable
to give gram quantities of 140. Dissolution of 140 and commercially available 1,4-
cyclohexanedione in ethanol followed by the addition of a small amount of aqueous KOH
gave tetramethylpentacene quinone 141 in 85% yield. One thing to note is the
insolubility of 141. While pentacene quinone 19, which has been prepared numerous
times in our group, has poor solubility, it is still possible to obtain both \(^1\)H and \(^{13}\)C NMR
spectra for it. However, the tetramethyl derivative 141 seems to be completely insoluble.
In fact, we have previously observed reduced solubility upon adding four methyl groups
to the terminal rings of numerous anthracene and pentacene systems, as will be discussed
later.

The quinone was converted directly to the pentacene using a modified Meerwein-
Ponndorf-Verley (MPV) reduction.\textsuperscript{147} The active species was prepared by refluxing
pieces of aluminum foil in dry cyclohexanol with a small amount of HgCl\(_2\) and a drop of
CCl\(_4\) for one day. Quinone 141 was added and the resulting mixture boiled for three
days, at which point it had turned the characteristic deep blue color of a pentacene. After
workup, 134 was obtained in 96% yield. NMR analysis was not a viable option as 134
has poor solubility. Only a \(^1\)H NMR spectrum has been reported in the literature for 134

123
and this was in deuterio o-dichlorobenzene at 120 °C. Thus, our uncharacterized 134 was simply refluxed in o-dichlorobenzene in the presence of three equivalents of [60]fullerene in the dark under N₂ for 24 hours to afford, after purification, [60]fullerene adduct 142 in 22% isolated yield (Scheme 67). Repeated purifications to remove excess [60]fullerene were required and this lowered the isolated yield. The solubility of 142 was sufficient to obtain both ¹H and ¹³C NMR spectra.

Scheme 67. Synthesis of 142.
Quinone 141 was also used in the synthesis of 135. Addition of phenyl lithium to a suspension of 141 in dry toluene at -78 °C gave the diphenylated diol 143, albeit in low yield, 32% (Scheme 68). Again, the four methyl groups severely reduce the solubility of this pentacene species. While NMR spectra for 143 were consistent with its structure, they were not conclusive owing to the poor signal to noise ratio associated with the poorly soluble compound. Diol 143 was aromatized using conditions employed in our group for the conversion of diols to acenes. Thus, compound 143 was boiled in acetic acid in the presence of KI to give dark blue solids. The solids were filtered and collected to give pentacene 135 in 39% yield. This yield is in stark contrast to yields obtained for diphenyl pentacene 23 which are upwards of 85%. The discrepancy is related to the difficulties in manipulating poorly soluble compounds. A $^1$H NMR spectrum was taken for 135, and while the signals are broadened, they are in the correct regions of the spectrum and are consistent with the structure of 135. Compound 135 was subsequently boiled in CS$_2$ in the presence of five equivalents of [60]fullerene to afford bis[60]fullerene adduct 144 in 44% isolated yield. Once again, multiple purifications via flash column chromatography were required to remove excess [60]fullerene (Scheme 68).
Scheme 68. Synthesis of 144.

As with 6, bisadduct 144 was quite soluble, enabling facile acquisition of $^1$H and $^{13}$C NMR spectra. These spectra confirm the formation of $C_{2v}$ cis-144 rather than the corresponding $C_{2h}$ trans isomer. Thus, the 6,13-diphenyl substituents give rise to 5 $^1$H NMR signals, indicative of slowly rotating (on the NMR time scale) phenyl groups in the
C$_{2v}$ symmetric 144. The corresponding C$_{2h}$ symmetric trans structure would show only 3
$^1$H NMR signals arising from the phenyl substituents, irrespective of the rate of rotation.

The final pentacene to be prepared was 136. We had previously prepared
tetraphenylpentacene in our group via construction of quinone 25 and subsequent
conversion to the acene.\textsuperscript{149} Thus, it was decided to approach the synthesis of 136 via
quinone 145 according to Scheme 69.

Compound 25 was synthesized in our group by reacting commercially available
diphenylisobenzofuran and p-benzoquinone and obtaining the double Diels-Alder adduct,
which was then dehydratively aromatized to give the pentacene.\textsuperscript{149} We decided to use an
analogous approach using dimethyl diphenylisobenzofuran 146. The synthesis of 146 was
achieved using two different approaches. The first approach mirrored work reported by
Cava and VanMeter\textsuperscript{125} and modified by our group.\textsuperscript{96} Thus, dimethyl butadiene and
maleic anhydride were refluxed in benzene to give Diels-Alder adduct 147 in 99\% yield
(Scheme 70). This was then aromatized by refluxing in o-dichlorobenzene with excess
10\% Pd/C to give 148 in 68\% yield. Friedel-Crafts acylation using benzene and AlCl$_3$ as
catalyst gave keto-acid 149 in 98\% yield. This was reductively cyclized to lactone 150 in
97\% yield by stirring in 10\% aqueous NaOH with excess NaBH$_4$. Finally, lactone 150
was converted to lactol 151 in 82\% yield by addition of phenylmagnesium bromide in dry
THF (Scheme 70).
When lactol 151 was boiled in benzene in the presence of \( p \)-benzoquinone and excess \( p \)-TsOH using a Dean-Stark trap, quinone 145 was prepared, albeit in yields ranging from 16 to 50% with no reproducibility (Scheme 69).

**Scheme 69.** One-pot synthesis of 145.
Scheme 70. Synthesis of lactol 151.

The reaction is striking given the number of steps that occur in one pot. Successively, 151 is dehydrated to isobenzofuran 146, two molecules of 146 are undergo successive Diels-Alder cyclization with p-benzoquinone, and the resulting adduct is dehydratively aromatized. Although intriguing, it was nonetheless desired to develop a higher yielding, more reproducible synthesis of 145. Thus, a direct preparation of 146 was attempted.

The literature reveals that 146 has been prepared from an acid-catalyzed dehydration of 152 (Scheme 71).\textsuperscript{150}
Compound 152 was synthesized via Diels-Alder addition of dimethylbutadiene to dibenzoylethylene 153, which was itself synthesized\textsuperscript{151} in two steps (Scheme 72). Thus, commercially available 1,2-dibenzoylethylene was brominated in acetic acid to give dibromide 154 in 69\% yield. Boiling 154 in acetone with two equivalents of triethylamine afforded, after two recrystallizations, 153 in 76\% yield. The literature\textsuperscript{151} indicates that the Diels-Alder reaction between dimethylbutadiene and 153 should be performed with care as heating for too long or at too high a temperature or in too concentrated a solution could result in unwanted side products and loss of yield. The literature reaction was reportedly performed in a mixture of methanol and benzene as it was reported that refluxing in benzene alone would lead to multiple products. In this author’s hands, just the opposite result was obtained. Thus, heating in methanol and benzene gave a very complex product mixture with trace amounts of what looked like 152 present in the \textsuperscript{1}H NMR spectrum. However, if the reaction was carried out in boiling benzene for 14-16 hours, 152 was prepared cleanly in 89\% yield. Refluxing 152 in benzene with dry \textit{p}-TsOH for 90 minutes gave a mixture of 146 and the hydrolyzed by-product dimethylidibenzoylbenzene. Recrystallization from absolute ethanol gave 146 pure in 53\% yield as a bright yellow powder that exhibited an intense blue fluorescence in solution. Compound 146 was then refluxed in ethanol with \textit{p}-benzoquinone to give
endo,exo-diendoxide 155 in 97% yield. This reaction was very clean and afforded one diastereomer of 155 as the sole product. Dehydrative aromatization by refluxing in benzene with p-TsOH through a Dean-Stark trap gave 145 in 47% yield (Scheme 72).

Scheme 72. Improved synthesis of 145.
Compound 145 was reduced to dihydropentacene 156 by refluxing it in a mixture of HI (47%) and acetic acid for five days in the dark under N₂. In this way, compound 156 was obtained in 67% yield. From here, all attempts at preparing, isolating, and characterizing pentacene 136 failed. These included oxidation with DDQ, 10% Pd/C, S₈/triglyme, and reduction of quinone 145 to a diol and subsequent reaction with KI/HOAc. However, when 156 was boiled in toluene in the presence of two equivalents of DDQ and three equivalents of [60]fullerene, pentacene 136 was prepared and trapped in situ to give [60]fullerene adduct 157 in 10% isolated yield (Scheme 73). Repeated purifications were needed to remove excess [60]fullerene and these steps adversely impacted the isolated yield.

Scheme 73. Synthesis of 157.
With all three pentacenes prepared and their fullerene adducts synthesized, we sought to further functionalize the pentacene backbones to use them in a cyclacene assembly. We decided first to try to functionalize the pentacene quinones prior to conversion to the pentacenes and reaction with [60]fullerene. In particular, we wanted to place aldehydes at the methyl sites. Our first approach involved halogenation of the methyl groups. The resulting halides could be displaced by hydroxide, which could then be oxidized to aldehydes. Finally, protection of the aldehydes would allow us to convert the quinones to pentacenes. Deprotection could then easily be effected after either reduction of the pentacene to its “protected” form, or on the fullerene adduct itself.

Unfortunately, halogenation of the terminal methyls was never achieved. Various conditions, involving NCS, NBS, and Br₂ as halogenating agents failed to give us the desired mono(halomethyl) groups on the end of the pentacenes. Instead, complex mixtures of various halogenated compounds, too complex to analyze or separate, were obtained. We also sought to oxidize the terminal methyl groups directly. A variety of conditions were tried, but none with success. Brute-force KMnO₄ oxidations in refluxing CHCl₃ and HOAc were both tried and both gave an insoluble oil. Dimethyl dioxirane and “purple benzene” were also tried but to no avail. Additionally, considering that it is known in the literature that [60]fullerene sensitizes singlet oxygen formation, some ^1O chemistry was attempted. Bisadduct 144 was dissolved in benzene and stirred. Air was bubbled through and the flask was irradiated for 1 month. The reaction was followed by TLC and it was found that no reaction was occurring. All of these failures may be due to the poor solubility or insolubility of the methylated acene compounds. With these
disappointing results in hand, we decided instead to build in the desired functionality earlier in the synthesis.

Since aldehydes are the most desired functional group to be placed at the ends of acenes, we decided to include protected alcohols, specifically benzyl protected alcohols, in the acene synthesis. Thus, the synthesis of a phthalic dialdehyde with bis(benzyloxymethyl) groups in the 4,5 positions was attempted (compound 163, Scheme 74). Rebek reported\textsuperscript{152} the preparation of the corresponding diol. Thus Rebek’s synthesis was utilized to prepare the diol, which could then be oxidized to the dialdehyde using Swern oxidation conditions worked out in our lab over the last few years.

The synthesis began with reduction of commercially available diethyl-3,4-furan dicarboxylate with LAH in refluxing ether overnight in 50% yield (Scheme 74). The resulting diol 158 was then benzylated via deprotonation by NaH in DMF, followed by addition of benzyl bromide, to give 159 in 73% yield. Compound 159 was then reacted in a Diels-Alder fashion with commercially available DMAD by heating the two reagents neat in an oil bath. In this way, Diels-Alder adduct 160 was obtained in 91% yield. Since the resulting endoxide is tetrasubstituted, our usual acid-mediated dehydration conditions would not work to aromatize 160. Instead of a dehydration, we needed a deoxygenation. Rebek reported\textsuperscript{152} a reaction utilizing a Ti\textsuperscript{0} catalyst which is preformed in the reaction. However, Rebek’s conditions were not giving the desired product in good yield. It was found, however, that Wong had reported\textsuperscript{153} alternative conditions for a similar deoxygenation reaction using the same preformed Ti\textsuperscript{0} catalyst. Wong’s conditions differed mainly in reaction time and the addition of triethylamine. Using Wong’s conditions afforded aromatized 161 cleanly and reproducibly in 74% yield.
Compound 161 was then reduced from the diester to the diol using LAH in refluxing THF for three hours to give 162 in 48% yield. Compound 162 was finally oxidized using a Swern oxidation to give dialdehyde 163 in 64% yield (Scheme 74).

Scheme 74. Synthesis of dialdehyde 163 (see references 152 and 153).

With 163 in hand, we planned on utilizing the tandem aldol-dehydration chemistry we have used in our group to prepare acene quinone systems. Thus, the dialdehyde and commercially available 1,4-cyclohexanedione were added to 95% ethanol and stirred. To this partially dissolved mixture was added a small amount of aqueous KOH. As usual during these reactions, the mixture instantly turned black upon addition of the aqueous KOH. Over the course of the next minute or two, the solution turned a
brownish/yellow color as the solid quinone began to precipitate out of solution. Simple vacuum filtration and washing with water afforded quinone 164 (Scheme 75).

\[
\begin{align*}
&\text{OBn} & \text{CHO} \\
&\text{OBn} & \text{CHO} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn} \\
&\text{OBn} & \text{OBn}
\end{align*}
\]

163

\[
\begin{align*}
\text{EtOH} & \text{KOH} \\
\rightarrow
\end{align*}
\]

164

Scheme 75. Synthesis of quinone 164.

With 164 in hand, we intended to use our standard phenylation conditions to introduce phenyl substituents. However, repeated attempts at adding phenyl lithium to a solution of the quinone in dry toluene at -78 °C did not produce the diphenyl diol. When the reaction was repeated in dry THF, however, the diphenyl diol was obtained.\textsuperscript{154} Another member of the Miller group was then able to aromatize the diol to prepare the pentacene, which in turn gave the cis-bis[60]fullerene adduct when reacted with [60]fullerene.\textsuperscript{154} Deprotection with TMSI gave the iodomethyl species, and studies are currently ongoing to prepare cyclacene precursors from this compound.\textsuperscript{154}

Simultaneously, an alternative approach toward an aldehyde decorated acene was studied. This approach uses a functionalized isobenzofuran as illustrated in Scheme 76.
In order to pursue this route, isobenzofuran 165 was first prepared. There is only one reported synthesis of 165 in the literature, spanning two short papers by Lepage.\textsuperscript{155,156} It was decided to adopt this synthetic route in order to prepare 165. Lepage reported the preparation of 165 as arising from reduction of 167. Compound 167 could be prepared by adapting a synthesis of a related compound from a report by Krapcho\textsuperscript{157} in 1993. Thus, the preparation of 165 was attempted (Scheme 77).

Commercially available diethylfuran-3,4-dicarboxylate was hydrolyzed to the diacid 168 by NaOH in a MeOH/H\textsubscript{2}O mixture.\textsuperscript{157} Diacid 168 was then converted to diacid chloride 169 by refluxing with SOCl\textsubscript{2} in toluene.\textsuperscript{157} Compound 169 was immediately reacted with commercially available diphenyl furan in a Freidel-Crafts acylation reaction in the presence of AlCl\textsubscript{3} to give 167 in 78% yield. It was found that upon simply adding acetone to the crude brown residue, bright yellow 167 precipitates and can be filtered and washed to give pure compound. Compound 167 was then reduced in refluxing ethanol with KBH\textsubscript{4} according to the literature\textsuperscript{155,156} to give intermediate diol 170. The Lepage synthesis stated that a simple acid quench of the excess reducing agent would also dehydrate diol 170 to give isobenzofuran 165. Repeated attempts at this
reaction failed. However, the author of this dissertation discovered that if 10% HCl in
HOAc was added to the reaction mixture when it was still quite warm, conversion to 165
took place almost instantly. This could be observed by watching the dark red reaction
mixture turn bright yellow with an intense blue fluorescence almost immediately upon
addition of HCl/HOAc mixture. In this way, 165 was finally prepared (Scheme 77).

Scheme 77. Synthesis of isobenzofuran 165 (see references 155, 156, and 157).
With 165 in hand, the Diels-Alder reaction with benzoquinone, as outlined in Scheme 76, was attempted. However, upon repeated attempts at this reaction, no Diels-Alder adduct was observed to form. When 165 was refluxed in ethanol with benzoquinone, standard conditions for isobenzofuran addition to benzoquinone, no reaction was observed. Additionally, changing the temperature (by changing solvent), length of reaction time, and addition of Brønsted or Lewis acid catalysts had no effect. This was not entirely surprising, as it was expected that the two aldehyde groups would partially deactivate the isobenzofuran ring system. However, it was thought that this could be circumvented in some way. A closer look at the literature\textsuperscript{155,156} showed that the preparation of 165 was not reported for use as a Diels-Alder diene. In fact, the authors were more interested in further functionalizing the aldehyde groups and then opening up the isofuran moiety.

Since the aldehyde groups deactivate the isobenzofuran ring system via a resonance withdrawal of electron density, it was decided to convert the aldehyde groups into less offending acetals. Conversion of 165 to 171 would be ideal since the cyclic acetals could only weakly deactivate the isobenzofuran via inductive, not resonance, effects (Scheme 78).

![Scheme 78. Deactivation of aldehydes in 165 to give 171.](image)
Although acetal formation was observed, the crude product mixture invariably contained starting material 165, mono-protected product, and desired product 171. Optimization of this reaction would possibly aid in subsequent Diels-Alder chemistry.

In addition to a pentacene derived from 164, heptacene 172 is also desired (Scheme 79), as the resulting phenyl substituted heptacene would add three molecules of [60]fullerene and would be a larger cyclacene “building block” than the [60]fullerene bisadduct that would be obtained from a pentacene.

**Scheme 79.** Retrosynthetic analysis for formation of functionalized heptacene 172.

Dialdehyde 163 is a key intermediate in our proposed synthesis of 172. However, in addition, we also need to prepare bis-diketone 173 (Figure 39).

**Figure 39.** Bis-diketone 173.
We envisioned 173 to form via a simple reduction of diquinone 70 (Scheme 80).

![Scheme 80. Reduction of 70 to 173.](image)

Even though 70 has been reported in the literature,\textsuperscript{114} its synthesis is rather long and complicated. Thus, we set out to devise an alternate synthesis that would afford 70 easily and in large quantities. A retrosynthetic analysis showed that if we could prepare sultine 174 (Figure 40), it could be reacted in a Diels-Alder fashion with benzoquinone to give a molecule that is only a few steps removed from 70.

![Figure 40. Sultine 174.](image)

Thus, the synthesis of sultine 174 was undertaken according to the method of Kotha and Ghosh.\textsuperscript{158} Commercially available 2,3-dimethylphenol was O-methylated using dimethyl sulfate in aqueous sodium hydroxide to give 175 (Scheme 81).\textsuperscript{159} Compound 175 was then brominated \textit{para} to the methoxy group to give 176.\textsuperscript{159} Nucleophilic aromatic substitution in freshly prepared sodium methoxide in the presence of freshly purified Cul and DMF gave 2,3-dimethyl-\textit{p}-dimethoxy benzene 177 very
Compound 177 was brominated using NBS and benzoyl peroxide (as radical initiator) in refluxing benzene to give 178. Finally, 178 was converted cleanly and easily to sultine 174 by stirring in DMF with Rongalite and tetrabutylammonium bromide (as phase-transfer catalyst). In this way, sultine 174 was prepared from cheap, readily available materials on a multi-gram scale (Scheme 81).

Scheme 81. Synthesis of sultine 174 (see references 158, 159, and 160).

Sultine 174 was boiled in toluene in the presence of benzoquinone to give a mixture of Diels-Alder adduct 179 and the aromatized Diels-Alder adduct 180 (Scheme 82). Previous work in our group focused on a tedious attempt at separating the two compounds which always resulted in loss of material on the silica column (owing to the fact it barely moves on silica) and the resulting partial aromatization of 179 to 180. In this author’s case, the mixture was simply refluxed in benzene in the presence of excess DDQ to convert everything in the mixture to 180. Compound 180 was then stirred at
room temperature in a 1:1 (v/v) mixture of water and acetonitrile in the presence of excess CAN to give, after workup, diquinone 70 (Scheme 82) in 86% yield.

Scheme 82. Synthesis of 70 from 174.

In this way, 70 was prepared and collected without purification steps and in gram quantities. Next, reduction of the two conjugated alkenes in 70 was needed in order to produce 173. Applying Lepage’s or Miller’s conditions for reducing alkenes (as utilized in the preparation of 102), 70 was heated in a mixture of HOAc and HCl in the presence of SnCl2. However, initial results showed incomplete reduction of 70. Longer reaction times seemed to hasten decomposition of 70. Concurrently, reduction of 70 was attempted using H2 gas in the presence of 10% Pd/C. While it seemed to be a much cleaner reduction, it too produced a mixture of starting material and what appeared to be desired product 173. Since these incomplete reductions were obtained using the “balloon” method with H2 at atmospheric pressure, it was postulated that this reduction would proceed faster and more efficiently under increased pressure of H2 in a stainless
steel bomb. This is something that should be tried in the future in order to prepare and eventually.

