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Tridecacyclene: Synthesis and Structural Properties of Non-Planar Polycyclic Aromatic Hydrocarbons and Studies Towards a Fragment of the Fullerene C240

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TRIDECACYCLENE: SYNTHESIS AND STRUCTURAL PROPERTIES OF NON-PLANAR POLYCYCLIC AROMATIC HYDROCARBONS AND STUDIES TOWARDS A FRAGMENT OF THE FULLERENE C_{240}

A Dissertation Presented

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Daniel Sumy

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ABSTRACT

While investigating strategies to prepare precursors to highly strained buckybowls, we focused our attention on the Lewis acid aldol cyclization of 1-acenaphthenone derivatives which has been shown to produce a cyclic tetramer as a byproduct. Surprisingly, despite the interesting structural and electronic properties that have recently been observed as a result of the incorporation of eight-membered rings into polycyclic aromatic hydrocarbons, this cyclic tetramer has largely been ignored. As a result of this, we set our sights on the isolation and characterization of this cyclic tetramer.

The initial approach employed subjecting 1-acenaphthenone to the most common conditions used in trimerization—TiCl$_4$ in boiling o-dichlorobenzene. Surprisingly, this resulted in exclusive formation of the cyclic tetramer, which we have named tridecacyclene. The results of these studies were promising, establishing structural characterization and supramolecular assemblies with C$_{60}$ in the solid-state. The optoelectronic properties revealed a significantly lower reduction potential (~0.4 eV) than the trimeric species of 1-acenaphthenone. This is attributed to the central eight-membered ring of tridecacyclene. Reduction proceeded through two single-electron processes.

Further examining the electrochemical properties, we were able to gain new insight into the relation of structure and aromaticity. Reduction of tridecacyclene with potassium metal allowed us to characterize the radical anion and dianion through NMR and UV-Vis spectroscopy. Solid-state analysis of the dipotassium adduct revealed that despite the propensity of the reduced form of cyclooctatetraene derivatives to flatten as the molecule adopts a Hückel aromatic core, tridecacyclene maintains its tub shape. Significant bond equalization was observed in the center eight-membered ring—a strong indication of a delocalized $\pi$-system. This was supported by harmonic oscillator model of aromaticity calculations of the central ring with the value increasing from 0.09 to 0.48 where a value of 1 indicates a fully aromatic ring.

Tridecacyclene represents the precursor to a fragment of the fullerene C$_{240}$. A broad variety of reactions to facilitate the necessary strain inducing C–C bonds to form the fragment have been attempted. To date, we have not been able to synthesize the fragment. However, the parent molecule tridecacyclene shows great promise in the development of non-aqueous redox flow batteries and is currently being explored for this purpose in our laboratory.
CITATIONS

Material from this dissertation has been published in the following form:


DEDICATION

For all of the time we spent together fishing on the Westfield river and all the great memories I have of those days, this work is dedicated to the memory of my grandfather, Donald Kordana.
ACKNOWLEDGEMENTS

In the pursuit of a Ph.D. in chemistry there exists a multitude of ups, downs and all emotions in-between. Through these experiences, we rely on our family and peers to get through the challenges of research. Because of this, there are several people I would like to thank.

At the forefront, my advisor Adam Whalley has been everything and more than one can ask for in an advisor. His unwavering support to both me and the rest of the group made working in the group the best part of walking onto campus every day. More importantly, he has been an excellent friend to me and I always enjoyed our excursions out into the woods to find creeks and rivers to catch trout in. I also greatly enjoyed his subtle references to *Seinfeld*. Professor Matthias Brewer, for accepting me into the program is something I am very grateful for and your support has been invaluable in both my research and professional career. (And it was great to stop and chat VWs with you—specifically, the perils of a 40-year-old electrical system) Professors Matthew Liptak and Adrien del Maestro for sitting on my graduate studies committee and offering excellent advice and helping me through graduate school.

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vast library of pop hits from the mid 2000s, and admittedly we briefly considered throwing it out the window. Team Vortex, for being the exclusive cool-kids club (not) of the entering class into the department in 2012 and keeping us all together even as we fell down the rabbit hole of research. And for the Chem Department, for all those rambunctious nights out downtown where all of our conversations circled back to research, Ramya, Sarah, Magenta, Christine, Nick, Ellie, Jordan, Ariel, Natalie, Teruki, Sandy, Joel, and Corinne. Mona, for being a great friend and sharing all those high fives with me.