3.4 Preparation of a Flexible Bis[60]Fullerene Adduct for Dynamic NMR Studies

Perhaps the most striking result of our group's work on the addition of [60]fullerene to large acenes is the observation that the cis-[60]fullerene adducts are obtained exclusively. The syn-diastereoselective addition of [60]fullerenes is attributed to favorable \( \pi-\pi \) stacking interactions between adjacent [60]fullerenes, which greatly stabilize the resulting structure. According to modeling and an X-ray crystal structure of 6, adjacent fullerenes are approximately 3.20 Å apart at the points of closest contact, an ideal distance for \( \pi-\pi \) stacking between [60]fullerenes. It was postulated by Miller and Mack that the addition of the first fullerene occurs readily as a standard Diels-Alder reaction, which is also readily reversible. Subsequent fullerenes can add either to the same (syn) face of the acene or to the opposite (anti) face. However, addition to the syn face results in favorable \( \pi-\pi \) interactions which stabilize the structure significantly and thereby retard retro Diels-Alder reaction.

Briggs and Miller reported the synthesis and characterization of two bis[60]fullerene adducts of tetraphenyl heptacene quinone 8. This quinone can be viewed as having two isolated anthracene moieties on either side of the quinone ring. Anthracene is the smallest acene that will undergo Diels-Alder cycloaddition with [60]fullerene. Thus, it was not surprising that [60]fullerene added to each side of 8. What was striking, however, and what lent further credence to the hypothesis that the \( \pi-\pi \)
stacking between [60]fullerenes is important is that both cis and trans bis[60]fullerene adducts of 8 form with virtually no preference. The [60]fullerene moieties in these adducts are too far removed from one another (~6 Å) to enjoy π-π stacking interactions. Additionally, and perhaps most exciting, was the fact that the two [60]fullerene adducts of 8 are thermally unstable. It was found that by simply heating these compounds slightly above room temperature to remove CS₂ solvent, the products underwent a retro Diels-Alder reaction to give [60]fullerene and quinone 8. By contrast, all cis-bis[60]fullerene adducts known in which the [60]fullerene moieties are properly spaced to enjoy π-π stacking interactions are thermally stable to at least 100 °C.

Given that π-π stacking interactions are key to the observed syn-diastereoselectivity in reactions of [60]fullerene and large acenes, we attempted to quantify the strength of this interaction. Müllen reported¹⁶⁴ in 1993 the preparation of a Diels-Alder [60]fullerene adduct (181) of o-quinodimethane arising from iodine-induced debromination of α,α'-dibromo-o-xylene (Scheme 83).

```
  \[
  \begin{array}{c}
  \text{Br} \\
  \text{Br} \\
  \text{Kl} \\
  \text{C}_{60} \\
  \text{181}
  \end{array}
  \]
```

Scheme 83. Müllen's synthesis of 181 (see reference 164).
Almost as an aside, Mullen briefly described the preparation of bis[60]fullerene adduct 182 formed from bis-o-quinodimethane formation and subsequent reaction with two equivalents of [60]fullerene (Scheme 84).

It should be noted that the bis-o-quinodimethane/diradical depicted in Scheme 84 almost certainly does not form. More likely, this reaction involves stepwise formation of separate o-quinodimethanes on each side of the starting material, followed in each case by addition to [60]fullerene. This diradical intermediate is only illustrative. Most importantly, however, Mullen demonstrated that bis[60]fullerene adducts of bis-o-quinodimethanes can indeed be prepared. Mullen’s synthesis of 182 was repeated in our group and by the author of this dissertation. With this proof of concept in place, and noticing that 182 maps directly onto the bis[60]fullerene adducts of pentacene, it was decided to prepare an analogous bis[60]fullerene adduct that maps directly onto the bis[60]fullerene adduct of 6,13-diphenylpentacene 6. It was postulated that 183, once prepared, would be conformationally mobile. That is, the methylene groups attaching the
fullerene to the benzene ring could invert to give an equilibrium mixture of cis- and trans- conformations. Thus, it was decided to prepare 183 to determine if one conformation (cis or trans) was preferred over the other and if so, a way to potentially measure this preference (Figure 41).

![Image of 183](image)

**Figure 41.** Flexible bis[60]fullerene adduct 183.

In order to prepare the flexible bisadduct 183, tetrakis(bromomethyl)terphenyl 184 was first prepared (Scheme 85). This was synthesized by brominating commercially available duroene in the open positions on the benzene ring to give p-dibromoduroene 185. This was then reacted with commercially available phenyl boronic acid in a Suzuki coupling reaction with Pd(PPh₃)₄ as catalyst to give tetramethyl terphenyl 186.₁⁶⁵ After much trial and error trying to brominate the methyl groups, it was found that simple NBS bromination using 8 equivalents of NBS gave 184 cleanly (Scheme 85).₁⁶⁶
With 184 in hand, the synthesis of 183 was next attempted. This was achieved by boiling 184 in toluene in the presence of excess [60]fullerene with KI and 18-crown-6 (as phase transfer catalyst). In theory, this should produce the bis[60]fullerene adduct as an equilibrium mixture of cis- and trans- conformations (Scheme 86).
Scheme 86. Synthesis of 183 in possible equilibrium.

An equilibrium mixture of conformations, however, was not observed. Instead, $^1$H NMR spectra indicated the sole presence of the cis- conformer. This was evidenced by the $^1$H NMR spectrum (Figure 42) which shows five $^1$H signals for the five protons of the phenyl substituents plus an AB quartet for the methylene (benzylic) protons. This can only be rationalized by considering a cis- conformer of 183 that is slow to invert on the NMR timescale. Compound 183 was very difficult to purify as it co-eluted with [60]fullerene under all conditions tested. Thus, it was impossible after numerous columns to obtain 183 in a completely pure state.
The corresponding *trans*-conformer of 183 has $C_{2v}$ symmetry and would give rise to only three aromatic signals due to the phenyl substituents. The presence of an AB quartet for the methylene protons further confirms that 183 is indeed "locked" into one conformation, at least on the NMR timescale. If a time-averaged structure were present, the methylene protons would give rise to a singlet. Since the molecule is "locked" into a *cis*-conformation, the methylene protons are diastereotopic, and thus show an AB pattern.

With this result in hand, a VT NMR study of the purified compound should be attempted. At elevated temperatures, it should be possible to interconvert *cis*- and *trans*-
In this way, information about the energetics of interconversion, and consequently the strength of the [60]fullerene-[60]fullerene π-π stacking interaction should be obtained. Since it was impossible at the time of this writing to obtain 183 free of [60]fullerene and other impurities due to rather poor solubility and the fact that it nearly co-elutes with [60]fullerene on a chromatography column, this was not attempted.
CHAPTER 4

CONCLUSIONS AND FUTURE DIRECTIONS

It has been shown that HI and HOAc will reduce acenes and acene quinones cleanly to give hydrogenated acenes. In the case of acenes smaller than five rings, reduction occurs solely on the internal rings, leaving the terminal rings intact. For pentacenes the internal rings are non-equivalent but reduction is nonetheless selective, generally producing hydrogenated acenes with either the center ring or alternating internal rings reduced. However, when phenyl substituted acenes with five or more rings are reduced, the reactions proceed in a highly regioselective fashion leaving the internal terphenyl moieties intact. In all cases, the hydrogenated acenes are more soluble than the acene quinones or acenes. The hydrogenated acenes are also stable under ambient conditions and they can be converted to the corresponding acenes via simple dehydrogenations using DDQ, Pd/C, or even elemental sulfur. In this way, a method to “protect” acenes as hydrogenated species has been developed.

The synthesis of large acenes, namely nine and eleven ring acenes, was studied. After much effort, two tetraaryl nonacene triquinones, 99 and 108, were prepared.
Attempts to reduce the quinone functionalities in order to then access the acenes for reactions with [60]fullerene proved problematic and ultimately unsuccessful. Alternative methods of reduction should be attempted in the future. One reduction that should be attempted is a dissolving metal reduction, also known as a Birch reduction. Additionally, a recent report in the literature demonstrated BH$_3$THF as an effective reductant for acene quinones. This should also be attempted on 99 and 108.

Also for the future, compound 47 should be revisited. It is believed that the
phenyl substituents are negatively impacting the CAN oxidation of 9,10-diphenyl-
1,4,5,8-tetramethoxyanthracene, possibly via steric repulsion. A way to test this
hypothesis would be to functionalize the phenyl groups in such a way that they would be
tethered to the adjacent oxygens to keep them in the same plane as the anthracene
backbone (see model compound above). This approach could also be tested on 79, which
likely suffers from the same effect. An alternative approach would be to prepare a 9,10-
dichloro or 9,10-dibromo 1,4,5,8-tetramethoxyanthracene followed by a CAN oxidation
to the corresponding diquinone. If successful, the phenyl groups could be added last via
a Pd-mediated coupling reaction. Still other approaches to 47 that could be tested involve
the intermediacy of the parent diquinone 70. Subjecting 70 to either halogenation or
Grignard conditions could prove useful. Selective halogenation in the 9,10 positions
could be followed by a Pd-mediated coupling reaction to afford 47 in two steps from 70.
A selective Grignard (conjugate) addition across the 9,10 positions would provide 47 in
one step from 70. Unlike organolithiums, Grignard reagents are known to occasionally
undergo conjugate additions across acene quinones. Either of these approaches, if

Model compound for future study (right).
successful, would be welcome as an easy, high-yielding synthesis of 70 has been described in this dissertation.

The synthesis of functionalized acenes for use as cyclacene building blocks was studied. Three methylated pentacenes and their corresponding [60]fullerene adducts were synthesized. Attempts to functionalize the methyl groups on the end of the pentacenes proved unsuccessful, most likely owing to the poor solubility of the methylated systems. An alternate approach at building functionality into the acenes at an earlier stage was also undertaken. A pentacene quinone with (benzyloxy)methyl groups (164) was prepared and this work was carried on further by other members of the group. Additionally, a diphenylisobenzofuran containing aldehyde groups (165) was prepared.

Attempts to react this directly with benzoquinone failed. Preparation of a protected analogue of this isobenzofuran was moderately successful, although optimization of the protection was not achieved. One way in which this problem may be circumvented would be to start with compound 140, which is dimethyl-o-phthalaldehyde. The two
aldehydes could be protected with ethylene glycol, and then the methyl groups brominated to give the bis(bromomethyl) compound. This material could then be converted to o-quinodimethane via action of iodide and reacted \textit{in situ} with the desired dienophile, thus eliminating the need to work directly with a deactivating, isofuran system. Work is currently underway in the Miller group on this route.
CHAPTER 5

EXPERIMENTAL SECTION

5.1 General Methods

$^1$H NMR Spectra: $^1$H NMR spectra were obtained on either a Bruker AM 360 FT-NMR operating at 360.134 MHz, 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 ($\delta_H$) values are reported in parts per million (ppm) relative to (CH$_3$)$_4$Si (TMS) unless otherwise noted.

$^{13}$C NMR Spectra: $^{13}$C NMR spectra were obtained on either a Bruker AM 360 FT-NMR operating at 90.556 MHz, 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 ($\delta_C$) values are reported in parts per million (ppm) relative to (CH$_3$)$_4$Si (TMS) unless otherwise noted.

5.2 Solvents

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

Acetic Acid (CH$_3$CO$_2$H) was obtained from VWR Chemical Co.

Acetic Anhydride ((CH$_3$CH$_2$CO)$_2$O) was obtained from Fisher Scientific Co.

Acetone (reagent grade) was obtained from Pharmco.

Benzene (C$_6$H$_6$) was obtained from EM Science.
Carbon Disulfide (CS$_2$) was obtained from EM Science.

Carbon Tetrachloride (CCl$_4$) was obtained from Aldrich Chemical Co.

Chloroform (CHCl$_3$) 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 (CH$_2$Cl$_2$) was obtained from Fisher Scientific Co.

Diethyl Ether ((CH$_3$CH$_2$)$_2$O) was obtained from Pharmco.

N,N-Dimethylformamide (CH$_3$CON(CH$_3$)$_2$) was obtained from Fisher Scientific Co. and obtained dry and oxygen-free from the solvent purification system.

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

1,4-Dioxane ((CH$_2$CH$_2$)$_2$O$_2$) was obtained from Aldrich Chemical Co.

Ethanol (anhydrous) was obtained from Pharmco.

Ethanol (95%) was obtained from Pharmco.

Ethyl Acetate (CH$_3$CO$_2$CH$_2$CH$_3$) was obtained from Fisher Scientific Co.

Heptanes were obtained from Fisher Scientific Co.

Hexanes were obtained from Fisher Scientific Co.

Methanol (CH$_3$OH) was obtained from Pharmco.

$N$-Methylpyrrolidinone (NMP) was obtained from Aldrich Chemical Co.

Nitrobenzene (PhNO$_2$) was obtained from Fisher Scientific Co.

Pyridine (C$_5$H$_5$N) was obtained from Aldrich Chemical Co. and dried over molecular sieves.

1,1,2,2-Tetrachloroethane (Cl$_2$CHCHCl$_2$) was obtained from Aldrich Chemical Co. and dried over molecular sieves.

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Tetrahydrofuran (THF) was obtained from Fisher Scientific Co. and obtained dry and oxygen-free from the solvent purification system.

Toluene (PhCH₃) was obtained from Fisher Scientific Co. and obtained dry and oxygen-free from the solvent purification system.

Triglyme (CH₃O(CH₂CH₂O)₂CH₃) was obtained from Fisher Scientific Co.

Xylenes were obtained from Fisher Scientific Co.

5.3 Column Chromatography

Sand was obtained from Fisher Scientific Co.

Silica Gel (230-400 mesh) was obtained from Natland International Co.

5.4 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.

9,10-Anthracene quinone (C₁₄H₈O₂) was obtained from Aldrich Chemical Co.

1,4-Benzoquinone (C₈H₄O₂) 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.

*tert*-Butylbenzene (C₆H₅C₄H₉) was obtained from Alfa Aesar Chemical Co.

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

Copper (Cu°) was obtained from Aldrich Chemical Co.

Copper (II) cyanide (CuCN) was obtained from Aldrich Chemical Co.

18-Crown-6 was obtained from Aldrich Chemical Co.

1,4-Cyclohexanedione (C₆H₈O₂) was obtained from Aldrich Chemical Co.

1,8-Diamino-4,5-dihydroxyanthracene-9,10-quinone (C₁₄H₁₀O₄N₂) was obtained from Aldrich Chemical Co.

1,2-Dibenzoylethane (C₆H₅COCH₂CH₂COC₆H₅) was obtained from Alfa Aesar Chemical Co.

1,2-Dibenzoylethylene (C₆H₅COCHCHOC₆H₅) was obtained from Aldrich Chemical Co.

1,3-Dichlorobenzene (MDCB) was obtained from Aldrich Chemical Co.

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

2,3-Dicyano-1,4-benzoquinone (C₂H₄O₂N₂) was obtained from Aldrich Chemical Co.

Diethyl-3,4-furandicarboxylate (C₁₀H₁₂O₃) was obtained from Aldrich Chemical Co.

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

1,8-Dihydroxy-9,10-anthracene quinone (C₁₄H₉O₄) was obtained from Aldrich Chemical Co.

1,4-Dihydroxybut-2-yne (C₄H₆O₂) was obtained from Aldrich Chemical Co.
Diisobutylaluminum hydride (DIBAL-H) was obtained from Aldrich Chemical Co.

2,5-Dimethoxymethylenetetrahydrofuran (C₆H₁₂O₃) was obtained from Aldrich Chemical Co.

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

2,3-Dimethylbutadiene (C₆H₁₀) was obtained from Alfa Aesar Chemical Co.

9,10-Diphenylanthracene (C₂₆H₁₈) was obtained from Aldrich Chemical Co.

2,5-Diphenyl-1,4-benzoquinone (C₁₈H₁₂O₂) was obtained from Lancaster Chemical Co.

trans,trans-1,4-Diphenylbutadiene (C₁₆H₁₄) was obtained from Acros Organics Co.

2,5-Diphenylfuran (C₁₆H₁₂O) was obtained from Alfa Aesar Chemical Co.

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

6,13-Diphenylpentacene 23fC₄H₂₄ was prepared according to the literature.⁸⁴

Disperse Blue 1 was obtained from Acros Organics Co.

Durene (C₁₀H₁₄) was obtained from Aldrich Chemical Co.

Ethyl benzoylacetate (C₁₁H₁₂O₃) was obtained from Alfa Aesar Chemical Co.

Ethylene Glycol (HOCH₂CH₂OH) was obtained from Fisher Scientific Co.

[60] Fullerene (C₆₀) was obtained from Merck Chemical Co.

Fumaryl Chloride (C₄H₂O₂Cl₂) was obtained from Alfa Aesar Chemical Co.

Hydriodic Acid (HI) was obtained from Aldrich Chemical Co.

Hydrochloric acid (HCl) was obtained from EM Science.

Hydroquinone (C₆H₆O₂) was obtained from Fisher Scientific Co.

Hydroxylamine-O-sulfonic acid was obtained from Aldrich Chemical Co.

Iodine (I₂) was obtained from Aldrich Chemical Co.

Iodobenzene (C₆H₅I) was obtained from Aldrich Chemical Co.

Iron (Fe⁹) was obtained from Aldrich Chemical Co.
Lithium aluminum hydride (LiAlH₄) was obtained from Aldrich Chemical Co.

Magnesium 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.

Oxalyl chloride (C₂O₂Cl₂) was obtained from Lancaster Chemical Co.

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

6,13-Pentacenequinone 19 (C₂₂H₁₂O₂) was prepared according to the literature.⁶⁰

Phenyllithium (C₆H₅Li) was obtained from Aldrich Chemical Co.

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

o-Phthalaldehyde (C₆H₅(CHO)₂) was obtained from Acros Organics Co.

Piperidine (C₅H₁₁N) 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 iodate (KIO₃) was obtained from Aldrich Chemical Co.

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

Pyromellitic anhydride was obtained from Aldrich Chemical Co.

Quinizarin (C₁₄H₈O₄) was obtained from Aldrich Chemical Co.

Rongalite (HOCH₂SO₂Na₂H₂O) 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 cyanide (NaCN) was obtained from Aldrich Chemical Co.

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

Sodium hydride (NaH) was obtained from Aldrich Chemical 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.

Sulfur (S₈) was obtained from Aldrich Chemical Co.

Sulfuric acid (H₂SO₄) was obtained from EM Science.

1,2,4,5-Tetrabromobenzene (C₆H₄Br₄) was obtained from Aldrich Chemical Co.

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

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

5,7,12,14-Tetraphenylpentacene-6,13-quinone 25 (C₄₆H₂₈O₂) was prepared according to the literature.⁹⁴

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.

Triethylamine ((CH₃CH₂)₃N) was obtained from Aldrich Chemical Co.

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

Trimethylsilyl chloride (TMSCl) was obtained from Aldrich Chemical Co.
Trimethylsilyltrifluoromethane sulfonate (TMSOTf) was obtained from Alfa Aesar Chemical Co.

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

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

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

1,4,5,8-Tetraphenyl-9,10-anthraquinone (18). 1.00g (4.85 mmol) of trans, trans-1,4-diphenylbutadiene and 0.25g (2.31 mmol) of 1,4-benzoquinone were placed in a round bottom flask with 10 mL of nitrobenzene. The resulting suspension was refluxed for 6 hours and allowed to cool to room temperature overnight. The resulting solids were filtered, washed with acetic acid, and dried to give 0.30g (25% yield) of quinone 18 as light brown solids, mp: 346-350°C (lit: 355 °C). \(^1\)H NMR (CDCl\(_3\)) δ 7.30-7.34 (m, 20H), 7.52 (s, 4H).

Reduction of 18 to give 1,4,5,8-Tetraphenyl-9,10-dihydroanthracene. 0.1 lg (.215 mmol) of quinone 18 was added to a suspension of 23.5g of 47% HI and 150 mL acetic acid. The suspension was heated with stirring under N\(_2\) in the dark for five days. The cooled mixture was quenched with saturated aqueous bisulfite and the mixture extracted with CH\(_2\)Cl\(_2\). The organic extracts were washed with aqueous bisulfite, water, brine, and dried over CaCl\(_2\). The solvent was removed to give 0.10g (100% yield) of the product as a light yellow solid. \(^1\)H NMR (CDCl\(_3\)) δ 3.87 (s, 4H), 7.21-7.33 (m, 20H); \(^13\)C NMR (CDCl\(_3\)) δ 31.31, 126.33, 126.68, 127.65, 128.98, 136.60, 138.84, 140.35.