None of this could have been possible without my family. Mom, thank you for all the support you’ve given me over the past five years. You’ve always had the best advice and have been there when I needed it most, whether it be a broken-down Jeep, stress, or moving to a new apartment. Dad for always finding time to come visit me, go to car shows and supporting me through graduate school. Dave, for helping me keep my cars on the road and always providing support when I needed it. Mindy, you’ve grown so much over the past years and have been a wonderful mother to Derek. Uncle Kenny, for always taking time to talk careers with me and helping me in my pursuit of a job post-graduation. Grandma, for helping me move, coming up to visit me with Mom, and keeping an eye out for furniture for my apartment at the second-hand store.
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CHAPTER ONE: NONPLANAR AROMATIC HYDROCARBONS AND THEIR APPLICATIONS

1.1. Introduction

As the world continues to exploit fossil fuel reserves, there has been a growing concern over both the depletion of these resources and the consequences of increasing the concentration of atmospheric carbon dioxide—a known greenhouse gas. Unfortunately, modern society has grown dependent on the services and materials provided from these resources, and simply scaling back consumption of fossil fuels without a viable alternative would greatly decrease quality of life and have severe economic ramifications. As such, interest in developing new types of energy that are both renewable and more efficient at producing power than what is currently available has been a growing field over the past few decades. The past 30 years have shown new development in using carbon-based materials to meet these demands. Carbon allotropes, which include carbon nanotubes (CNTs), graphene, and fullerenes (Figure 1.1) have garnered an important focus in energy research as their unique electronic properties and extreme durability show potential for use in energy storage, superconductors, nanodevices and lightweight materials.\(^1\) Of these allotropes, the fullerenes, which are well known for their spherical structure

Figure 1.1: Allotropes of carbon have become attractive candidates for energy technology due to their exceptional electronic and physical properties.

are non-planar polycyclic aromatic hydrocarbons (PAHs) and consist of a carbon skeleton where curvature is introduced through pentagonal rings incorporated within the larger hexagonal network. Fullerenes are known to exist in a variety of sizes but research has been focused mostly on buckminsterfullere, C\textsubscript{60}, which was first isolated by Smalley in 1985 while exploring the mechanisms of formation of long-chain carbon molecules in space.\textsuperscript{2} Through vaporization of graphite by laser irradiation Smalley was able to repeatedly detect a high concentration of a cluster of 60 carbon atoms through time of flight mass spectrometry (TOFMS). The only structure they argued that could possibly exist to allow a cluster of 60 carbon atoms was the truncated icosahedron. Unfortunately, they could only speculate to the spherical structure, as they had no further means of characterization.

To study the structure, a scalable synthesis of C\textsubscript{60} was needed and in 1990 Huffman and coworkers reported the first macroscopic synthesis of C\textsubscript{60} through evaporation of graphitic carbon utilizing graphitic electrodes under an atmosphere of

high-pressure helium. The resulting soot was removed from the collecting surface and dispersed in benzene to dissolve the C\textsubscript{60}. The fullerene suspension was filtered to remove insoluble impurities and concentrated under gentle heating to reveal a black crystalline solid. A separate synthesis reported by Johnson produced buckminsterfullerene on a gram scale through the combustion of graphite. Soot collected from the combustion of graphite contained high levels of C\textsubscript{60} and smaller amounts of a slightly larger fullerene, C\textsubscript{70}. Furthermore, they were able to control the ratio of C\textsubscript{60} to C\textsubscript{70} through the flame conditions with higher pressures yielding larger amounts of C\textsubscript{70}.\textsuperscript{3} X-ray powder (XRD) and single-crystal X-ray diffraction (SC-XRD) studies on the fullerene material suggested that the fullerenes pack tightly in an ordered array and confirmed the structure theorized by Smalley.\textsuperscript{4,5}

The large-scale syntheses of C\textsubscript{60} made the study of their structure and electronic properties more accessible. However, there were still obstacles to overcome with C\textsubscript{60} as these syntheses required large amounts of solvent to both prepare and use the fullerene, as solubility was still quite limited. Fortunately, C\textsubscript{60} was easy to functionalize with reactivity similar to alkenes.\textsuperscript{6} Thus a library of substituted buckminsterfullerene derivatives was prepared through nucleophilic, radical and cycloaddition reactions with

\textsuperscript{3} Howard, J.B.; Mckinnon, T.J.; Makarovsky, Y.; Lafleur, A.L.; and Johnson, M.E. \textit{Nature} 1991, 139–141
Scheme 1.1: The reactivity of buckminsterfullerene allowed for the synthesis of a variety of derivatives. Some selected examples include (a) $[3 + 2]$ cycloaddition with azomethine ylides (b) Carbene addition to give PCBM (c) Bingel-Hirsch reaction d) $[3 + 2]$ cycloaddition with dienes e) organometallic additions

[6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) prepared by Wudl arguably the most widely used fullerene derivative (Scheme 1.1).$^7$

The study of C$_{60}$ revealed some unique properties, one of which was the electron accepting ability. In 1986, it was theorized that C$_{60}$ contained a triply degenerate LUMO capable of accepting six electrons.$^8$ Subsequent electrochemical studies produced the di,$^9$ tri,$^{10}$ tetra$^{11}$ and penta-anions$^{12}$ with Echegoyen demonstrating the hexanion in 1992.$^{13}$ As

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a result buckminsterfullerene has been extensively used in the development of bulk heterojunctions for organic photovoltaics with the fullerene acting as the electron acceptor.\textsuperscript{14}

Despite all the fascinating properties and uses that fullerenes have demonstrated, there still was an opportunity to develop this new field of chemistry, known as fullerene chemistry, further. As demonstrated, fullerenes are isolated as a product of combustion of carbon—a process that requires harsh conditions and tedious purification to remove any undesired fullerene sizes. Additionally, while \textit{C}_{60} has proved accessible and to an extent \textit{C}_{70}, accessing larger fullerenes still remains a formidable challenge. Thus, attention was drawn to the synthesis of easier to prepare materials that might mimic the properties of fullerenes.

Non-planar aromatics became the focus of this research with the most common examples being small, bowl-shaped fragments of fullerenes known as buckybowls. These PAHs contained the same carbon framework as fullerenes and with that may exhibit very similar properties. Thus, a synthesis of a buckybowl could allow much broader access to the novel properties seen in fullerenes without the associated limitations on synthesis (ie, a much larger library of different sized fragments could be synthesized rather than the

\begin{itemize}
\item Xie, Q.; Perez-Cordero, E.; and Echegoyen \textit{J. Am. Chem. Soc.} 1992, 114, 3978–3980
\end{itemize}
few examples of fullerenes available). The following sections of this chapter will focus on key developments in the synthesis of buckybowls and the observed electrochemical and supramolecular properties. The final sections will explore the Lewis-acid mediated cyclization of 1-acenaphthenone and 1-indene derivatives used extensively in the preparation of precursors to buckybowls and C\textsubscript{60}, highlighting the opportunity to tune this reaction for preparation of a new class of non-planar PAHs with a central eight-membered ring. The importance of this and significance to the work done in the Whalley research lab will be outlined with a research plan.

1.2 Buckybowls

Nearly two decades before Smalley’s landmark discovery of C\textsubscript{60}, a small bowl-shaped hydrocarbon was reported by Barth and Lawton.\textsuperscript{15} This non-planar PAH which was dubbed corannulene, (Figure 1.2) consists of a central five-membered ring flanked by five fused hexagonal rings, making it a part of the [\(n\)]circulene family of PAHs. When compared to C\textsubscript{60}, it becomes apparent that this compound makes up a small bowl-shaped fragment of the curved surface. Unfortunately, Barth and Lawton’s synthesis of corannulene was both lengthy and low yielding (~0.6 % overall) and limited the ability to study it further. As a result, there were no developments in the synthesis or studies on its

Figure 1.2: Open geodesic polyarenes or more commonly referred to as buckybowls represent a portion of the curved surface of a fullerene.

properties until the discovery and isolation of $C_{60}$ and SWCNTs fueled research into curved aromatic systems.

Typically, buckybowls are synthesized to represent the most common fullerene, $C_{60}$ but bowl-shaped fragments of larger fullerenes are beginning to be explored. The Scott laboratory reported an improved synthesis of corannulene in 1991$^{16}$ with Siegel and coworkers reporting their own methodology the following year.$^{17}$ Quickly buckybowls of various sizes were reported by a number of research groups with Rabideau and coworkers reporting hemibuckminsterfullerene in 1996,$^{18}$ a representation of exactly one half of buckminsterfullerene. Shortly thereafter Scott and coworkers reported the synthesis of

circumtrindene, which represented 60% of the curved surface of buckminsterfullerene.\textsuperscript{19} Finally, sumanene was reported in 2003 by Hirao and coworkers, which unlike prior fragments, contained three benzylic positions that allow further functionalization (Figure 1.2).\textsuperscript{20} These are just a selection of the fullerene fragments reported in the past few decades and they represent the range of size and methods of synthesis. The methods developed for the synthesis of these buckybowls was key to the chemical synthesis of C\textsubscript{60}, and they will be discussed more in depth in the following sections. Buckybowls were also seen as a starting point for the synthesis of SWCNTs, with researchers envisioning the buckybowl serving as the end cap of the nanotube from which they synthetically extend a nanotube from.