Reduction of 23 to give 5,7,12,14-Tetrahydro-6,13-diphenylpentacene. A mixture of 23.5 g of HI (47%) and 150 mL of acetic acid was prepared in a 250 mL round bottom
flask. To this stirred solution was added 0.11g (0.255 mmol) of 23. The resulting suspension was refluxed in the dark under N₂ for 5 days with stirring. Upon completion, the initially brown/purple suspension had become a light yellow solution. The reaction was cooled to room temperature and to it was added saturated aqueous bisulfite solution. The reaction was then extracted with CH₂Cl₂ and the organic layers washed with aqueous bisulfite, water, brine, and dried over CaCl₂. The solvent was removed to give light yellow solids (0.11g, 100% yield) as product. ¹H NMR (CDCl₃) δ 3.65 (s, 8H), 7.01-7.09 (m, 7H), 7.30-7.33 (m, 4H), 7.51-7.61 (m, 9H); ¹³C NMR (CDCl₃) δ 34.82, 126.13, 127.34, 127.41, 128.89, 129.94, 132.94, 137.43, 138.40.

Reduction of 25 to give 6,13-Dihydro-5,7,12,14-tetraphenylpentacene. 23.5g of HI (47%) and 150 mL of acetic acid were combined in a 250 mL round bottom flask. To this was added, with stirring, 0.11g (0.179 mmol) of quinone 25. The resulting light yellow suspension was refluxed in the dark under N₂ for 5 days with stirring. Upon completion, the reaction was a colorless, clear solution. To the cooled solution was added saturated aqueous bisulfite solution. The reaction was extracted with CH₂Cl₂, the organic layers washed with aqueous bisulfite, water, brine, and dried over CaCl₂. Upon removal of the solvent, 0.09g (87% yield) of product was obtained as a light yellow solid. ¹H NMR (CDCl₃) δ 3.71 (s, 4H), 6.90-7.38 (m, 33H); ¹³C NMR (CDCl₃) δ 32.94, 124.72, 126.31, 126.64, 127.98, 130.14, 131.22, 134.12, 135.94, 138.65.

7,16-Heptacenequinone (29). A 500 mL three-necked round bottom flask was fitted with the following: a reflux condenser, a Claisen adapter, and three pressure-equalizing
dropping funnels with stoppers. To the three-neck flask was added 150 mL of ethanol. To the three dropping funnels were added the following solutions: 1.45 g (7.88 mmol) of naphthalene-2,3-dicarboxaldehyde in 40 mL of THF, 0.5 g (4.37 mmol) of 1,4-cyclohexanedione in 40 mL of THF, and 0.30 g (4.85 mmol) of KOH in 1 mL water diluted with 15 mL ethanol. The three solution were added dropwise simultaneously to refluxing ethanol with stirring over 3 hours. Yellow solids formed immediately. After the three hour period, the mixture was cooled to room temperature, the solids filtered, washed with acetone, and dried to give 1.20 g (66% yield) of quinone 29 as an insoluble yellow powder. MALDI-TOF M.S. confirmed the molecular weight of 408.

6,10,17,21-Nonacenediquinone (30). 4.00 g (5.23 mmol) of octabromo compound 32 was suspended in dry DMF, and to this was added 2.72 g (13.07 mmol) 33 and 9.40 g (62.72 mmol) of NaI. The reaction was heated to 120 °C in an oil bath under N₂ for 24 hours. Upon reaching 55°C, all of the reactants were dissolved. After 24 hours, the brown reaction mixture was cooled to room temperature and poured into aqueous sodium bisulfite. The brown solids were filtered, washed with copious amounts of water, acetone, and dried to give 2.64 g (94% yield) of diquinone 30 as dark brown solids.

1,2,4,5-Tetrakis(dibromomethyl)benzene (32). 5.0 g (37.31 mmol) of durene was dissolved in 200 mL of CCl₄ in a 3-neck round bottom flask fitted with a reflux condenser and a pressure-equalizing addition funnel. The solution was heated to reflux by shining a light on it. 102.7 g (642.9 mmol) of Br₂ was added dropwise over 3.5 hours. HBr evolution was detected by gas escaping out the top of the condenser. (Note: The
reaction must be performed in a fume hood). The reaction was heated with the light for 3 days. At this point, white solids were floating in the solution. The mixture was cooled to room temperature and the solids filtered and washed with boiling CHCl₃ to give 25.04g (88% yield) of 32 as a white powder. Compound 32 was insoluble in every organic solvent tried. Due to the extreme insolubility, ¹H NMR shifts aren’t reported although the broad signals in the attempted NMR are consistent with the product.

**1,4-Anthraquinone (33).** 0.225g (1.56 mmol) of 1,4-dihydro-1,4-epoxynaphthalene, 0.370g (1.57 mmol) of di(2-pyridyl)-tetrazine, and 0.169g (1.56 mmol) of 1,4-benzoquinone were placed in a 25 mL round bottom flask. To this solid mixture was added 5 mL of CHCl₃, and the resulting solution instantly bubbled, liberating N₂ gas. After 5 minutes, the bubbling had ceased and the color of the solution was a clear red color. The solution was diluted with 20 mL of CHCl₃, washed with two 20 mL portions of 0.5M aqueous HCl, the organic layer separated, dried over CaCl₂, and the solvent evaporated to give the crude endoxide intermediate as a brown/yellow solid residue. To the residue was added 50 mL of glacial acetic acid and 1.50g of anhydrous sodium acetate. The resulting mixture was refluxed for 1 hour under N₂. After cooling to room temperature, the mixture was poured into 150 mL of water, the solids filtered and washed with water, and dried to yield 0.101g (31% overall yield) of quinone 33 as a gray/brown solid.

**Alternative procedure for the synthesis of 33:** 10.0g (41.66 mmol) of commercially available quinizarin was suspended in 150 mL of methanol. The suspension was cooled to 0°C in an ice bath, and 6.40g (166.6 mmol) of NaBH₄ was added slowly in small
portions to control foaming. After all of the NaBH₄ was added, the resulting orange solution was stirred at 0°C for 1 hour. 100 mL of 6M aqueous HCl was dripped in, the solids filtered and dried in the oven to give 8.60g (99% yield) of 33 as an orange/brown powder. ¹H NMR (CDCl₃) δ 7.06 (s, 2H), 7.69 (MM', 2H), 8.04 (AA', 2H), 8.61 (s, 2H).

8,19-Nonacenequinone (34). The following three solutions were added simultaneously to 100 mL of refluxing THF: 0.93g (3.97 mmol) of dial 36 in 250 mL of THF, 0.33g (2.94 mmol) of 1,4-cyclohexanedione in 250 mL of THF, and 1.00g of KOH in 25 mL of water. The solutions were added over 3 hours and the THF solution became dark red upon their addition. The mixture was cooled to room temperature, the solids filtered, washed with acetone, and dried to give 1.00g (100% yield) of quinone 34 as an insoluble red powder. MALDI-TOF M.S. confirmed the molecular weight of 508.

9,22-Undecacenequinone (35). Tetracene dial 37 (0.58g, 2.04 mmol) was suspended in 100 mL ethanol and refluxed with stirring. Added to this were 0.22g (1.95 mmol) of 1,4-cyclohexanedione in 150 mL ethanol and 0.65g (11.7 mmol) of KOH in 50 mL water. These two solutions were added dropwise with stirring over 3 hours. The resulting suspension was cooled to room temperature and the solids were collected by vacuum filtration and dried. 0.88g (78% yield) of quinone 35 was obtained as a dark green solid. MALDI-TOF M.S. confirmed the molecular weight of 608.
Anthracene-2,3-dicarboxaldehyde (36). In a 50 mL round bottom flask was combined the following: 2.00g (15 mmol) of o-phthalaldehyde, 4.00g (30 mmol) of 2,5-dimethoxytetrahydrofuran, 1.5 mL of glacial acetic acid, 1.5 mL of water, and 2 drops of piperidine. The resulting light yellow mixture was refluxed for 24 hours, upon which time it became red. The mixture was cooled, at which point it had turned mostly solid. The solids were filtered, washed with copious amount of each: 10% HCl, water, methanol, and ether, and dried. The resulting orange/red solid was collected, recrystallized from benzene, and dried to give 0.93g (27% yield) of 36 as a light red powder. $^1$H NMR (CDCl$_3$) δ 7.64 (MM', 2H), 8.09 (AA', 2H), 8.61 (s, 2H), 8.63 (s, 2H), 10.64 (s, 2H); $^{13}$C NMR (CDCl$_3$) δ 126.58, 127.73, 128.62, 129.50, 131.97, 133.74, 136.38, 192.40.

Tetracene-2,3-dicarboxaldehyde (37). In a 50 mL round bottom flask was combined the following: 2.00g (15 mmol) of o-phthalaldehyde, 8.16g (62 mmol) of 2,5-dimethoxytetrahydrofuran, 3 mL of glacial acetic acid, 1 mL of water, and 3 drops of piperidine. The resulting light yellow mixture was refluxed 24 hours, upon which time it turned a dark red. The solution was cooled, at which point it had solidified almost completely. The solids were filtered and washed with copious amounts of the following: 10% HCl, water, methanol, and ether, and dried. The resulting dark red solids were recrystallized from acetic acid, collected, and dried to give 0.76g (18% yield) of 37 as a red solid. $^1$H NMR (CDCl$_3$) δ 7.52 (MM', 2H), 8.07 (AA', 2H), 8.62 (s, 2H), 8.76 (s, 2H), 8.87 (s, 2H), 10.64 (s, 2H).
9,10-Dihydro-9,10-diphenylanthracenes (38 and 39). The exact procedure as above for the other HI/HOAc reductions was used starting from 0.11 g (0.333 mmol) of 9,10-diphenylanthracene. All other amounts remained the same. The reaction gave 0.11 g (100% yield) of 38 and 39. $^1$H NMR (CDCl$_3$) $\delta$ 5.16 (s), 5.24 (s), 6.98-7.25 (m); $^{13}$C NMR (CDCl$_3$) $\delta$ 49.97, 50.40, 126.14, 126.44, 126.48, 126.55, 128.16, 128.44, 128.59, 129.23, 129.25, 129.37, 138.45, 139.32, 143.72, 144.40.

1,2-Dicyano-3,6-dimethoxybenzene (49). 1.00 g (6.25 mmol) of 2,3-dicyanohydroquinone was dissolved in 33 mL of 2-butane. To this solution was added 6.72 g (5.0 mL, 53.33 mmol) of dimethyl sulfate and 8.00 g (57.88 mmol) of anhydrous K$_2$CO$_3$. The solution was refluxed for 18 hours. After approximately 2 hours, solids were forming in the reaction mixture. After 18 hours, the reaction was cooled to room temperature and vacuum filtered. The solid residue was added to 125 mL of water to remove excess K$_2$CO$_3$, and the solids filtered, washed with much water, and dried. The crude solids were recrystallized from acetic acid, filtered, and dried to give 1.07 g (91% yield) of 49 as a white powder. $^1$H NMR (d$_6$-DMSO) $\delta$ 3.90 (s, 6H), 7.60 (s, 2H).

4,7-Dimethoxyphthalic anhydride (50). To 1.00 g (5.32 mmol) of 49 was added 5 mL of concentrated H$_2$SO$_4$. The resulting mixture instantly turned a light yellow color. This mixture was heated in a hot water bath at approximately 97 °C for 3 hours. The mixture was then cooled to room temperature, left to sit overnight, and the solids filtered over a glass frit. The solids were washed with much water, dried, and collected to give 0.96 g.
(87% yield) of anhydride 50 as a yellow powder. mp: 259 °C (lit: 95 259-260 °C). $^1$H NMR (d$_6$-DMSO) $\delta$ 3.93 (s, 6H), 7.60 (s, 2H).

4,7-Dimethoxy phthalide (51). 0.10g (.481 mmol) of 50 was dissolved in glacial acetic acid and heated to 100 °C in an oil bath. To the green solution was added, in portions, zinc dust with stirring. The zinc dust was added to the solution until the solution turned colorless and the fluorescence disappeared. The solution was cooled, filtered to remove zinc dust, and poured into CH$_2$Cl$_2$. The solution was washed with saturated sodium bicarbonate, water, brine, and then dried over CaCl$_2$. The solvent was evaporated to yield 0.087g (94% yield) of 51 as a light yellow solid.

Alternative method for the preparation of 51: To 0.10g (.481 mmol) of 50 dissolved in ethanol was added, in portions, 0.40g (9.62 mmol) of NaBH$_4$. This must be added slowly to control the foaming that occurs. After complete addition, the bright yellow solution was refluxed until it turned colorless and did not fluoresce (approximately 4 hours). The reaction was cooled to room temperature and concentrated HCl was dripped in slowly to decompose any excess NaBH$_4$. Water and ethyl acetate were added to the mixture and the water layer extracted with ethyl acetate. The combined organic extracts were washed with water, brine, and dried over CaCl$_2$. The solvent was evaporated to give 0.92g (99% yield) of 51 as a light yellow powder. $^1$H NMR (CDCl$_3$) $\delta$ 3.85-3.93 (d, 6H), 5.17 (d, 2H), 6.83-7.15 (m, 2H).

5,8-Diphenyl-5,8-dihydro-naphthalene-1,4-diol (53). 0.10g (.318 mmol) of 54 was placed in a mixture of 5 mL concentrated HCl and 25 mL ethanol. The mixture was
heated to boiling for approximately 15 minutes, until all of the solids were dissolved. The solution was cooled to room temperature, poured into CH₂Cl₂, and to this was slowly added saturated sodium bicarbonate solution. The organic layer was separated, washed with water, dried over CaCl₂, and the solvent evaporated to yield 0.09g (90% yield) of 53 as fluffy white solids. mp: 208-210 °C (lit: 210-211 °C). ¹H NMR (CDCl₃) δ 4.20 (s, 2H), 4.77 (s, 2H), 5.86 (s, 2H), 6.67 (s, 2H), 7.32-7.34 (m, 10H); ¹³C NMR (CDCl₃) δ 41.60, 115.39, 124.80, 126.92, 126.97, 127.86, 129.06, 143.00, 147.56.

5,8-Diphenyl-4a,5,8,8a-tetrahydro-[1,4]naphthoquinone (54). 1.00g (4.85 mmol) of trans, trans-1,4-diphenyl-1,3-butadiene and 1.00g (9.25 mmol) of 1,4-benzoquinone were placed in a 125 mL Erlenmeyer flask. To this mixture was added 50 mL of glacial acetic acid. The mixture was allowed to sit, uncovered, at room temperature for 3 weeks, at which point large, yellow prisms had been deposited on the bottom of the flask. The prisms were picked out of the flask with tweezers, rinsed with acetone, and dried to yield 0.50 g (33% yield) of 54. ¹H NMR (CDCl₃) δ 3.74-3.93 (m, 4H), 5.91 (s, 2H), 6.26 (s, 2H), 7.18-7.40 (m, 10H); ¹³C NMR (CDCl₃) δ 41.83, 51.95, 126.90, 128.07, 128.78, 129.42, 139.66, 198.95.

1,4-Dimethoxy-but-2-yne (55). 2.00g (23.25 mmol) of 1,4-butynediol was dissolved in 30 mL of water. To this was added alternately, with stirring, portions of powdered NaOH (2.10g, 52.32 mmol total) and dimethyl sulfate (6.59g, 5.0 mL, 52.32 mmol total). The reaction temperature during addition was kept below 40 °C by ice bath cooling. After the addition was complete, the mixture was heated to 90 °C for 3 hours in an oil bath. 30 mL.
of ice water was then added to the mixture and it was allowed to cool to room
temperature. The aqueous phase was extracted with diethyl ether (5 x 50 mL), the ether
layers dried over CaCl₂, and the solvent evaporated to give 1.37g (52% yield) of 55 as a
light yellow oil. ¹H NMR (CDCl₃) δ 3.30 (s, 6H), 4.06 (s, 4H).

1,8-Dimethoxy-9,10-anthraquinone (56). In a 500 mL 3-neck round bottom flask fitted
with a reflux condenser, two glass stoppers, and magnetic stirring was dissolved 3.00g
(12.5 mmol) of commercially available 1,8-dihydroxyanthraquinone and 15.76g (12 mL,
125 mmol) of dimethyl sulfate in 175 mL of dry THF. To this was added, in portions,
1.50g (62.5 mmol) of sodium hydride with continuous stirring. The initially light orange
solution bubbled and turned a deep red color upon addition of NaH. The mixture was
stirred at room temperature, under N₂, for 24 hours, upon which time saturated aqueous
ammonia solution was added slowly to quench the reaction. This must be added slowly,
as vigorous foaming occurs as it is added. This mixture is stirred three hours at room
temperature, poured into 500 mL of water, and the precipitated yellow solids filtered,
washed with water, and dried to give 3.35g (86% yield) of 56 as a yellow powder. Due
to the water sensitivity of subsequent reactions planned for this material, it was
recrystallized from toluene to give 2.26g (68% yield) of 56 as bright gold flakes. ¹H
NMR (CDCl₃) δ 4.01 (s, 6H), 7.31 (d, 2H), 7.65 (t, 2H), 7.84 (d, 2H); ¹³C NMR (CDCl₃)
δ 56.75, 118.29, 119.12, 124.26, 134.08, 134.98, 159.66, 183.07, 184.24.

Mixture of cis- and trans-1,8-Dimethoxy-9,10-diphenylanthracene-9,10-diol (57). To
a flame-dried 3-necked round bottom flask, flushed with N₂, was added 200 mL of dry
toluene and 1.00g (3.73) of recrystallized 56. This suspension was cooled to -78 °C in a dry ice/acetone bath and was stirred for 10 minutes. To this was added, dropwise over 15 minutes, 10mL (11.19 mmol) of a 1.8M solution of phenyl lithium. The resulting suspension was stirred and then warmed to room temperature over 2 hours. After stirring at room temperature 1 additional hour, at which point it was a red solution, the reaction was quenched by slow addition of saturated ammonium chloride solution. The layers were separated, the organic layer dried over CaCl₂, and the solvent evaporated to give 1.01g (64% yield) of 57 as a yellow powder. ¹H NMR (CDCl₃) δ 3.35 (s, 6H), 5.18 (s, 1H), 6.22 (s, 1H), 6.65-7.66 (m, 24H); ¹³C NMR (CDCl₃) δ 55.40, 72.66, 73.44, 111.59, 120.70, 121.77, 125.46, 126.67, 126.75, 127.57, 128.14, 128.90, 130.07, 140.94, 142.03, 148.56, 150.03, 156.62.

1,8-Dimethoxy-9,10-diphenylanthracene (58). 0.55g (3.203 mmol) of KI was placed in 20 mL of glacial acetic acid and to this was added 0.34g (0.802 mmol) of diol 57. The resulting mixture was heated to reflux for 2 hours with stirring. The initially yellow solution turned dark red/brown upon completion of reflux. The mixture was then cooled to room temperature, the acetic acid evaporated, and the resulting solids gravity filtered and washed with H₂O and dried to give 0.27g (87% yield) of 58 as shiny brown solids. ¹H NMR (CDCl₃) δ 3.34 (s, 6H), 7.15-7.61 (m, 16H); ¹³C NMR (CDCl₃) δ 55.69, 104.70, 119.81, 123.66, 124.36, 125.12, 125.21, 127.13, 127.21, 128.38, 128.48, 128.71, 131.15, 131.91, 136.67, 147.26, 157.77.

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1,8-Dibenzyloxy-9,10-anthraquinone (59). To a 250 mL round bottom flask was added 1.00 g (4.16 mmol) of 1,8-dihydroxyanthraquinone, 11.52 g (83.33 mmol) of anhydrous K₂CO₃, 7.11 g (41.66 mmol) of benzyl bromide, and 150 mL of acetone. The resulting mixture was refluxed with stirring for two days. The reaction was cooled and the solids vacuum filtered and washed with water, hexanes, and dried. The crude solid was recrystallized from acetic acid to give 1.34 g (77% yield) of 59 as shiny gold flakes. ¹H NMR (CDCl₃) δ 5.33 (s, 4H), 7.32-7.43 (m, 14H), 7.85 (d, 2H); ¹³C NMR (CDCl₃) δ 71.21, 119.49, 120.27, 124.95, 126.79, 127.77, 128.61, 133.71, 134.93, 136.56, 158.27, 182.31, 183.97.

1,8-Dibenzyloxy-9,10-diphenylanthracene-9,10-diol (60). To a flame-dried 300 mL 3-neck round bottom flask flushed with N₂ was added 1.00 g (4.166) of quinone 59 and 200 mL of dry toluene. The suspension was cooled to -78 °C and stirred for 10 minutes. To the suspension was then added 11.57 mL (20.83 mmol) of PhLi (1.8M solution) dropwise over 15 minutes. The suspension was stirred and allowed to warm to room temperature over 2 hours and then stirred at room temperature an additional hour. The resulting solution was then quenched with saturated aqueous NH₄Cl, the toluene layer isolated, dried over CaCl₂, and the solvent removed to give a yellow, waxy solid. To the solid was added hexanes and the resulting suspension was filtered, rinsed with hexanes, and dried to give 0.85 g (62% yield) of diol 60 as a fine white powder. ¹H NMR (CDCl₃) δ 4.77 (d, 2H), 4.99 (d, 2H), 5.30 (s, 1H), 6.26 (s, 1H), 6.72 (m, 2H), 6.92-7.48 (m, 26H); ¹³C NMR (CDCl₃) δ 69.20, 72.64, 72.90, 111.66, 121.50, 124.70, 125.59, 126.20, 126.67, 127.23, 127.30, 127.40, 127.49, 127.90, 127.95, 129.50, 138.87, 140.94, 147.61, 149.85, 154.94.
1,8-Dibenzylxoy-9,10-diphenylanthracene (61). 0.30g (0.521 mmol) of diol 60 was dissolved in 40 mL of acetic acid and to this was added 0.56g (8.59 mmol) of zinc dust. The resulting suspension was refluxed under N₂ for 45 minutes, upon which time it was a dark green color. The reaction was filtered hot, the zinc dust rinsed with additional acetic acid, and the filtrate cooled to room temperature. Upon addition of water, green solids precipitated out of solution. These were collected via vacuum filtration, washed with water, and dried to give 0.25g (89% yield) of 61 as a green powder.¹ H NMR (CDCl₃) δ 4.49 (s, 4H), 6.42-7.42 (m, 32H); ¹³C NMR shifts are not reported because it is not known which are due to the product and which are impurities.

1,4,5,8-Tetrahydroxy-9,10-anthraquinone (62). Commercially available Disperse Blue 1 was obtained from Acros and was extracted off of the polymer dispersal agent via continuous Soxhlet extraction with acetone. The recovered Disperse Blue 1 from the acetone extracts was used without further purification. 0.50g (1.86 mmol) of Disperse Blue 1 was placed in a 100 mL round bottom flask and to this was added 50 mL of 1M NaOH in water. This solution was heated to 90 °C in an oil bath, with stirring. To this was added, in portions, 1.00g of sodium dithionite in 5 mL of water. Upon addition of the dithionite solution, the dark blue solution turned a rusty red color. This solution was stirred for four hours, upon which evolution of ammonia ceased. The solution was cooled to room temperature and air was bubbled through it for 30 minutes. After aeration, the solution was acidified by dripping in concentrated HCl slowly, upon which time the solution became a deep wine red color. The solution was stirred a few minutes more and then filtered over a frit, washed with water, and dried to yield 0.29g (57%) of a.
mixture of *leuco*-quinone 64 and 62 as a dark red/black solid. 0.24 g of the mixture was placed in 20 mL of nitrobenzene and 1 mL of pyridine and refluxed for 2 hours, upon which time the initially dark red/bronze colored solution had turned a dark purple/pink color. The mixture was cooled to room temperature and filtered over a frit. The solids were washed with nitrobenzene, ethanol, and ether to give 0.15g (63% yield) of 62 as shiny black solids. $^1$H NMR (CDCl$_3$) $\delta$ 7.32 (s, 4H), 12.42 (s, 4H).

**1,8-Dihydroxy-4,5-dinitro-9,10-anthraquinone (66).** Commercially available 1,8-dihydroxyanthraquinone (5.0g, 20.83 mmol) was added to a suspension of 3.00g (48.53 mmol) of boric acid in 60.0 g of fuming sulfuric acid (27-33% oleum). The resulting solution instantly turned a dark purple color. This solution was cooled in an ice bath and to it was added 31% by weight HNO$_3$ in water (total mass 10.0g) dropwise over 1 hour with stirring. The internal reaction was monitored and not allowed to get above 25 °C. After complete addition of the nitrating agent, the resulting brown mixture was quenched with water, the solids filtered, washed with 90% H$_2$SO$_4$ until the washings were yellow in color, and then washed with water and dried. The resulting golden/yellow solids were placed in 250 mL of a 25:5:1 mixture of ethanol:benzene:DMF, and refluxed with stirring overnight. The initial suspension was a dark red solution with solids floating in it upon completion of reflux. The mixture was cooled, filtered, the solids washed with water, and dried to give 3.72g (54%) of 66 as a golden/yellow powder, with the 2,5-dinitrated isomer being the only other species present. $^1$H NMR (CDCl$_3$) $\delta$ 7.40 (d, 2H), 7.89 (d, 2H), 8.07 (s, 2H).
1,4,5,8-Tetramethoxy-9,10-anthraquinone (67). To a mixture of 2.60 g (18.8 mmol) of anhydrous K$_2$CO$_3$ in 15 mL of 2-butanone was added 0.27 g (0.99 mmol) of tetrahydroxy compound 62. To this was added 2.66 g (2.0 mL, 21.08 mmol) of dimethyl sulfate, and the resulting mixture was refluxed with stirring for 2 days, upon which it became a murky brown color. After 2 days, the mixture was cooled, poured onto crushed ice, and extracted with CHCl$_3$. The combined CHCl$_3$ extracts were washed with water, dried over CaCl$_2$, and evaporated to give a brown residue. This residue was mixed with 200 mL of 2.5M NaOH, extracted with CHCl$_3$, and the combined organic extracts washed with water, dried over CaCl$_2$, and evaporated to give brown/yellow solids, which analyzed for 0.17 g (53% yield) of 67. This was recrystallized from 5:1 EtOAc/CHCl$_3$ to purify 67, giving a yellow/brown powder in high purity. $^1$H NMR (CDCl$_3$) $\delta$ 3.92 (s, 12H), 7.15 (s, 4H).

1,4,5,8-Tetramethoxy-9,10-diphenylanthracene-9,10-diol (68). 0.13 g (0.396 mmol) of tetramethoxyquinone 67 was dissolved in dry THF and cooled to -78 °C under N$_2$. To this was added 1.1 mL of a 1.8M solution of phenyllithium dropwise. The solution was stirred for 30 minutes at -78 °C and then warmed to room temperature. After stirring for 2 hours at room temperature, an aqueous solution of acetic acid was added. The resulting solution turned light yellow and white solids precipitated. The solids were collected by vacuum filtration washed with water, and dried to give 0.13 g (68% yield) of diol 68. $^1$H NMR (d$_6$-DMSO) $\delta$ 3.23 (s, 12H), 5.23 (s, 2H), 6.80 (s, 4H), 7.14-7.55 (m, 10H).
1,4,5,8-Tetramethoxy-9,10-diphenylanthracene (69). 0.09g (1.85 mmol) of diol 68 was suspended in 200 mL of acetic acid. To this was added 2.00g (30.59 mmol) of zinc dust. The resulting mixture was heated to reflux with stirring for 45 minutes under N₂. The initially orange suspension was a light yellow by the end of the reaction. The reaction was cooled, the zinc dust filtered off, and water added to the filtrate. Bright yellow solids precipitated, and these were collected by vacuum filtration, washed with water, and dried to give 0.075g (90% yield) of anthracene 69 as a yellow powder. ¹H NMR (CDCl₃) δ 3.22 (s, 12H), 6.54 (s, 4H), 7.21-7.31 (m, 10H). ¹³C NMR (CDCl₃) δ 56.0, 106.0, 124.58, 125.19, 125.64, 128.74, 133.91, 146.59, 149.52, 151.57.

Anthracene-1,4,5,8-tetraone (70). In a round bottom flask, sultine 174 (4.00g, 17.54 mmol), benzoquinone (3.79g, 35.08 mmol), and 100 mL of toluene were combined and refluxed 24 hours. The initially light yellow solution was dark red with solids floating in it upon completion of reflux. The solvent was removed to give dark red solids 179 and 180, which were immediately dissolved in 200 mL of benzene. To this mixture was added DDQ (15.92g, 70.15 mmol) and it was refluxed with stirring overnight. The mixture was cooled, the solvent removed, and the solids washed with absolute ethanol until the washings were colorless. The resulting dark red solids 180 were dried, placed in a round bottom flask, and to them was added 100 mL of a 1:1 v/v mixture of water/acetonitrile. To this was added, with stirring, ceric ammonium nitrate (20.20g, 36.85 mmol). This mixture was stirred overnight, at which point it had become bronze in color. The mixture was extracted with CHCl₃, washed with water, dried, and the solvent
removed to give 70 as light brown solids (1.50g, 86% yield). $^1$H NMR (CDCl$_3$) $\delta$ 7.14 (s, 4H), 8.80 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 125.29, 134.62, 138.93, 182.90.

1,4-Bis(trimethylsilyl)-2,5-diphenyl-3,6-dihydroxybenzene (71). To a round bottom flask was added 76 (0.20g, 0.36 mmol) and 20% aqueous methanol. This mixture was refluxed with stirring and followed by TLC until there was a spot that did not move up the plate. This took approximately four days. At this time, the solvent was removed to leave light brown solids of 71 (0.12g, 82% yield). $^1$H NMR (CDCl$_3$ w/no TMS) $\delta$ -0.09 (s, 18H), 4.60 (s, 2H), 7.35-7.48 (m, 10H); $^{13}$C NMR (CDCl$_3$ w/no TMS) $\delta$ 1.15, 126.00, 128.73, 129.50, 131.30, 133.41, 138.01, 151.18.

2,5-Diphenylhydroquinone (73). 1.50g (5.77 mmol) of commercially available 2,5-diphenylbenzoquinone was placed in a round bottom flask with 30 mL of glacial acetic acid and 3.00g (45.87 mmol) of zinc dust. The resulting mixture was stirred at room temperature for one hour and then refluxed for 30 minutes. The mixture was filtered hot, the zinc dust on the filter washed with hot acetic acid (2 x 3 mL) and the filtrate heated back to reflux. Hot water was added dropwise through the top of the condenser to the refluxing filtrate. Upon sufficient addition, the hydroquinone precipitated from the refluxing solution. Additional water was added to ensure complete precipitation, and the mixture was then cooled to room temperature. The solids were filtered, washed with hot water, and dried to give 1.35g (89% yield) of hydroquinone 73 as cream/white fluffy granular solids. $^1$H NMR (CDCl$_3$) $\delta$ 6.91 (s, 2H), 7.39-7.53 (m, 10H); $^{13}$C NMR (CDCl$_3$) $\delta$ 102.66, 117.45, 128.37, 128.88, 129.29, 129.66, 137.01, 146.58.
2,5-Dibromo-3,6-diphenylhydroquinone (74). 1.00g (3.82 mmol) of hydroquinone 73 was placed in a three-neck flask fitted with magnetic stirring, a condenser, and a pressure-equalizing dropping funnel. 30 mL of CHCl₃ was added and the mixture was stirred and cooled to 10 °C with a cold water bath. Bromine (1.95g, 0.63 mL, 12.20 mmol) in 5 mL of CHCl₃ was added rapidly dropwise. The mixture was allowed to warm to room temperature and stirred eight hours. The CHCl₃ was evaporated using no external heating and the resulting orange solids were placed in a round bottom flask. 75 mL of 95% ethanol and 1.00g (5.27 mmol) of SnCl₂ was added. The mixture was refluxed until it turned a light yellow color, upon which time 6M HCl was added dropwise through the top of the condenser. The acid was added until white solids began to precipitate from the solution. Additional 6M HCl was added to ensure complete precipitation, the mixture cooled to room temperature, and then placed in the refrigerator overnight. The solids were filtered, washed with 6M HCl, hot water, and dried to give 1.56g (98% yield) of dibromide 74 as a white powder. ¹H NMR (CDCl₃) δ 5.28 (s, 2H), 7.36-7.58 (m, 10H); ¹³C NMR (CDCl₃) δ 111.71, 128.63, 128.80, 129.14, 129.83, 135.97, 144.26.

1,4-Dibromo-2,5-diphenyl-3,6-bis(trimethylsilyloxy)benzene (75). To a flame-dried three-neck flask was suspended 1.00g (2.38 mmol) of hydroquinone 74 in 30 mL of dry toluene. To this was added, with stirring, 2 mL of dry pyridine, upon which the hydroquinone went into solution. The solution was heated to reflux under N₂ and 1.60g (1.90 mL, 14.57 mmol) of TMSCl was dripped in over one hour. The resulting mixture was refluxed for six hours, cooled to room temperature, and the solids filtered. The filtrate was evaporated to give 1.20g (90% yield) of 75 as light yellow solids. ¹H NMR
(CDCl₃ w/no TMS) δ -0.15 (s, 18H), 7.30-7.46 (m, 10H); ¹³C NMR (CDCl₃ w/no TMS) δ 0.27, 117.59, 127.95, 128.10, 128.23, 130.75, 135.23, 138.72.

1,4-Bis(trimethylsilyl)-2,5-diphenyl-3,6-bis(trimethylsilyloxy)benzene (76). To a flame-dried three-neck flask under N₂ was added 1.00g (1.77 mmol) of dibromide 75 and 75 mL of dry toluene. To this was added, with stirring, 0.37g (15.96 mmol) of sodium metal in pieces. The resulting mixture was heated to reflux and to this was added, dropwise, 0.81g (1.00 mL, 7.43 mmol) of TMSCl over 30 minutes. The resulting mixture was refluxed with stirring for two days. The mixture was then cooled, the dark blue solids filtered, and the filtrate evaporated to give 0.87g (89% yield) of 76 as light yellow solids. ¹H NMR (CDCl₃ w/no TMS) δ -0.32 (s, 18H), -0.08 (s, 18H), 7.33 (br.s, 10H); ¹³C NMR (CDCl₃ w/no TMS) δ 0.64, 2.54, 127.72, 128.20, 132.99, 133.93, 140.24, 141.52, 153.55.

1,2,4,5-Tetrabromo-3,6-diiodobenzene (77). In a 125 mL Erlenmeyer flask was stirred I₂ (21.3g, 83.92 mmol) and KI0₃ (2.55g, 11.91 mmol) in 30 mL of concentrated H₂SO₄ for 30 minutes. At this time, a suspension of 1,2,4,5-tetrabromobenzene (6.00g, 15.22 mmol) in 35 mL of concentrated H₂SO₄ was added in one portion and the mixture stirred for 5 days at room temperature. After this period of time, the mixture was purged into 300 mL of ice water and sodium bisulfite was added, with stirring, under the mixture turned yellow. The solids were filtered, washed with water, and dried to give the product 77 in 89% yield (8.81g) as an off-white powder. The material is quite insoluble and was analyzed by melting point (lit: 328-331 °C, exp: 326-330 °C).
4,11-Diphenyl-4,11-oxo-3a,4,11,11a-tetrahydro-anthra[2,3-c]furan-1,3-dione (80). 
Isonaphthofuran 27 (0.38g, 1.18 mmol) was suspended in 10 mL of benzene. To this was added, with stirring, 0.12g (1.18 mmol) of maleic anhydride. The initially red suspension lightened up to give a clear yellow solution over 10 minutes. The benzene was evaporated off by blowing N2 over the solution to give 0.44g (89% yield) of Diels-Alder adduct 80 as a white solid. $^1$H NMR (Benzene-d$_6$) $\delta$ 3.67 (s, 2H), 7.00 (m, 2H), 7.17-7.26 (m, 5H), 7.35-7.43 (m, 7H), 8.11-8.13 (m, 4H); $^{13}$C NMR (Benzene-d$_6$) $\delta$ 56.41, 91.08, 120.66, 127.03, 127.35, 128.55, 128.79, 129.08, 129.30, 133.39, 136.68, 141.41, 168.36.

4,11-Diphenyl-anthra[2,3-c]furan-1,3-dione (81). 0.10g (0.24 mmol) of Diels-Alder adduct 80 was dissolved in 25 mL of benzene. To this was added 0.28g (1.67 mmol) of dried $p$-toluenesulfonic acid and the resulting mixture was refluxed for six hours through a Dean-Stark trap for azeotropic removal of water. The initially light yellow mixture had become an orange mixture with a deep blue-green fluorescence upon this time. The mixture was cooled, washed with saturated aqueous sodium bicarbonate, water, brine, and dried over CaCl$_2$. Evaporation of the benzene gave 0.80g (84% yield) of 81. $^1$H NMR (CDCl$_3$) $\delta$ 7.44-7.55 (m, 12H), 7.2-7.843 (m, 2H), 8.38 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 120.50, 128.16, 128.56, 128.73, 129.17, 129.63, 129.83, 132.79, 133.19, 133.81, 143.96, 161.98.

4,11-Diphenyl-3H-anthra[2,3-c]furan-1-one (82). Anhydride 81 (0.11g, 0.275 mmol) was suspended in 60 mL of dry THF in a round bottom flask. To this suspension was added, with stirring, NaBH$_4$ (0.21g, 5.50 mmol). The resulting red mixture was refluxed.
overnight. Upon heating, the mixture turned a grey-blue color. After cooling to room temperature, the reaction was quenched with concentrated HCl, upon which time it became a light yellow solution with an intense blue fluorescence. Water was added and the reaction was extracted with CH₂Cl₂, and the organic extracts washed with water, brine, dried, and the solvent evaporated. The crude material was examined by TLC and it was found the major spot was bright yellow with an intense yellow glow when viewed under longwave UV light. This band was isolated via preparative TLC (CH₂Cl₂ eluant) to give pure 82 as a yellow powder (0.07g, 66% yield). ¹H NMR (CDCl₃) δ 5.26 (s, 2H), 7.40-7.65 (m, 12H), 7.87-7.92 (m, 2H), 8.37 (s, 1H), 8.47 (s, 1H); ¹³C NMR (CDCl₃) δ 68.12, 118.93, 124.77, 126.14, 127.08, 128.12, 128.44, 128.53, 128.63, 129.15, 129.53, 130.16, 131.45, 132.33, 132.82, 133.02, 134.68, 136.08, 136.22, 142.50, 169.64.

4,11-Diphenyl-1,3-dihydroanthra[2,3-c]furan-1-ol (83). In a flame-dried 100 mL round bottom flask was placed lactone 82 (0.25g, 0.647 mmol), and 75 mL of dry CH₂Cl₂. This solution was cooled, under N₂, to -78 °C by means of a dry ice-acetone bath. To this was added, slowly and dropwise, DIBAL-H (0.184g, 0.220 mL, 20 wt% solution in toluene). The resulting solution was stirred at -78 °C for 1.5 hours, at which point methanol was dripped in slowly to quench. The mixture was then allowed to warm to room temperature and the poured into more CH₂Cl₂. The mixture was washed with brine, filtered through Celite, and dried over CaCl₂. The solvent was removed without heat, by blowing a stream of N₂ over it. Lactol 83 was obtained in 72% yield (0.18g) as a yellow powder. ¹H NMR (CDCl₃) δ 2.95-2.96 (d, 1H), 4.91-4.94 (d, 1H), 5.31-5.34 (d, 1H), 6.40-6.41 (d, 1H), 7.10-7.25 (m, 2H), 7.37-7.60 (m, 12H), 7.81-7.85 (m, 2H), 8.27-
8.28 (d, 2H); $^{13}$C NMR (CDCl$_3$) δ 71.19, 100.33, 124.65, 125.55, 125.82, 125.93, 127.87, 127.88, 128.17, 128.29, 128.35, 128.51, 129.61, 129.65, 129.70, 131.15, 131.48, 131.52, 131.63, 131.95, 134.58, 135.00, 135.58, 137.20, 138.60.

1,3,7,9-Tetrakis(4-tert-butylphenyl)anthra[2.3-c:6,7-c']-difuran-5,11-dione (84). To a dried 100 mL two-neck heart-shaped flask flushed with N$_2$ was added 100 (0.50g, 1.288 mmol), 1,4-cyclohexanedione (0.072g, 0.644 mmol) and 33 mL of degassed ethanol. The resulting mixture was sonicated for 10 minutes and then stirred under N$_2$ for 10 minutes to give a finely dispersed solution. To this was added, via syringe in one portion, aqueous KOH (0.76M, 1.33 mL). The initially light yellow suspension instantly turned dark purple. The mixture was stirred under N$_2$ in the dark at room temperature for approximately 3 hours. At this time, the mixture was diluted with water, extracted with CHCl$_3$, and the extracts dried and the solvent removed. Care was taken to avoid light exposure. The resulting purple solid was subjected to very quick TLC and $^1$H NMR analysis. TLC (CHCl$_3$ eluant) showed one purple spot that ran with the solvent front, while the $^1$H NMR shows essentially quantitative conversion to the bisfuran (0.52g, 100% yield). The material was used immediately as is. $^1$H NMR (CDCl$_3$) δ 8.90 (s, 4H), 7.92 (d, 8H), 7.55 (d, 8H), 1.41 (s, 36H). This material is very light sensitive; however, it appears to be quite stable to heat and air in the absence of light. However, it was used as is in the next reaction.

2,5-Diphenylfuran-3,4-dicarboxaldehyde (85). To a flame-dried round bottomed purged with N$_2$ was added 90 mL of dry dichloromethane. To this was added oxalyl
chloride (1.29g, 0.87 mL, 10.16 mmol). The resulting mixture was cooled, with stirring, to -78 °C and to this was added dry DMSO (1.59g, 1.45 mL, 20.38 mmol) in a little dichloromethane dropwise. This mixture was stirred for 2 minutes and to it was then added a solution of diol 89 (0.93g, 3.32 mmol) in dichloromethane with a little DMSO to effect solution. The resulting mixture was stirred for 25 minutes and then to it was added dropwise triethylamine (5.17g, 7.18 mL, 51.09 mmol). The mixture was stirred 5 minutes and the cold bath was then removed and the mixture allowed to warm to room temperature. The mixture was poured into water, extracted with CHCl₃, the extracts washed with water, dried, and the solvent evaporated to give orange solids. The solids were redissolved in CHCl₃ and the solution washed with water and then brine to remove the last traces of DMSO and triethylamine. The CHCl₃ layer was dried and the solvent evaporated to give dialdehyde 85 as orange solids (0.90g, 98% yield). ¹H NMR (CDCl₃) δ 7.53-7.55 (m, 6H), 7.95-7.97 (m, 4H), 10.43 (s, 2H); ¹³C NMR (CDCl₃) δ 121.39, 127.88, 128.61, 128.93, 131.09, 159.48, 186.92.

3,4-Dibromo-2,5-diphenylfuran (86). Method A: In a 125 mL Erlenmeyer flask was dissolved 2,5-diphenylfuran (3.00g, 13.63 mmol) in 35 mL of benzene. To this was added N-bromosuccinimide (5.34g, 30 mmol) and the resulting mixture stirred at room temperature and followed by TLC until no starting material remained (about 3 days). The mixture was then filtered through silica, the filtrate washed with water, dried, and evaporated to give 86 as an orange powder (4.30g, 83% yield). ¹H NMR (CDCl₃) δ 7.37-7.49 (m, 6H), 8.03-8.06 (m, 4H); ¹³C NMR (CDCl₃) δ 102.38, 102.51, 125.69, 128.68, 129.16, 148.17.
Method B: In a 250 mL round bottom flask, 2,5-diphenylfuran (2.00g, 9.09 mmol) was dissolved in 45 mL CHCl₃ and cooled in an ice bath to 0 °C. To this was added, via a dropping funnel, bromine (2.90g, 0.93 mL, 18.18 mmol) in CHCl₃ over 15 minutes. Upon complete addition, the ice bath was removed and the reaction stirred an additional 15 minutes. The solvent was evaporated to give a brown oil that solidified on standing to give a tan solid. The solids were transferred, with 20 mL methanol, to a glass frit (with no vacuum applied) and ground into a powder. The vacuum was applied to remove the methanol, the vacuum shut off, and 10 mL of methanol added and the solids again ground under the methanol to a powder. The vacuum was applied again to draw off the methanol and this time, with the vacuum still on, the solids were rinsed with 10 mL methanol. The solids were collected and dried to give 86 as a white powder (3.15g, 92%) with identical NMR spectra to the material obtained via method A.

3,4-Dicyano-2,5-diphenylfuran (87). In a flame-dried 100 mL round bottom flask was dissolved 86 (2.13g, 5.63) in 20 mL of N-methylpyrrolidinone (dried over 4A molecular sieves) under N₂. Upon complete dissolution, copper (I) cyanide (2.02g, 22.53 mmol) was added and the resulting mixture refluxed under N₂ for 5 hours. The reaction was cooled to room temperature and poured into 400 mL of H₂O. The reaction flask was rinsed out with a solution of NaCN (7.40g in 74 mL of water) and the mixture stirred 10 minutes. Water (100 mL) was added and the solids filtered, washed with water, and dried to give tan/brown solids. These solids were rinsed with hot heptane until the washings were clear, and the heptane was evaporated to give orange solids which were a mixture of 87 and the mono-cyano derivative. The solids were recrystallized from heptane to give
dicyano furan 87 as the sole product (0.878g, 58% yield) as orange crystals. $^1$H NMR (CDCl$_3$) $\delta$ 7.53-7.56 (m, 6H), 8.02-8.07 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 94.23, 111.65, 125.74, 126.22, 129.42, 131.59, 159.04.

2,5-Diphenylfuran-3,4-dicarboxylic acid (88). To a 100 mL round bottom flask was added dicyano furan 87 (0.659g, 2.44 mmol), ethylene glycol (52 mL) and 3M aqueous NaOH (5.3 mL). The resulting suspension was heated to reflux with stirring, at which point it became an orange solution. The hydrolysis was monitored by checking the evolution of ammonia by holding a piece of wet pH paper at the top of the condenser. When ammonia evolution ceased (approximately 5 days), the solution, which had lightened in color considerably, was cooled to room temperature, diluted with water, and acidified with 10% HCl. The mixture was extracted with CHCl$_3$, dried, and the solvent evaporated to give a gummy solid that was ground under H$_2$O until it became a powder. The solids were filtered, washed with water, and dried thoroughly to give diacid 88 as a white powder (0.629g, 84% yield). $^1$H NMR (d$_6$-DMSO) $\delta$ 7.50-7.54 (m, 6H), 7.85-7.88 (m, 4H).

2,5-Diphenyl-3,4-hydroxymethylfuran (89). Method A: To a flame-dried round bottomed flask purged with nitrogen was added diacid 88 (0.49g, 1.59 mmol) and 10 mL of dry THF. This mixture was cooled to 0 °C and to this was added, with stirring, BH$_3$THF (4.13 mL, 4.136 mmol) dropwise. The resulting mixture was allowed to warm to room temperature overnight, quenched with a 1:1 mixture of THF and water, and the solvent removed. The residue was dissolved in dichloromethan, washed with water,
dried, and the solvent evaporated. The resulting solids were recrystallized from CHCl₃ to give diol 89 as a white powder (0.17g, 38% yield).

**Method B:** To a flame-dried 2 neck flask purged with nitrogen and fitted with a reflux condenser was added 100 mL of dry ether. This was cooled to 0 °C and to this was added, with stirring, LAH (1.19g, 31.42 mmol). After stirring for 10 minutes, a solution of diester 90 in ether was added dropwise (1.27g, 3.49 mmol). The resulting mixture was allowed to warm to room temperature and stirred overnight. The excess LAH was quenched by careful addition of ethyl acetate. Water was added and the mixture neutralized by addition of 10% HCl. The resulting mixture was extracted with ethyl acetate, the extracts washed with water, dried, and the solvent removed to give pure diol 89 as a white solid (0.93 g, 95% yield). NMR data for the products obtained from each method were identical. \(^1\)H NMR (CDCl₃) \(\delta 4.84 (s, 4H), 7.36 (t, 2H), 7.46 (t, 4H), 7.67 (d, 4H); \(^{13}\)C NMR (CDCl₃) \(\delta 55.81, 121.79, 126.75, 128.13, 128.75, 130.37, 150.24.\)

**Ethyl-2,5-diphenylfuran-3,4-dicarboxylate (90).** Ethyl dibenzoylsuccinate 97 (6.16g, 16.12 mmol) was placed in a 125 mL Erlenmeyer flask and to it was added 61.6g of concentrated sulfuric acid. The resulting mixture was stirred magnetically until all of the solids dissolved, giving a brown solution. The solution was stirred overnight and then poured onto ice at which point an oil separated out. The resulting mixture was extracted with ether, the ether extracts washed with water, dried, and the solvent removed to give furan 90 as a viscous orange oil that slowly crystallized on standing. \(^1\)H NMR (CDCl₃) \(\delta 1.29 (t, 6H), 4.32 (q, 4H), 7.37-7.41 (m, 6H), 7.84-7.87 (m, 4H); \(^{13}\)C NMR (CDCl₃) \(\delta 13.61, 60.99, 115.34, 126.92, 128.07, 128.47, 129.11, 152.76, 163.25.\)
Ethyl Dibenzoylsuccinate (97). To a 250 mL round bottomed flask was added 50 mL of absolute ethanol. To this was added, with stirring, sodium metal (2.30g, 100 mmol). Upon complete dissolution of the sodium, ethyl benzoyleacetate (19.2g, 100 mmol) was dripped in and the resulting mixture stirred one hour at room temperature. The solvent was then removed under vacuum at room temperature, and to it was added dry ether (150 mL). To this suspension was added a solution of I₂ in THF (25.38g, 100 mmol in 50 mL) via a dropping funnel. The resulting brown solution was poured into a solution of aqueous sodium bisulfite and the mixture extracted with ether. The extracts were washed with water, dried, and the solvent evaporated to give a yellow oil. When placed in the refrigerator, the oil completely crystallized. The solids were triturated with a small amount of cold methanol and filtered. Compound 97 was obtained as a white powder (6.87g, 36% yield). ¹H NMR (CDCl₃) δ 0.96 (t, 6H), 3.95 (q, 4H), 5.61 (s, 2H), 7.49-7.63 (m, 6H), 8.14-8.17 (m, 4H); ¹³C NMR (CDCl₃) δ 13.46, 53.10, 61.92, 128.47, 129.29, 133.63, 136.03, 166.98, 193.91.

1,3,7,9-Tetraphenylanthraf[2.3-c:6,7-c']-difuran-5.11-dione (98). To a round bottom flask was added 85 (0.20g, 0.73 mmol), 1,4-cyclohexanedione (0.04g, 0.36 mmol), and 20 mL of ethanol. This mixture was sonicated for thirty minutes. Then, 2 mL of 0.76M aq. KOH was added. The mixture immediately became dark red and was stirred in the dark at room temperature for 24 hours. At this time, water was added and the mixture made basic by addition of solid Na₂CO₃. The mixture was poured into a large volume of water and the solids filtered, washed with water, and dried to give 98 (0.16g, 75% yield).
as dark red solids. These solids were kept in the dark and under N\textsubscript{2}. They appeared to be stable to heat and air in the absence of light. They were used as is for the next reaction.

6,10,17,21-Tetraphenyl-5,8,11,16,19,22-nonacenehexaone (99). A 10 mL round bottom flask was flame-dried and purged with N\textsubscript{2}. To it was added freshly sublimed 1,4-naphthoquinone (0.013g, 0.085 mmol), bisisobenzofuran 98 (0.011g, 0.019 mmol), and 5 mL of CHCl\textsubscript{3}. TMSOTf (0.256g, 0.210 mL, 1.15 mmol) was added in one portion and the flask covered, wrapped in foil, and stirred at room temperature for 24 hours. The reaction was then quenched with water, made basic with solid Na\textsubscript{2}CO\textsubscript{3}, and extracted with CHCl\textsubscript{3}. The organic extracts were washed with water, dried, and the solvent removed to give brown solids. These were triturated with acetone to give yellow solids which were shown in the 'H NMR spectrum to be 99 with an impurity present. This impurity could not be removed by column chromatography. 'H NMR (CDCl\textsubscript{3}) δ 7.41-7.44 (m, 6H), 7.58-7.62 (m, 8H), 7.70-7.77 (m, 10H), 8.08-8.09 (m, 4H), 8.54 (s, 4H).

2,5-Bis(4-tert-butylphenyl)-3,4-diformylfuran (100). To a flame-dried 100 mL round bottom flask purged with N\textsubscript{2} was added 16 mL of dry CH\textsubscript{2}Cl\textsubscript{2} and oxalyl chloride (0.72 mL, 8.19 mmol). The resulting solution was cooled, with stirring, to -78 °C and stirred for 5 minutes. To this was added, dropwise, a solution of dry DMSO (1.20 mL, 16.39 mmol) in a small amount of CH\textsubscript{2}Cl\textsubscript{2}. The resulting mixture was stirred for 2 minutes. A solution of diol 107 (1.05g, 2.67 mmol) in CH\textsubscript{2}Cl\textsubscript{2} with a tiny amount of DMSO (to solublize 107) was added dropwise. The mixture was stirred at -78 °C for 25 minutes, and then triethylamine (5.76 mL, 41.09 mmol) was added dropwise. The mixture was
stirred for 5 minutes, the cooling bath removed, and the mixture was allowed to warm to room temperature. The mixture was poured into water, the organic layer removed, and the water layer extracted with CHCl₃. The combined organic extracts were washed with water, dried, and the solvent removed to give a yellow oil that solidified on standing to give a yellow solid. The solid was recrystallized from the smallest amount possible of hot heptanes. The solids were collected via vacuum filtration and dried to give 100 as a pale yellow powder (0.987g, 95% yield). ¹H NMR (CDCl₃) δ 1.36 (s, 18H), 7.54 (XX', 4H), 7.90 (AA', 4H), 10.43 (s, 2H); ¹³C NMR (CDCl₃) δ 31.20, 35.10, 121.03, 125.20, 125.92, 128.42, 154.62, 159.67, 187.04.

(E)-1,4-Bis(4-tert-butylphenyl)but-2-ene-1,4-dione (101). A 100 mL 3-neck round bottom flask was flame-dried and flushed with N₂. To it was added AlCl₃ (13.4g, 100 mmol) and 1,1,2,2-tetrachloroethane (TCE) (30 mL). The resulting suspension was cooled to 0 °C in an ice bath and stirred. Fumaryl chloride (6.40g, 4.53 mL, 42 mmol) and tert-butylbenzene (16.85g, 19.44 mL, 126 mmol) were combined and stirred to give a uniform solution. This was then added to the AlCl₃/TCE mixture via an addition funnel over 45 minutes. The initially yellow suspension became a blood-red color upon addition of the two reactants. After the addition was complete, the mixture was stirred for 15 minutes, and the ice bath was removed. The mixture was then stirred for at least 2.5 hours (although letting it stir overnight did not affect the yield). The mixture was poured over HCl/ice and poured into a separatory funnel. The organic layer was removed, the aqueous layer extracted with CHCl₃, and the combined organic layers washed with water and dried. After removal of the solvent, the remaining oil was left on the rotary evaporator.
and the vacuum and heating increased until all that was left was an orange paste. This paste was recrystallized from 95 % ethanol to give 101 as bright yellow plates (7.15g, 49% yield). \( ^{1}H\) NMR (Acetone-\(d_{6}\)) \( \delta \) 1.36 (s, 18H), 7.66 (XX', 4H), 7.95 (s, 2H), 8.07 (AA', 4H); \( ^{13}C\) NMR (Acetone-\(d_{6}\)) \( \delta \) 32.22, 36.71, 127.71, 130.61, 136.69, 159.22, 190.79.

**1,4-Bis(4-tert-butylphenyl)butane-1,4-dione (102).** A 250 mL 3-neck round bottom flask was flame-dried and flushed with N\(_2\). The flask was fitted with a reflux condenser and to it was added SnCl\(_2\)2H\(_2\)O (4.28g, 18.99 mmol), 35 mL of HOAc, and 5.33 mL of HCl. The resulting suspension was stirred and heated to 50 °C in a warm water bath until it became a clear solution. To this was added, in one portion, 101 (5.65g, 16.23 mmol). The mixture was stirred until it became a homogenous solution, and was then stirred an additional 5 minutes. The orange solution was immediately poured onto ice, and the resulting tan solids were filtered, washed with water, and dried. The solids were recrystallized from ethanol to give a white powder. The mother liquor was evaporated and recrystallized from hexanes to give a second crop of light yellow solids, which were combined with the first crop to give 102 (4.93g, 87% yield). \( ^{1}H\) NMR (Acetone-\(d_{6}\)) \( \delta \) 1.35 (s, 18H), 3.43 (s, 4H), 7.57 (XX', 4H), 8.00 (AA', 4H); \( ^{13}C\) NMR (Acetone-\(d_{6}\)) \( \delta \) 32.33, 33.99, 36.59, 127.32, 129.76, 130.61, 136.69, 159.22, 190.45.

**2,5-Bis(4-tert-butylphenyl)furan (103).** Diketone 102 (4.78g, 13.65 mmol) was placed in a flame-dried 250 mL 2-neck flask flushed with N\(_2\). To it was added 65 mL of BF\(_3\)OEt\(_2\). The mixture became reddish brown and eventually became homogenous. The
mixture was stirred at room temperature for 42 hours. After the first day, it became a reddish heterogenous mixture. At the end of 42 hours, the mixture was poured over ice to give tan solids. The solids were filtered, washed with water, dried, and recrystallized from absolute ethanol to give white needles. A second crop of crystals was grown by evaporating the mother liquor, recrystallizing the residue from absolute ethanol, and combing the solids. Compound 103 was obtained in 90% yield (4.10g). $^1$H NMR (Acetone-d$_6$) $\delta$ 1.34 (s, 18H), 1.51 (s, 2H), 7.50 (XX', 4H), 7.73 (AA', 4H); $^{13}$C NMR (Acetone-d$_6$) $\delta$ 32.51, 36.14, 108.80, 125.21, 127.52, 130.02, 152.16, 155.02.

3,4-Dibromo-2,5-bis(4-tert-butylphenyl)furan (104). Furan 103 (2.12g, 6.38 mmol) was dissolved in 45 mL of CHCl$_3$ in a 250 mL round bottom flask. The solution was cooled in an ice bath and to it was added, dropwise, a solution of bromine (2.04g, 0.65 mL, 12.76 mmol) in CHCl$_3$ over 15 minutes. Upon complete addition, the ice bath was removed and the solution stirred an additional 15 minutes. The solvent was then evaporated to give an oil, which solidified either upon standing or cooling in an ice bath. The solid was triturated with 20 mL of methanol to give a white powder. This was filtered through a fritted funnel via vacuum filtration. The vacuum was shut off and 10 mL of methanol was added to the powder and the solids ground under the methanol. The vacuum was reapplied, the solvent drawn off, and the solids washed with 10 mL of methanol with the vacuum left running. The solids were dried to give 104 as a white powder (2.57g, 82% yield). $^1$H NMR (Acetone-d$_6$) $\delta$ 1.35 (s, 18H), 7.58 (XX', 4H), 7.98 (AA', 4H); $^{13}$C NMR (Acetone-d$_6$) $\delta$ 32.42, 36.36, 103.15, 127.30, 127.56, 128.06, 150.14, 153.89.
3,4-Dicyano-2,5-bis(4-tert-butylyphenyl)furan (105). A modification of the literature preparation was devised. Dibromofuran 104 (2.76g, 5.63) was dissolved in 15 mL of anhydrous 1-methyl-2-pyrrolidinone (NMP) in a flame-dried, N₂ purged 50 mL round bottom flask to give a light yellow solution. To this was added CuCN (2.02g, 22.53 mmol) and the resulting red/black mixture was refluxed with stirring for 5 hours. The mixture was then allowed to cool to room temperature and poured into 220 mL of water. The reaction flask was rinsed out with aqueous NaCN (4.00g in 41 mL of water) and stirred for 10 minutes. Water (54 mL) was added, and the resulting mixture was filtered, washed with water, and dried to give grey solids. These solids were placed in a Sohxlet thimble and the cyanofurans extracted through the Sohxlet extractor using heptane for 6 hours. The resulting orange solution was evaporated and the solids recrystallized from heptanes to give selectively the dicyanofuran 105 as white needles. A second crop was grown from the mother liquor by evaporating the mother liquor and recrystallizing it from heptane to give a small amount of additional product. After recrystallization, 105 was obtained as fluffy white needles (1.78g, 83% yield). ¹H NMR (CDCl₃) δ 1.37 (s, 18H), 7.56 (XX', 4H), 7.96 (AA', 4H); ¹³C NMR (CDCl₃) δ 30.77, 34.86, 93.13, 111.65, 123.32, 125.33, 126.10, 154.99, 158.86.

2,5-Bis(4-tert-butylyphenyl)-3,4-dicarboxyfuran (106). Dicyanofuran 105 (0.950g, 2.48 mmol) was suspended in 76 mL of ethylene glycol and to it was added 8 mL of 3M aqueous NaOH. The resulting suspension was stirred and heated to reflux. After about one hour, the mixture became a bright yellow solution. The solution was refluxed and the reaction monitored by holding a piece of wet pH paper over the top of the condenser.
When the pH was neutral, indicating no more evolution of ammonia, heating was stopped and the solution cooled to room temperature. The solution was diluted with 180 mL of water and acidified with 10% aqueous HCl. Upon acidification, the white suspension was extracted with CHCl₃, the extracts dried, and the solvent evaporated to give a viscous oil that slowly started to crystallized. Approximately 75 mL of water was added and the oil triturated until it became tan solids. The solids were filtered, washed with water, and dried to give diacid 106 as a tan powder (1.00 g, 96% yield). ¹H NMR (CDCl₃) δ 1.36 (s, 18H), 7.50 (XX', 4H), 7.82 (AA', 4H); ¹³C NMR (CDCl₃) δ 31.02, 34.74, 113.48, 125.34, 125.62, 127.88, 153.16, 155.87, 168.83.

2,5-Bis(4-tert-butylphenyl)-3,4-bis(hydroxymethyl)furan (107). To a flame-dried 100 mL round bottom flask flushed with N₂ was added diacid 106 (1.47 g, 3.50 mmol) and 30 mL of dry THF. The resulting pale yellow solution was cooled in an ice bath and to it was added, very slowly and dropwise, a 1 M solution of BH₃ THF in THF (9.10 mL, 9.10 mmol) with stirring. The addition needs to be done slowly as there is vigorous evolution of hydrogen. After the addition was complete, the ice bath was removed and the mixture was stirred at room temperature for 24 hours. At this time, the reaction was very carefully quenched by dropwise addition of a 1:1 mixture of THF and water. After the quench was complete, the solution was placed on the rotary evaporator and the volatile organics removed. To the resulting suspension was added water and CH₂Cl₂. Extraction with CH₂Cl₂ followed by filtration through a small amount of Celite gave a clear solution. Evaporation of the solvent gave diol 107 as white solids (1.10 g, 80% yield). ¹H NMR (CDCl₃) δ 1.35 (s, 18H), 2.89 (br, 2H), 4.80 (s, 4H), 7.47 (XX', 4H), 7.59 (AA',

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6,10,17,21-Tetrakis(4-tert-butylphenyl)-5,8,11,16,19,22-nonacenehexaone (108). To a flame-dried 100 mL round bottom flask flushed with N2 was added 1,4-naphthoquinone (sublimed, 0.50g, 3.20 mmol) and a solution of bisfuran 84 in dry CHCl3 (75 mL) (approximately 0.52g, 0.64 mmol). The resulting dark purple solution was stirred in the dark under N2 and to it was added, in one portion via syringe, trimethylsilyl trifluoromethansulfonate (TMSOTf, 7.65 mL, 39.6 mmol). The resulting mixture was stirred at room temperature in the dark under N2 for 48 hours. At this time, the now brown reaction mixture was diluted with water and to this was added, in portions (careful to avoid foaming up) solid Na2CO3 until the pH was basic. The mixture was poured into a separatory funnel, diluted with water, and extracted with CHCl3. The CHCl3 extracts were washed with water, dried over CaCl2, and the solvent removed to give a brown residue. This residue was triturated with acetone and vacuum filtered to give an orange solid. The solid was washed on the frit with acetone until the washings were clear, and then collected. TLC analysis (CHCl3 eluant) showed two spots: a yellow spot running near the solvent front and a much fainter spot (Rf=0.7). The crude product was purified via flash column chromatography with CHCl3 as eluant, the top golden band collected, and the solvent removed to give pure 108 as a yellow solid (0.18g, 26% yield). 1H NMR (CDCl3) δ 1.50 (s, 36H), 7.23 (XX', 8H), 7.61 (AA', 8H), 7.68 (MM', 4H), 8.04 (AA', 4H), 8.64 (s, 4H); 13C NMR (CDCl3) δ 31.49, 34.82, 125.58, 127.04, 128.40, 130.70, 131.39, 133.86, 134.77, 135.46, 137.83, 145.62, 150.60, 181.68, 183.92.
**1,5-Dichloro-2,4-dinitrobenzene (113).** To a round bottom flask was added 70.0g (694 mmol) of KNO₃ and 250 mL of concentrated sulfuric acid. Once all of the KNO₃ was dissolved, m-dichlorobenzene (50.0g, 340 mmol) was added and the biphasic mixture was stirred vigorously. As the mixing proceeded, the mixture gradually turned a bright yellow color and the internal temperature rose to 90 °C. Stirring was continued for 3 hours and the resulting suspension was poured over 750g of crushed ice. The resulting solids were filtered, washed with water, hexanes, and dried. The crude solids were recrystallized from 95% ethanol and dried to give 50.9g (63% yield) of 113 as shiny light yellow flakes. mp: 95-97°C (lit: 103°C). **Caution:** 113 is known to be a severe skin irritant and blistering agent and should be handled carefully with gloves at all times. ¹H NMR (CDCl₃) δ 7.84 (s, 1H), 8.56 (s, 1H); ¹³C NMR (CDCl₃) δ 123.27, 132.32, 135.14, 145.38.

**1,3-Diamino-4,6-dinitrobenzene (114).** A 500 mL 3-neck round bottom flask was charged with 17.00g (71.73 mmol) of 113 and 150 mL of ethylene glycol. The resulting suspension was stirred and heated to 140 °C in an oil bath, at which point it became a light yellow solution. Ammonia gas was bubbled into the solution at such a rate that it was just absorbed. The solution changed to an orange color after one hour. Upon 3 hours of gas bubbling in, the solution was a dark orange and began to develop a cloudiness. After an additional 30 minutes, orange/brown solids precipitated out of solution. Ammonia addition was continued for an additional 90 minutes, and then the solution was cooled to room temperature. The solids were filtered, washed with boiling water, boiling ethanol, and dried to give 12.4g (80% yield) of 114 as an orange/brown
powder. mp: 299-306 °C (lit: 300 °C with sublimation). \( ^1 \)H NMR (CDCl\textsubscript{3}) \( \delta \) 6.21 (s, 1H), 7.70 (br.s, 4H), 8.90 (s, 1H); \( ^{13} \)C NMR (CDCl\textsubscript{3}) \( \delta \) 135.19, 160.95, 164.91, 186.19.

1,5-Bis(acetylamino)-2,4-dinitrobenzene (115). To a 100 mL round bottom flask was added 7.30g (36.86 mmol) of 114, 75 mL of acetic anhydride, and 4 drops of concentrated H\textsubscript{2}SO\textsubscript{4}. The resulting suspension was stirred and heated to reflux, at which point it became a dark red solution. The solution was refluxed for 5 minutes, cooled to room temperature, and poured slowly into 400 mL of water with stirring. The resulting solids were filtered, washed with water, and dried to give 9.25g (89% yield) of 115 as a light yellow/orange powder. The crude product was pure enough for use in subsequent reactions, but it can be recrystallized from acetic acid if an analytically pure sample is necessary. \( ^1 \)H NMR (CDCl\textsubscript{3}) \( \delta \) 2.36 (s, 6H), 8.60 (s, 1H), 8.79 (s, 1H), 10.87 (s, 2H); \( ^{13} \)C NMR (CDCl\textsubscript{3}) \( \delta \) 23.66, 116.50, 123.34, 134.69, 136.28, 168.80.

1,7-Diacetyl-1,7-dihydrobenzo[1,3-d: 4,5-d']bistriazole (117). 2.00g (7.14 mmol) of 115 was suspended in 30 mL of absolute ethanol with 0.5g of Pd/C (10%). To this suspension was fitted a hydrogen balloon, and hydrogen gas was allowed to enter the system. The reaction was monitored by TLC until an immovable spot was the sole spot present (ethyl acetate eluant). The resulting suspension was filtered, the filtrate diluted with 70 mL of water, and the resulting mixture filtered one last time. This mixture was cooled to 0 °C in an ice bath and to it was added 3.33 mL of concentrated HCl. A solution of 1.48g (21.4 mmol) of NaNO\textsubscript{2} in 7 mL of water was dripped in over 30 minutes, upon which time the initially dark red solution lightened up to orange and a
solid precipitated out of solution. The resulting suspension was filtered and the resulting tan solids washed with water and dried to give 0.87g (50% yield) of 117. $^1$H NMR (d$_6$-DMSO) δ 2.98 (s, 6H), 8.83 (s, 1H), 9.27 (s, 1H); $^{13}$C NMR (d$_6$-DMSO) δ 23.16, 97.36, 111.86, 111.91, 131.55, 144.45, 169.71.

**Benzo[1,2-\textit{d}; 4,5-\textit{d}']bistriazole (118).** 0.73g (2.99 mmol) of 117 was suspended in a 50% aqueous ethanol solution. To this was added 1 mL of concentrated sulfuric acid, and the resulting suspension was heated to reflux for one hour, upon which time it became a light yellow solution. The mixture was cooled to room temperature and the ethanol allowed to evaporate. The resulting suspension was chilled overnight and the white solids filtered, washed with water, and dried to give 0.43g (92% yield) of 118. $^1$H NMR (d$_6$-DMSO) δ 7.96-8.79 (br.m, 2H), 15.77-15.82 (br, 2H).

**Benzo[1,2-\textit{d}; 4,5-\textit{d}']bistriazole-1,7-diamine (112) and benzo[1,2-\textit{d}; 4,5-\textit{d}']bistriazole-1,5-diamine (119).** To a 300 mL 3-neck flask was dissolved 10.76g of KOH in 110 mL of water. To this solution was added 3.26g (20.38 mmol) of benzobistriazole 118. The resulting solution was heated to 65 °C in an oil bath and to it was added in portions over 1 hour 9.21g (81.50 mmol) of hydroxylamine-O-sulfonic acid. Each portion added was accompanied by foaming and a tan murkiness that disappeared after a few minutes. After complete addition, the mixture was stirred at 65-70 °C for 1 hour. The mixture was then cooled, filtered, and continuously extracted with ether for one week. The ether was evaporated to yield 1.00g (26% yield) of the 1,5-, 1,6-, and 1,7-diamino isomers. The desired 1,5- and 1,7- isomers were obtained by recrystallization from ethanol. The first
solids precipitated were the 1,5-isomer 119 (0.30g). Subsequent filtration of the formed solids from the filtrate gave a mixture of 119 and 1,7-isomer 112 (0.11g). These were suitable for use as bisbenzyne equivalents in subsequent chemistry.

2,5-Bis(trimethylsilyl)-1,4-bis(triflyloxy)benzene (121). 1.00g (3.94 mmol) of hydroquinone 125 was dissolved in 25 mL of dry pyridine under N2 and cooled to 0 °C. 2.79g (1.67 mL, 9.88 mmol) of triflic anhydride was added dropwise, upon which a white solid precipitated. The mixture was warmed to room temperature and then heated to 50°C with stirring for one hour. After cooling to room temperature, the pyridine was evaporated to yield a brown solid mass with white solids mixed in. These solids were placed on a filter and washed with copious amounts of boiling hexanes until all of the white solids appeared to be off of the filter. The hexane filtrate was evaporated to give light yellow solids, which were recrystallized from hexanes to give 1.66g (81% yield) of 121 as off-white solids. $^1$H NMR (CDCl$_3$) $\delta$ 0.39 (s, 18H), 7.46 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ -1.28, 113.16, 116.69, 120.24, 123.77, 126.95, 137.41, 153.07.

2,5-Dibromohydroquinone (122). 11.0g (101 mmol) of hydroquinone was dissolved in 250 mL of glacial acetic acid. To this was added 32.0g (11 mL, 200 mmol) of bromine dissolved in 20 mL of glacial acetic acid dropwise. The resulting solution was stirred at room temperature for one hour and poured into 1 liter of water. The solution was allowed to stand overnight, upon which off-white needles had precipitated out. The solids were filtered, washed with water, and dried to give 7.11g (26% yield) of 122. $^1$H NMR (CDCl$_3$) $\delta$ 5.14 (s, 2H), 7.16 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 109.88, 118.55, 146.74.
1,4-Dibromo-2,5-bis(trimethylsilyloxy)benzene (123). 2.0g (7.46 mmol) of hydroquinone 122 was suspended in 30 mL of dry toluene in a flame-dried three-neck flask. To this was added 3 mL of dry pyridine, upon which 122 went into solution. The solution was heated to reflux under N2 and to this was added dropwise 4.86g (5.70 mL, 44.77 mmol) of TMSCl over one hour. Upon addition of TMSCl, white solids began to precipitate. The mixture was refluxed with stirring for six hours, cooled to room temperature, and the white solids filtered. The filtrate was evaporated to dryness to give 2.53g (82% yield) of 123 as light yellow solids. \(^1\)H NMR (CDCl3 w/no TMS) \(\delta\) 0.28 (s, 18H), 7.03 (s, 2H); \(^13\)C NMR (CDCl3 w/no TMS) \(\delta\) 0.22, 113.91, 124.12, 147.26.

1,4-Bis(trimethylsilyl)-2,5-bis(trimethylsilyloxy)benzene (124). 2.00g (4.85 mmol) of 123 was suspended in 50 mL of dry toluene in a flame-dried three-neck flask under N2. To this was added, in pieces, 0.50g (21.84 mmol) of sodium metal. The resulting suspension was heated to reflux. At this time, 1.10g (1.30 mL, 10.19 mmol) of TMSCl was dripped in over 30 minutes. The resulting mixture was refluxed overnight and then cooled to room temperature. The resulting dark blue solids were filtered off and the filtrate evaporated to give 1.60g (83% yield) of 124 as fluffy yellow solids. \(^1\)H NMR (CDCl3 w/no TMS) \(\delta\) 0.25 (s, 18H), 0.31 (s, 18H), 6.77 (s, 2H); \(^13\)C NMR (CDCl3 w/no TMS) \(\delta\) -1.10, 0.64, 122.42, 131.56, 153.92.

2,5-Bis(trimethylsilyl)hydroquinone (125). 1.00g (2.51 mmol) of tetra-TMS compound 124 was dissolved in 40 mL of dry dioxane. To this was added 2.5 mL of 6M HNO3 and the resulting solution was stirred at room temperature for 30 minutes. The solution was
poured into 80 mL of water, extracted with chloroform, the organic phase dried, and the solvent evaporated to give light yellow solids. After recrystallization from hexanes, 0.42g (66% yield) of 125 was obtained as an off-white solids. \(^1\)H NMR (CDCl\(_3\) w/no TMS) \(\delta\) 0.29 (s, 18H), 4.48 (s, 2H), 6.67 (s, 2H); \(^13\)C NMR (CDCl\(_3\) w/no TMS) \(\delta\) -0.82, 120.87, 128.22, 154.13.

**Mixture of 4,6-dibenzoyl-isophthalic acid (126) and 2,5-dibenzoyl-terephthalic acid (127).** A 250 mL 3-neck round bottom flask was fitted with a reflux condenser, drying tube, and glass stoppers. To the flask was added 5.00g (22.94 mmol) of pyromellitic anhydride and 150 mL of benzene. To this suspension was added with stirring, 12.23g (91.74 mmol) of AlCl\(_3\) was added in portions and the resulting mixture was refluxed for 3 hours. The mixture was then cooled to room temperature and ice chips added slowly with stirring. Concentrated HCl was added, at which point the dark brown/orange mixture became white. The benzene was evaporated and the aqueous suspension filtered, washed with copious amounts of water, and the solids dried in the oven to give 8.57g (100 % yield) of 126 and 127 as a white powder. \(^1\)H NMR (d\(_6\)-DMSO) \(\delta\) 7.53-8.56 (m, 24H), 13.74 (br, 4H); \(^13\)C NMR (d\(_6\)-DMSO) \(\delta\) 128.73, 128.77, 128.95, 129.15, 130.64, 133.28, 133.44, 133.51, 136.22, 136.26, 142.06, 144.83, 165.44, 165.70, 195.00, 195.05.

**Mixture of 3,5-diphenyl-5,6-dihydro-3H-2-oxa-s-indacene-1,7-dione (128) and 3,7-diphenyl-3,7-dihydro-benzo[1,2-c;4,5-c']difuran-1,5-dione (129).** To a large Erlenmeyer flask was placed 12.35g (32.08 mmol) of keto-acid mixture 126 and 127. To this was added enough 10% aqueous sodium hydroxide to effect solution. With stirring,
12.35g (311.22 mmol) of NaBH₄ was added and the resulting mixture stirred at room temperature for three days. At this point, the pH was adjusted to approximately 8 by addition of concentrated HCl. 2.50g (64.16 mmol) of NaBH₄ was added and the mixture stirred at room temperature for two days. The mixture was then acidified with concentrated HCl and the solids filtered and washed with water and dried to give 11.29g (100% yield) of bis-lactones 128 and 129 as a white solid. ¹H NMR (d₆-DMSO) δ 2.50 (s, 4H), 6.80-6.88 (m, 4H), 7.32-7.45 (m, 22H), 7.97 (s, 2H), 8.37 (s, 2H); ¹³C NMR (d₆-DMSO) δ 81.95, 120.34, 126.41, 126.84, 126.93, 127.07, 128.95, 129.15, 130.31, 136.02, 136.13, 150.50, 155.43, 155.63, 168.30, 168.45.

Mixture of 1,3,5,7-Tetraphenyl-5,7-dihydro-1H,3H-benzo[1,2-c;4,5-c']difuran-1,7-diol (130) and 1,3,5,7-tetraphenyl-5,7-dihydro-1H,3H-benzo[1,2-c;4,5-c']difuran-1,5-diol (131). To a flame-dried 250 mL round bottom flask flushed with N₂ was added 4.00g (11.70 mmol) of lactones 128 and 129 and 150 mL of dry THF. The resulting suspension was cooled to 0 °C in an ice bath and to it was added 16.4 mL (49.12 mmol) of a 3M solution of phenylmagnesium bromide dropwise over 20 minutes. The reaction became a deep red/brown solution at this time. The mixture was allowed to warm to room temperature overnight and was then quenched with aqueous NH₄Cl. The resulting mixture was extracted with ether and the ether extracts washed with water, brine, and dried over CaCl₂. The ether was removed by blowing N₂ over it in the hood. It is imperative that no heat be used in this evaporation. The resulting orange viscous oil was triturated with hexanes until it became a bright yellow powder. The solids were filtered, rinsed with hexanes, and dried to give 4.10g (70% yield) of lactols 130 and 131.
1,2,4,5-Tetrabenzoylbenzene (132). In a 125 mL Erlenmeyer flask was combined 75 mL of concentrated HNO₃ and 75 mL of glacial acetic acid. To this was added, with stirring, 133 (1.70g, 3.54 mmol) in one portion. The orange 133 instantly became white upon contact with the acid solution. After all the 133 was added, the resulting mixture was stirred until the color was completely gone, and then stirred an additional 10 minutes. The mixture was poured into 200 mL of water, the solids filtered, washed with water, and dried to give 132 as a white powder (1.68g, 96% yield). $^1$H NMR (CDCl₃) δ 7.38-7.43 (m, 8H), 7.52-7.57 (m, 4H), 7.72-7.84 (m, 10H); $^{13}$C NMR (CDCl₃) δ 128.82, 130.10, 130.39, 133.94, 136.37, 141.65, 195.29.

5,6-Dibenzoyl-1,3-diphenylisobenzofuran (133). To a 100 mL round bottom flask was dissolved KOH in 50 mL of 95% ethanol. To this was added, simultaneously, furan dialdehyde 85 (1.00g, 3.62 mmol) and commercially available dibenzoyl ethane (0.90g, 3.78 mmol). The mixture instantly turned orange. The mixture was stirred and refluxed for 2 to 3 hours. Upon cooling, the solids were filtered, washed with cold ethanol, and dried to give 133 as a bright orange powder (1.33g, 77% yield). For prolonged storage, 133 was stored in the refrigerator in the dark, where it appeared to be stable indefinitely. $^1$H NMR (CDCl₃) δ 7.32-7.58 (m, 12H), 7.80-7.93 (m, 8H), 8.12 (s, 2H); $^{13}$C NMR (CDCl₃) δ 120.06, 124.87, 125.38, 128.27, 128.47, 129.23, 129.85, 130.45, 133.00, 136.73, 130.39, 133.94, 136.37, 141.65, 195.80.

2,3,9,10-Tetramethylpentacene (134). In a flame-dried round bottom flask was added aluminum foil (2.50g, 93 mmol), HgCl₂ (0.05g, 0.184 mmol), and dry cyclohexanol (100
mL). To this was added one drop of CCl₄ and the resulting mixture was refluxed, with stirring, under N₂ overnight (caution: bring to reflux slowly, as gas evolution is rapid upon reflux). In the morning, the mixture was a light grey suspension. The heat was shut off, the mixture allowed to cool to under reflux temperature, and quinone 141 (1.46g, 4.01 mmol) was added in one portion. The resulting mixture was brought back up to reflux and heated under N₂ with stirring in the dark for 3 days. After this time, the reaction was a dark blue color. The mixture was cooled to room temperature and filtered through a frit being careful to shield the solids from light. The solids were then washed successively with hot acetic acid (2 x 50 mL), 25% HCl (2 x 50 mL), hot H₂O (2 x 50 mL), and ethanol (2 x 50 mL). The solids were then collected, dried under vacuum, and stored in the refrigerator under N₂ in the dark. Pentacene 134 was obtained in 96% yield (1.28g) as deep blue solids.

2,3,9,10-Tetramethyl-6,13-diphenylpentacene (135). Potassium iodide (0.288g, 1.73 mmol) was added to 20 mL of acetic acid and the resulting suspension stirred. To this was added diol 143 (0.22g, 0.423 mmol). The resulting suspension was heated to reflux for 2 hours, upon which time it became a deep red/brown solution. The mixture was cooled to room temperature and the solids filtered and washed with water to give pentacene 135 as dark blue solids (0.07g, 35% yield). Because pentacenes are unstable in solution and in light, the product was kept dry under N₂ and in the dark at all times.

Dimethyl-4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (137). To a round bottom flask was added 3.88g (47.32 mmol) of 2,3-dimethyl-1,3-butadiene, 6.72g (47.32...
mmol) of dimethylacetylene dicarboxylate, and 40 mL of benzene. The mixture was refluxed with stirring overnight and the solvent removed. The resulting waxy solids were washed with hexanes, filtered, and dried to give 7.10g (67% yield) of 137 as light yellow solids. $^1$H NMR (CDCl$_3$) $\delta$ 1.62 (s, 6H), 2.88 (s, 4H), 3.73 (s, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 17.85, 34.01, 52.05, 121.42, 132.64, 168.30.

4,5-Dimethylphthalic acid dimethyl ester (138). To a round bottom flask was added 2.00g (8.92 mmol) of Diels-Alder adduct 137, 2.80g (23.72 mmol) of 10% Pd/C, and 100 mL of o-dichlorobenzene. The resulting mixture was refluxed with stirring for three days. The reaction mixture was then cooled down, filtered through Celite, and the solvent removed to give an orange oil that crystallized over time to give 1.63g (82% yield) of 138 as orange crystals. $^1$H NMR (CDCl$_3$) $\delta$ 2.21 (s, 6H), 3.80 (s, 6H), 7.40 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 19.77, 52.60, 129.57, 130.17, 140.41, 168.39.

(1,2-Hydroxymethyl)-4,5-dimethyl benzene (139). To a flame-dried 3-neck flask under N$_2$ was added dry THF. This was cooled to -78 °C and to this was added, slowly and in portions, 0.512g (13.51 mmol) of LAH with stirring. To the resulting grey suspension was added a solution of 1.50g (6.75 mmol) of diester 138 dropwise over 1 hour. The suspension at this time became a murky brown color. After addition was complete, the mixture was allowed to warm to room temperature over 2 hours and then refluxed overnight. At this time, the reaction was a muddy green color. It was cooled to 0oC and 15% aqueous NaOH was added very slowly dropwise to quench the reaction. The reaction was then diluted with ice water and THF. The mixture was extracted with
diethyl ether and the ether extracts washed with water, brine, and dried. Removal of the solvent gave white solids (0.85g, 76% yield) of 139. $^1$H NMR (CDCl$_3$) $\delta$ 2.24 (s, 6H), 3.26 (br, 2H), 4.63 (s, 4H), 7.10 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 19.28, 63.91, 131.31, 136.74.

**4,5-Dimethylbenzene-1,2-dicarbaldehyde (140).** A round bottom flask was flame-dried and to it was added 120 mL of dry CH$_2$Cl$_2$. Under N$_2$, 1.71 mL (2.52g, 19.88 mmol) of oxalyl chloride was added and the mixture stirred and cooled to -78 °C. To this was added 2.82 mL (3.11g, 39.75 mmol) of DMSO in dry CH$_2$Cl$_2$ dropwise. The mixture was stirred for 5 minutes and then to it was added a solution of 1.50g (9.04 mmol) of diol 139 in CH$_2$Cl$_2$/DMSO dropwise. After complete addition, the peach-colored slurry was stirred for 30 minutes. 22.5 mL (16.2g, 160.4 mmol) of triethylamine was added dropwise and then reaction was then allowed to warm to room temperature. The mixture was poured into water, the layers separated, and the organic layer washed with copious amounts of water, brine, dried, and evaporated to give brown solids. Column chromatography with CH$_2$Cl$_2$ as eluant gave two bands, the second of which was 0.97g (66% yield) of 140 as a light yellow solid. $^1$H NMR (CDCl$_3$) $\delta$ 2.40 (s, 6H), 7.72 (s, 2H), 10.48 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 19.93, 132.42, 134.20, 143.47, 192.27.

**2,3,9,10-Tetramethylpentacene-6,13-dione (141).** In a round bottom flask was dissolved 0.92g (5.68 mmol) of dialdehyde 140 and 0.353g (3.15 mmol) of 1,4-cyclohexanedicarboxylic anhydride in 60 mL of ethanol. To this was added dropwise, with stirring, 10 mL of 5% aqueous KOH. Upon addition of the first drop, the solution became black, then
brown, and solids precipitated. The mixture was stirred at room temperature for 1 hour and the refluxed for 2 hours. The reaction was cooled and the solids filtered, washed with water, and dried to give the quinone 141 as a brown powder (0.91g, 79% yield).

[60] Fullerene adduct of 2,3,9,10-tetramethylpentacene (142). To a 100 mL round bottom flask was added [60] fullerene (0.640g, 0.898 mmol) and 50 mL of o-dichlorobenzene. Upon complete dissolution of the [60] fullerene, pentacene 134 (0.100g, 0.299 mmol) was added and the resulting mixture was stirred and heated to reflux in the dark under N₂ for 24 hours. At this time, the reaction was cooled to room temperature and the solvent removed to give a brown solid. The solids were rinsed through a filter with CHCl₃ to remove the bulk of the remaining [60] fullerene and the resulting filtrate evaporated, dissolved in CS₂, and subjected to flash column chromatography (CS₂ eluant). The brown band containing the monoadduct, which ran behind [60] fullerene, was collected, the solvent removed, and the solids dried under vacuum to give the mono[60] fullerene adduct 142 as brown solids (0.07g, 22% isolated yield). ¹H NMR (CS₂/CDCl₃) δ 2.51 (s, 12H), 5.92 (s, 2H), 7.69 (s, 4H), 8.06 (s, 4H); ¹³C NMR (CS₂/CDCl₃) δ 20.20, 58.24, 71.95, 123.24, 127.69, 131.70, 135.41, 136.78, 137.79, 139.71, 141.34, 141.71, 141.85, 142.22, 142.80, 144.30, 145.05, 145.09, 145.12, 145.83, 146.05, 155.10.

2,3,9,10-Tetramethyl-6,13-diphenylpentacene-6,13-diol (143). Quinone 141 (1.67g, 4.58 mmol) was suspended in 250 mL of dry toluene under N₂ in a flame-dried roundbottom flask. This mixture was cooled to -78 °C and stirred for ten minutes. To
this was added, dropwise, phenyllithium (1.5 M solution, 12.23 mL, 18.35 mmol) over 15 minutes. The resulting mixture was allowed to warm to room temperature overnight and stirred at room temperature. At this time, the reaction was quenched with aqueous NH₄Cl, the layers separated, and the organic layer dried and evaporated to give the product 143 as a brown powder (1.46g, 61% yield).

cis-Bisfullerene[60] adduct of 2,3,9,10-Tetramethyl-6,13-diphenylpentacene (144). In a 250 mL round bottom flask was placed [60]fullerene (0.52g, 0.72 mmol) and 100 mL of CS₂. This mixture was stirred in the dark under N₂ for 20 minutes and to it was added pentacene 135 (0.04g, 0.08 mmol). The resulting mixture was refluxed overnight in the dark under N₂ with stirring. The resulting brown solution was evaporated and the crude solids purified via column chromatography three times with CS₂ eluant (Rf=0.85) and then preparative TLC (CS₂ eluant) to give the bisfullerene[60] adduct 144 as a brown powder (0.70g, 44% yield). ¹H NMR (CS₂/CDCl₃) δ 2.37 (s, 12H), 5.62 (s, 4H), 7.05 (d, 2H), 7.28-7.37 (m, 6H), 7.49 (t, 2H), 7.64 (d, 2H), 7.74 (t, 2H); ¹³C NMR (CS₂/CDCl₃) δ 20.25, 55.01, 72.71, 127.00, 128.17, 128.99, 129.12, 129.82, 130.16, 135.38, 135.98, 136.87, 137.17, 137.96, 139.18, 139.55, 139.85, 140.08, 141.64, 141.78, 142.08, 142.28, 142.67, 144.70, 144.76, 145.44, 145.59, 146.20, 146.23, 146.45, 146.52, 147.55, 155.57, 156.12.

2,3,9,10-Tetramethyl-5,7,12,14-tetraphenyl-pentacene-6,13-dione (145). To a 100 mL round bottom flask was added 0.58g (1.85 mmol) of lactol 151 and 0.10g (0.926 mmol) of benzoquinone. To this was added 50 mL of benzene and to the stirred suspension was
added 3.18 g (18.52 mmol) of p-toluenesulfonic acid. The resulting mixture was refluxed with stirring through a Dean-Stark trap to azeotropically remove water throughout the reaction. Reflux was maintained overnight and then reaction was then cooled. The benzene mixture was washed with aqueous saturated sodium bicarbonate, water, brine, and dried over CaCl₂. The resulting black solution was evaporated to give light brown solids. These were dissolved in a minimal amount of acetone and to the solution was added hexanes. The resulting orange/brown solids were filtered and dried to give 0.13 g (21% yield) of quinone 145. ¹H NMR (CDCl₃) δ 2.24 (s, 12H), 7.21-7.38 (m, 24H); ¹³C NMR (CDCl₃) δ 20.62, 127.10, 128.01, 130.26, 131.65, 133.58, 138.09, 138.54, 139.05, 189.30.

Alternative Procedure for Preparing 145. To a round bottom flask was added 0.40 g (0.568 mmol) of diendoxide 155, 0.66 g (3.84 mmol) of dried pTsOH, and 50 mL of benzene. The resulting mixture was refluxed with stirring overnight, cooled, and washed with aqueous saturated sodium bicarbonate. The organic layer was dried and evaporated to give a black residue. To this was added a small amount of ice cold acetone and the mixture filtered and washed with a little cold acetone to give 145 as yellow solids (0.18 g, 47% yield).

5,6-Dimethyl-1,3-diphenylisobenzofuran (146). A round bottom flask was charged with 1.50 g (4.74 mmol) of 152, 0.15 g (0.872 mmol) of dried p-TsOH, and 60 mL of benzene. The resulting light yellow solution was stirred and refluxed for 1.5 hours. After ten minutes, a bright blue fluorescence developed on the surface of the mixture. After the reaction was complete, it was cooled, washed with aqueous saturated sodium bicarbonate,
and dried. The solvent was removed to give light orange solids which were recrystallized from ethanol to give isobenzofuran 146 as bright yellow solids. These are stored in the dark in order to prevent decomposition. 0.97g (69% yield) were obtained in this way. \( ^1H \) NMR (CDCl\(_3\)) \( \delta \) 2.33 (s, 6H), 7.25 (t, 2H), 7.46 (t, 4H), 7.59 (s, 2H), 7.93 (d, 4H); \( ^13C \) NMR (CDCl\(_3\)) \( \delta \) 21.18, 118.58, 122.28, 124.74, 126.66, 129.07, 132.16, 135.74, 142.72.

5,6-Dimethyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (147). 5.44g (66.4 mmol) of commercially available 2,3-dimethyl-1,3-butadiene and 5.00g (51.0 mmol) of maleic anhydride were suspended in 20 mL of benzene. The resulting mixture was brought gently to a boil and then refluxed for 20 hours. The solution was cooled to room temperature and the solvent evaporated to give a milky-white liquid which, upon cooling, solidified to give 9.14g (99% yield) of 147 as a white powder. \( ^1H \) NMR (CDCl\(_3\)) \( \delta \) 1.70 (s, 6H), 2.26-2.46 (m, 4H), 3.31-3.35 (m, 2H); \( ^13C \) NMR (CDCl\(_3\)) \( \delta \) 19.52, 30.69, 40.61, 127.58, 174.72.

5,6-Dimethylisobenzofuran-1,3-dione (148). To a round bottom flask was added 5.00g (27.77 mmol) of Diels-Alder adduct 147, 3.39g (27.74 mmol) of 10% Pd/C, and 125 mL of o-dichlorobenzene. The resulting mixture was refluxed with stirring for three days. The mixture was then cooled, filtered through Celite, and the solvent evaporated to give solids floating in a small remaining amount of solvent. To this was added hexanes and the solids filtered, washed with hexanes, and dried to give 3.34 g (68% yield) of 148 as golden flakes. \( ^1H \) NMR (CDCl\(_3\)) \( \delta \) 2.46 (s, 6H), 7.74 (s, 2H); \( ^13C \) NMR (CDCl\(_3\)) \( \delta \) 21.19, 126.56, 129.61, 146.91, 163.50.
2-Benzoyl-4,5-dimethylbenzoic acid (149). To a flame-dried 3-neck round bottom flask was added the following: 3.00g (17.04 mmol) of anhydride 148 and 150 mL of benzene. The flask was fitted with a reflux condenser with drying tube and stoppers. To the resulting stirred suspension was added 8.70g (65.11 mmol) of AlCl₃ in two portions. The initially light brown suspension became a dark red solution upon addition of the AlCl₃. The resulting mixture was refluxed with stirring for approximately 18 hours and then cooled to room temperature. Ice chips were added very slowly to the cooled mixture until no more bubbling was noted. To the resulting biphasic mixture was added concentrated HCl. The mixture was placed on the rotary evaporator to remove the benzene and the aqueous suspension filtered, washed with copious amounts of water, and dried to give 4.22g of keto-acid 149 as a light brown powder (98% yield). 

$^{1}$H NMR (CDCl₃) δ 2.21-2.25 (m, 6H), 7.00-7.74 (m, 7H), $^{13}$C NMR (CDCl₃) δ 19.55, 19.96, 125.37, 128.31, 128.85, 129.35, 131.75, 132.93, 137.23, 138.31, 140.16, 142.81, 170.44, 197.55.

5,6-Dimethyl-3-phenyl-3H-isobenzofuran-1-one (150). Keto-acid 149 (4.0g, 15.75 mmol) was dissolved in enough 10% aqueous NaOH to effect solution. To the stirred solution was added 2.89g (76.37 mmol) of NaBH₄ and the resulting light brown mixture stirred at room temperature for 70 hours. At this point, the pH was adjusted to approximately 8 via addition of concentrated HCl. To the mixture was then added 0.60g (15.75 mmol) of NaBH₄ and the reaction was stirred at room temperature for 40 hours. Concentrated HCl was added to destroy any excess NaBH₄ and to acidify the solution, at which point it became a milky white/brown color. The resulting solids were filtered,
washed with water, and dried to give 3.62g (97% yield) of lactone 150 as a light brown powder. $^1$H NMR (CDCl$_3$) $\delta$ 2.30-2.37 (m, 6H), 6.32 (s, 1H), 7.24-7.38 (m, 6H), 7.70 (s, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 20.16, 20.95, 82.62, 123.62, 125.98, 126.04, 127.11, 129.08, 129.31, 137.06, 138.74, 144.77, 148.14, 171.08.

5,6-Dimethyl-1,3-diphenyl-1,3-dihydro-isobenzofuran-1-ol (151). A flame dried 100 mL round bottom flask was flushed with N$_2$ and in it was suspended 4.20g (17.65 mmol) of lactone 150 in 120 mL of dry THF. The suspension was cooled to 0 °C in an ice bath and to it was added dropwise over twenty minutes 20 mL (60.0 mmol) of a 3M solution of phenylmagnesium bromide. Upon complete addition of the Grignard reagent, the mixture became a deep red solution. The mixture was allowed to warm up to room temperature with stirring overnight. The reaction was quenched with aqueous NH$_4$Cl and extracted with ether. The ether extracts were washed with water, brine, and dried over CaCl$_2$. The ether was evaporated with no heat by blowing N$_2$ over it in the hood. It is imperative that no heat be used in this evaporation. The resulting orange viscous oil was triturated with hexanes until it became a very light orange solid. The solids were filtered, rinsed with hexanes, and dried to give 4.33g (77% yield) of lactol 151.

1,2-Dibenzoyl-4,5-dimethylcyclohexa-1,4-diene (152). To a round bottom flask was added 1.75g (7.47 mmol) of dibenzoylacetylene 153, 0.80g (9.72 mmol) of 2,3-dimethyl-1,4-butadiene, and 60 mL of benzene. The resulting mixture was refluxed with stirring for 6 hours, cooled to room temperature, and the solvent removed to give an orange oil that crystallized on the vacuum pump. The solids were recrystallized from ethanol to

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give pure 152 as light yellow solids (2.10 g, 89% yield). $^1$H NMR (CDCl$_3$) $\delta$ 1.74 (s, 6H), 3.13 (s, 4H), 7.25 (t, 4H), 7.40-7.49 (m, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 18.32, 35.71, 122.56, 128.47, 129.25, 133.17, 137.35, 138.58, 198.30.

**Dibenzoyl acetylene (153).** To a round bottom flask was added 3.93 g (9.924 mmol) of dibromide 154 and 40 mL of acetone. To the stirred suspension was added 2.10 g (20.8 mmol) of triethylamine and the resulting white suspension was heated to reflux for 1 hour. At this point, the reaction was a red solution with solids floating in it. The reaction was cooled to room temperature and the triethylammonium bromide filtered off. The solvent was evaporated to give red solids. These were recrystallized from absolute ethanol twice to give 1.89 g (81% yield) of 153 as light yellow crystals. $^1$H NMR (CDCl$_3$) $\delta$ 7.54 (t, 4H), 7.69 (t, 2H), 8.19 (d, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 86.08, 129.20, 130.03, 135.40, 176.78.

**2,3-Dibromo-1,4-diphenylbutane-1,4-dione (154).** In an Erlenmeyer flask was placed 1.18 g (5.00 mmol) of commercially available dibenzoylethylene and 20 mL of glacial acetic acid. The mixture was stirred and warmed slightly to affect solution. To this was added, dropwise, 0.79 g (0.25 mL, 4.94 mmol) of bromine. The resulting suspension was stirred at room temperature for one hour and then cooled to 0 °C. The solids were filtered and dried to give 1.37 g (69% yield) of 154 as a white powder. $^1$H NMR (CDCl$_3$) $\delta$ 5.97 (s, 2H), 7.54-7.70 (m, 6H), 8.10-8.14 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 41.42, 129.31, 134.21, 134.70, 190.84.
2,3,9,10-Tetramethyl-5,7,12,14-tetraphenyl-7,12:5,14-dioxido-5,5a,6a,7,12,12a,13a,14-octahydro-6,13-pentacenedione (155). A 50 mL round bottom flask was charged with 0.20 g (0.671 mmol) of isobenzofuran 146, 0.033 g (0.31 mmol) of 1,4-benzoquinone, and 20 mL of ethanol. The resulting bright yellow suspension was heated to reflux with stirring for 2 hours, upon which time it had become a white suspension. The solids were filtered and dried to give the double Diels-Alder adduct 155 as a white powder (0.210 g, 97% yield). $^1$H NMR (CDCl$_3$) $\delta$ 2.07 (s, 6H), 2.19 (s, 6H), 3.25 (s, 2H), 4.27 (s, 2H), 6.64-6.67 (m, 6H), 6.93 (s, 2H), 7.10 (t, 4H), 7.23-7.26 (m, 2H), 7.58-7.61 (m, 6H), 7.76-7.79 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 20.04, 20.20, 58.46, 64.54, 89.38, 92.17, 120.33, 123.83, 126.87, 128.05, 128.29, 128.59, 129.22, 134.52, 134.88, 136.74, 137.00, 144.00, 144.93, 205.66.

2,3,9,10-Tetramethyl-5,7,12,14-tetraphenyl-6,13-dihydropentacene (156). Hydriodic acid (47%, 25.0 g) and acetic acid (150 mL) were mixed in a round bottom flask. To this mixture was added, with stirring, quinone 145 (0.11 g, 0.164 mmol). The resulting yellow/brown solution was refluxed with stirring for 5 days in the dark under N$_2$. At this time, the dark brown reaction mixture was cooled and quenched with aqueous potassium bisulfite, at which point it became light yellow and solids precipitated. The solids were collected by vacuum filtration, washed with aqueous bisulfite, water, and dried to give dihydropentacene 156 as a white powder (0.07 g, 67% yield).

[60] Fullerene adduct of 2,3,9,10-Tetramethyl-5,7,12,14-tetraphenylpentacene (157). A 250 mL round bottom flask was charged with [60]fullerene (0.337 g, 0.468 mmol) and
120 mL of toluene. This mixture was stirred under N₂ for 20 minutes, and to it was added dihydropentacene 156 (0.100g, 0.156 mmol) and DDQ (0.07g, 0.313 mmol). The resulting mixture was stirred and refluxed under N₂ in the dark overnight. The resulting brown solution was evaporated and TLC analysis (CS₂ eluant) revealed a brown spot that traveled behind [60 fullerene. The crude solids were washed with ethanol until the washings were clear. The material was then subjected to column chromatography, followed by two preparative TLC plates (all using CS₂ eluant) to give monoadduct 157 as a brown powder (0.021g, 10% isolated yield). ¹H NMR (CS₂/CDCl₃) δ 2.25 (s, 12H), 5.75 (s, 2H), 6.93-6.95 (m, 4H), 7.13-7.15 (m, 4H), 7.21-7.24 (m, 5H), 7.30-7.33 (m, 8H), 7.36-7.39 (m, 5H); ¹³C NMR (CS₂/CDCl₃) δ 20.42, 52.43, 71.99, 127.03, 127.24, 128.20, 128.55, 130.47, 130.82, 131.30, 135.43, 136.56, 137.87, 139.97, 141.85, 142.05, 142.15, 142.60, 142.94, 144.65, 145.37, 145.42, 145.61, 146.20, 146.39, 147.51, 156.03.

3,4-Hydroxymethylfuran (158). Lithium aluminum hydride (3.57g, 94.33 mmol) was added in portions to 175 mL of dry ether in a flame dried N₂ purged 3-neck flask. To this was added, with stirring, diethyl-3,4-furandicarboxylate (5.00g, 23.58 mmol) dropwise. The resulting mixture was stirred at room temperature for 2 hours and then refluxed overnight. The mixture was cooled and quenched very carefully with ethyl acetate. It was then extracted with ether, the ether extracts washed with water, dried, and the solvent removed to give 158 as a colorless oil (1.50g, 50% yield). ¹H NMR (CDCl₃) δ 4.43 (s, 4H), 4.65 (br, 2H), 7.32 (s, 2H); ¹³C NMR (CDCl₃) δ 55.00, 124.64, 141.37.

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3,4-Benzoxymethylfuran (159). In 20 mL of DMF was dissolved 158 (1.50g, 11.72 mmol). The solution was cooled to 0 °C and to it was added, in portions, NaH (0.675g, 28.12 mmol). After stirring for 15 minutes, benzyl bromide (4.40g, 25.78 mmol) was added in dropwise over 1 hour. The mixture was warmed to room temperature, stirred 16 hours, and poured into water. The mixture was extracted with ether, the extracts dried, and the solvent removed to give 159 as a light yellow oil (2.63g, 73% yield). \( ^1H\) NMR (CDCl\(_3\)) \( \delta \) 4.39-4.46 (m, 8H), 7.25-7.35 (m, 12H); \( ^{13}C\) NMR (CDCl\(_3\)) \( \delta \) 62.65, 72.16, 121.91, 127.71, 127.89, 128.47, 138.27, 141.87.

5,6-Bis(benzyloxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (160). Dimethylacetylene dicarboxylate (1.16g, 8.18 mmol) and 159 (2.40g, 7.79 mmol) were combined and heated to 110 °C in an oil bath with stirring for 1 hour. Upon cooling, 160 was collected as an amber oil (3.20g, 91% yield). \( ^1H\) NMR (CDCl\(_3\)) \( \delta \) 3.71 (s, 6H), 4.28-4.52 (m, 8H), 5.69 (s, 2H), 7.28-7.33 (m, 12H); \( ^{13}C\) NMR (CDCl\(_3\)) \( \delta \) 52.31, 64.10, 72.45, 86.89, 127.79, 127.87, 128.47, 137.86, 148.73, 152.74, 163.14.

4,5-Bis(benzyloxymethyl)phthalic acid dimethyl ester (161). To a flame dried 3-neck round bottom flask purged with N\(_2\) was added 300 mL of dry THF. The flask was cooled to 0 °C and to it was added, slowly and dropwise, TiCl\(_4\) (11mL, 96.71 mmol). To the resulting bright yellow solution was added, in portions, LAH (1.35g, 35.55 mmol). Upon each addition, a black layer formed on top of the solvent, which eventually, with stirring, became uniformly green. Upon complete addition of the LAH, 18 mL of triethyl amine.

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was added. The resulting mixture was stirred and heated to reflux for 10 minutes. The mixture was cooled and a solution of endoxide 160 (3.20 g, 7.11 mmol) in dry THF was added. The mixture was refluxed with stirring for 24 hours, cooled to room temperature, and poured into 400 mL of water. The mixture was extracted with CH$_2$Cl$_2$, the extracts washed with water, dried, and the solvent removed to give 161 as a brown oil (2.30 g, 74% yield). $^1$H NMR (CDCl$_3$) $\delta$ 3.89 (s, 6H), 4.52-4.58 (m, 8H), 7.27-7.33 (m, 10H), 7.81 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 52.16, 68.29, 72.24, 127.37, 128.00, 128.26, 130.60, 137.12, 139.27, 167.43.

1,2-Bis(benzyloxymethyl)-4,5-bis(hydroxymethyl)benzene (162). In 50 mL of dry THF was dissolved 161 (2.30 g, 5.29 mmol). LAH (2.60 g, 68.7 mmol) was added in four portions, and the resulting mixture was stirred at room temperature 15 minutes and then refluxed with stirring under N$_2$ for 3 hours. The mixture was cooled, quenched carefully with ethyl acetate, water was added, and it was extracted with CH$_2$Cl$_2$. The extracts were dried and the solvent removed to give 162 as a brown oil (0.950 g, 48% yield). $^1$H NMR (CDCl$_3$) $\delta$ 4.47-4.52 (m, 12H), 7.26-7.31 (m, 12H); $^{13}$C NMR (CDCl$_3$) $\delta$ 63.53, 69.59, 72.80, 127.99, 128.15, 128.65, 130.41, 136.39, 138.11, 139.21.

1,2-Bis(benzyloxymethyl)benzene-4,5-dicarbaldehyde (163). To a flame dried N$_2$ purged round bottom flask was added 30 mL of dry CH$_2$Cl$_2$. Oxalyl chloride (0.68 mL, 7.69 mmol) was added and the mixture cooled to -78 °C. To this was added dry DMSO (1.10 mL, 15.43 mmol) in a little bit of CH$_2$Cl$_2$ very slowly dropwise. This was stirred 2 minutes, and then to it was added a solution of 162 (0.950 g, 2.51 mmol) in CH$_2$Cl$_2$ (with
a little bit of DMSO added) dropwise. The resulting mixture was stirred at -78 °C for 1 hour. Triethylamine (5.39 mL, 38.7 mmol) was added, the mixture stirred 5 minutes, and then allowed to warm to room temperature. The mixture was poured into water, extracted with CHCl₃, the organic extracts washed with water, brine, dried, and the solvent removed to give 163 as a brown oil (0.60g, 64% yield). ¹H NMR (CDCl₃) δ 4.57-4.62 (m, 8H), 7.30-7.34 (m, 10H), 8.05 (s, 2H), 10.49 (s, 2H); ¹³C NMR (CDCl₃) δ 68.38, 72.80, 127.63, 127.75, 128.30, 130.47, 135.21, 137.19, 142.28, 191.89.

2,3,9,10-Tetrakis(benzyloxymethyl)-6,13-pentacenequinone (164). Cyclohexane-1,4-dione (0.0374g, 0.334 mmol) and 163 (0.250g, 0.668 mmol) were combined in a round bottom flask and to them was added 20 mL of 95% ethanol. To this stirred mixture was added 5 mL of aqueous KOH. The initially light yellow solution immediately became black upon KOH addition, and after a few minutes, became brown with solids. This mixture was stirred at room temperature for 24 hours. Water was added and the solids were filtered, washed with water, washed with ethanol, and dried to give 164 (0.196g, 75% yield) as a brown powder. ¹H NMR (CDCl₃) δ 4.65-4.80 (m, 16H), 7.38-7.41 (m, 20H), 8.17 (s, 4H), 8.91 (s, 4H); ¹³C NMR (CDCl₃) δ 69.97, 73.08, 128.18, 128.84, 129.61, 129.69, 131.08, 134.95, 138.08, 138.70, 183.20.

1,3-Diphenylisobenzofuran-5,6-dicarbaldehyde (165). Absolute ethanol (100 mL) was used to dissolve quinone bisfuran 167 (1.00g, 2.94 mmol) in a round bottom flask. To this stirred solution was added KBH₄ (1.58g, 29.4 mmol) and the resulting mixture was refluxed under N₂ overnight. The heating was stopped and, while still warm, the mixture

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was acidified with 10% HCl in HOAc. The initially orange solution became yellow and developed an intensely glowing fluorescence on the surface. The mixture was kept in the dark, allowed to cool, and to it was added CHCl₃. The organic layer was washed with brine, dried, and rotovapped, being careful to do each step in the dark. The resulting bright orange solid was placed on the vacuum pump to dry and 165 (0.43g, 45% yield) was obtained as a bright orange solid. ¹H NMR (CDCl₃) δ 7.43 (t, 2H), 7.55 (t, 4H), 7.96 (4H), 8.46 (s, 2H), 10.44 (s, 2H); ¹³C NMR (CDCl₃) δ 120.49, 125.98, 129.31, 129.65, 130.12, 130.32, 132.90, 149.14, 192.10.

1,3-Diphenylbenzo[1,2-c;4,5-c']difuran-4,8-dione (167). To a flame dried round bottom flask purged with N₂ was added AlCl₃ (3.02g, 22.7 mmol), diphenyl furan (2.01g, 9.15 mmol), and 60 mL of dry CH₂Cl₂. To this was added, with stirring, a solution of diacid chloride 169 (1.48g, 7.63 mmol) in 50 mL of dry CH₂Cl₂. The mixture was stirred at room temperature for 18 hours and then refluxed an additional 6 hours. The mixture was cooled and ice chips were added, followed by concentrated HCl. The CH₂Cl₂ was evaporated off and the resulting brown residue was pumped on for 24 hours. The residue was triturated with cold acetone and filtered to give 167 (2.02g, 78% yield) as a bright yellow powder. ¹H NMR (CDCl₃) δ 7.51-7.53 (m, 6H), 8.17 (s, 2H), 8.38-8.40 (m, 4H); ¹³C NMR (CDCl₃) δ 121.05, 125.89, 128.46, 128.64, 131.20, 145.86, 156.50, 176.58.

Furan-3,4-dicarboxylic acid (168). To a round bottom flask was added diethylfuran-3,4-dicarboxylate (2.836g, 13.37 mmol) and 30 mL of MeOH/H₂O (5:1 v/v). To the resulting solution was added, dropwise over 45 minutes, 12 mL of 3M aqueous NaOH.
The resulting mixture was stirred for 90 minutes at room temperature, and then refluxed for 45 minutes. After cooling, the mixture was rotovapped to half its volume, acidified with 6M HCl, and extracted with ethyl acetate. The aqueous phase was saturated with NaCl, extracted with ethyl acetate, and the combined ethyl acetate extracts washed with brine, dried, and evaporated to give 1.59g (76% yield) of 168 as a tan/off-white powder.

**Furan-3,4-dicarbonyl dichloride (169).** To a round bottom flask was added diacid 168 (0.228g, 1.46 mmol), thionyl chloride (0.57 mL, 0.94g, 7.82 mmol), and 10 mL of toluene. The resulting mixture was refluxed for 3 hours, rotovapped to dryness, and placed on a vacuum pump for 24 hours to give 169 (0.27g, 98%) as a beige solid. It was used as is in the next reaction without further manipulations.

**5,8-Dimethoxy-1,4-dihydrobenzo[l,2]oxathiine-3-oxide (174).** Into a round bottom flask was placed 178 (6.30g, 19.44 mmol), Rongalite (5.98g, 38.88 mmol), tetrabutylammonium bromide (0.625g, 1.94 mmol), and 60 mL of dry DMF. The resulting mixture was stirred in the dark at room temperature for 24 hours. At this time, water was added, the mixture extracted with CH₂Cl₂, the organic layers washed with water, and dried. The solvent was removed on the rotary evaporator with the bath temperature never exceeding 40 °C. The residue was dried on the vacuum pump to give sultine 174 as white solids (4.00g, 96% yield). ¹H NMR (CDCl₃) δ 3.59-3.60 (m, 1H), 3.78-3.79 (m, 6H), 4.09-4.11 (m, 1H), 5.12-5.16 (m, 2H), 6.76 (s, 2H); ¹³C NMR (CDCl₃) δ 48.08, 55.69, 55.76, 56.59, 108.95, 109.11, 114.48, 121.81, 149.11, 151.20.
1-Methoxy-2,3-dimethylbenzene (175). Solid NaOH (23.27g, 582 mmol) was dissolved in 210 mL of water. To this solution was added, with stirring, 2,3-dimethylphenol (50.0g, 410 mmol). The solution was cooled to 0 °C and to it was added dimethyl sulfate (61.2g, 46.0 mL, 557 mmol) dropwise over 10 minutes. The resulting mixture was stirred for 30 minutes, warmed to room temperature, and refluxed 90 minutes. The mixture was cooled, extracted with ether, dried, and the solvent evaporated to give 175 as a light yellow oil (48.2g, 86% yield). $^1$H NMR (CDCl$_3$) δ 2.38 (s, 3H), 2.48 (s, 3H), 3.98 (s, 3H), 6.91 (d, 1H), 7.00 (d, 1H), 7.26 (t, 1H); $^{13}$C NMR (CDCl$_3$) δ 11.40, 19.89, 55.26, 107.71, 122.12, 124.82, 125.70, 137.64, 157.42.

1-Bromo-4-methoxy-2,3-dimethylbenzene (176). In a round bottom flask, 175 (48.0g, 353 mmol) was dissolved in acetic acid. To it was added a solution of bromine (66.1g, 22 mL, 413 mmol) in acetic acid dropwise with stirring over 1 hour. To the resulting mixture was added water (1700 mL) and Na$_2$SO$_3$ until the solution became light yellow/white. To this mixture was added 170 mL of CH$_2$Cl$_2$ and the resulting mixture was stirred for 30 minutes. The organic phase was collected placed in an Erlenmeyer flask, and to it was added 2M NaOH to wash it free of acids. The organic phase was collected, dried, and the solvent evaporated to give 176 as an orange oil (61.78g, 81% yield). $^1$H NMR (CDCl$_3$) δ 2.24 (s, 3H), 2.40 (s, 3H), 3.82 (s, 3H), 6.61 (d, 1H), 7.37 (s, 1H); $^{13}$C NMR (CDCl$_3$) δ 12.94, 19.89, 55.69, 109.35, 116.41, 127.04, 129.66, 136.90, 156.72.
1,4-Dimethoxy-2,3-dimethylbenzene (177). In a round bottom flask was placed 135 mL of dry methanol. To it was added, in portions, sodium metal (13.71g, 596 mmol) with stirring until all of the sodium was dissolved. To this solution was added 135 mL of dry DMF, bromo compound 176 (53.86g, 251 mmol), and freshly purified CuI (3.20g, 16.8 mmol). The resulting mixture was refluxed for 24 hours, cooled, and to it was added water. The resulting tan solids were filtered, washed with copious amounts of water, and dried to give 177 (40.0g, 96% yield) as tan solids. $^1$H NMR (CDCl$_3$) δ 2.19 (s, 6H), 3.80 (s, 6H), 6.68 (s, 2H); $^{13}$C NMR (CDCl$_3$) δ 12.02, 56.01, 107.75, 126.65, 151.85.

2,3-Bis(bromomethyl)-1,4-dimethoxybenzene (178). To a round bottom flask was added 177 (4.00g, 24.09 mmol), NBS (10.72g, 60.24 mmol), benzoyl peroxide (0.40g), and 300 mL of benzene. The resulting mixture was stirred and refluxed 24 hours. The mixture was cooled, quenched with aqueous sodium bisulfite, washed twice with water, and the benzene layer dried and evaporated to give light yellow solids of 178 (6.9 lg, 88%). $^1$H NMR (CDCl$_3$) δ 3.85 (s, 6H), 4.73 (s, 4H), 6.83 (s, 2H); $^{13}$C NMR (CDCl$_3$) δ 24.13, 56.44, 112.31, 126.58, 151.94.

cis-Bis[60]fullerene] adduct of 184 (183). 0.296g (.412 mmol) of [60]fullerene was dissolved in 120 mL toluene. To this solution was added 0.05g (.083 mmol) of 184, 0.07g (.412 mmol) of KI, and 0.35g (1.34 mmol) of 18-crown-6. The solution was degassed and then refluxed under N$_2$ in the dark for 24 hours. The initially purple solution was brown upon completion of reflux. The solvent was evaporated from the crude mixture and the resulting solids were purified by flash column chromatography.
with either 100% CS₂ or 100% toluene as eluant. The product eluted nearly on top of [60]fullerene and could not be separated completely. The product solids were then washed with CHCl₃ until the CHCl₃ washes were clear in color. The solids left in the filter paper were further purified by washing the crude solids in a Soxhlet extractor with refluxing THF to give the purified product as the solids left in the thimble. ¹H NMR (CS₂/CDCl₃) δ 4.39 (d, 4H), 4.63 (d, 4H), 6.84 (d, 2H), 7.11 (t, 2H), 7.33 (t, 2H), 7.57 (t, 2H), 7.64 (d, 2H).

1,2,4,5-Tetrakis(bromomethyl)-3,6-diphenylbenzene (184). To a suspension of 1.00g (3.5 mmol) of 186 in 50 mL of CCl₄ was added 5.00g (27.9 mmol) of N-bromosuccinimide and a spatula-tip of benzoyl peroxide. The suspension was refluxed for 24 hours, cooled to room temperature, and the solvent evaporated. The resulting orange solids were washed with copious amounts of boiling acetone to give 1.40g of 184 as a white powder in 67% yield. ¹H NMR (CDCl₃) δ 4.39 (br. s, 8H), 7.20-7.40 (m, 10H).

1,4-Dibromo-2,3,5,6-tetramethylbenzene (185). To a round bottom flask fitted with a reflux condenser was added durene (25.0g, 187 mmol), iodine (1.00g, 7.80 mmol) and 150 mL of CH₂Cl₂. This solution was stirred and bromine (24.0 mL, 74.6g, 467 mmol) in 100 mL CH₂Cl₂ was dripped in at room temperature under rigorous exclusion of light. A gas trap was installed at the top of the condenser to remove the formed HBr gas safely. The reaction was then refluxed for 1 hour, cooled, and 50 mL of 5M aq. NaOH was added. The layers were separated, and the organic layer was washed with water, dried,
and then placed in an ice bath. The formed solids were filtered, washed with water, and
dried to give **185** (50.6g, 93% yield). $^1$H NMR (CDCl$_3$) $\delta$ 2.47 (s, 12H); $^{13}$C NMR
(CDCl$_3$) $\delta$ 22.26, 128.09, 134.98.

**1,4-Diphenyl-2,3,5,6-tetramethylbenzene (186).** To a mixture of 2.00g (6.85 mmol) of
1,4-dibromodurene **185**, 3.34g (27.4 mmol) phenyl boronic acid, and 0.08g (.0686 mmol)
of tetrakis(triphenylphosphine) palladium was added 40 mL of toluene and 40 mL of 1 M
aqueous Na$_2$CO$_3$. The resulting mixture was refluxed under an N$_2$ atmosphere for 5 days
with vigorous stirring. Over this period of time, the reaction mixture went from light
yellow to green to a red color. After 5 days, the heating was stopped and the reaction was
poured into a separatory funnel. The layers were separated and the organic layer washed
with water, dried over CaCl$_2$, and the solvent evaporated to yield 1.65g (84% yield) of
**186** as an off white solid. The crude material is pure as is, although it can be
recrystallized from ethyl acetate; however, the slight solubility in ethyl acetate results in
some loss of product. $^1$H NMR (Benzene-d$_6$) $\delta$ 1.96 (s, 12H), 7.11-7.22 (m, 10H); $^{13}$C
NMR (Benzene-d$_6$) $\delta$ 18.20, 126.50, 128.61, 129.59, 131.85, 141.60, 143.44.
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FULLERENE-ACENE CHEMISTRY: PART I: STUDIES ON THE REGIOSELECTIVE REDUCTION OF ACENES AND ACENE QUINONES; PART II: PROGRESS TOWARD THE SYNTHESIS OF LARGE ACENES AND THEIR DIELS-ALDER CHEMISTRY WITH [60]FULLERENE

VOLUME 2

APPENDICES

BY

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B.S. University of New Hampshire, 2001

DISSERTATION

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%Int.  11 mV[sum= 219 mV] Profiles 1-20 Smooth Av 2

MW=308
Data: NQ;DHB matrix;1b_0001;J5 23 Jun 2004 15:41 Cal: Heather 23 Jun 2004 14:10
Kratos PC Axima CFRplus V2.3.4: Mode reflection_1ghz, Power: 90, P.Ext. @ 500 (bin 84)

%Int.  25 mV[sum= 686 mV] Profiles 1-27 Smooth Av 2

MW=508

34

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Kratos PC Axima CFRius V2.3.4: Mode reflectron_1ghz, Power: 98, P.Ext. @ 500 (bin 84)

%Int. 15 mV [sum: 136 mV] Profiles 1-9 Smooth Avg 2

MW=608

[Mass/Charge diagram]