1.2.1 Corannulene

Corannulene is arguably the most widely studied buckybowl, with numerous publications detailing synthetic procedures, electrochemical properties and applications in materials science. Prior to the isolation of C\textsubscript{60}, corannulene was largely ignored in part due to the lengthy synthetic procedure and dismal yield. The Scott laboratory described the synthesis of corannulene through a much simpler synthetic procedure. The synthesis built upon the work of Brown, who demonstrated that terminal acetylenes reversibly


\textsuperscript{20} Sakurai, H.; Daiko, T.; and Hirao, T. \textit{Science}, \textbf{2003}, \textit{301}, 1878
Scheme 1.2: The Scott laboratory kept refining their synthesis of corannulene, finally achieving a simple and efficient three-step route with 25% overall yield. This synthesis is attractive in that all reactions can be run with commonly available reagents.

rearrange to vinylidenes under flash vacuum pyrolysis (FVP).\(^{21}\) Scott saw the utility in this methodology and significantly shortened the synthetic procedure of corannulene from 17 steps to five while increasing the yield from 0.6% to 6.5%. The Brown rearrangement was the key step that induced strain into the molecule through the formation of two C–C bonds. Further improvements to the synthetic procedure in Scott’s lab shortened the synthesis to just three steps while improving the overall yield to 25%.\(^{22}\) As a result of the success of this method, FVP became popular in the synthesis of bowl-shaped PAHs, with many derivatives reported throughout the 1990s.\(^{23}\)

While FVP has been successful in the synthesis of a wide-variety of buckybowls, there are some downsides to this method. FVP requires heating of the precursors into the gas phase using extremely high temperatures—500 to 1200 °C. Material is passed through the oven under high vacuum and collected in a cold trap. Because of the high


Scheme 1.3: Siegel and coworkers devised a synthetic procedure that required no pyrolysis for the final bond-closing step. This methodology is tolerant of alkyl and chloro functional groups allowing for increased access to derivatives of corannulene.

Temperatures required there is little functional group tolerance and as a result the preparation of derivatives using FVP becomes very challenging. Furthermore, the process of vaporizing the sample and passing it through a heated oven limits the amount of material that can be prepared. Siegel and coworkers took a different approach, reporting a non-pyrolytic synthesis of a corannulene. The key step in the synthesis was the C–C bond formation utilizing a low-valent titanium species (initially the synthesis used TiCl$_3$ with LiAlH$_4$, but later studies found TiCl$_4$ with Zn–Cu returned higher yields) followed by oxidation with DDQ (Scheme 1.3). The milder nature of this synthesis allowed incorporation of functionality that would decompose under flash vacuum pyrolysis conditions.

The syntheses highlighted here showed the rapid development in the preparation of corannulene once the electronic properties of curved PAHs were realized and have allowed the preparation. The availability of these materials allowed further investigation into the electronic and supramolecular properties.

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1.2.2 Circumtrindene

While the synthesis of corannulene opened up an entire host of novel research, it represents only a fraction of the buckybowls prepared since the early 1990s. Circumtrindene, 2, which represents 60% of the curved surface of $C_{60}$ was reported in 1996 and is the largest fragment of $C_{60}$ known to date.\textsuperscript{19} Circumtrindene was synthesized from decacyclene, 1, a reagent that was commercially available in the 1990s (It has since been discontinued from all major chemical suppliers). Scott was able to effect the three-necessary carbon-carbon bond closures through FVP (Scheme 1.4).\textsuperscript{19a} Unfortunately, despite the success of FVP in the synthesis of corannulene the overall yield of circumtrindene was only 0.2%!

\begin{center}
\textbf{Scheme 1.4}: FVP of decacyclene, (1), afforded the closed fullerene fragment circumtrindene, (2), in 0.2% yield.
\end{center}
Scheme 1.5: Synthesis of 8-chloroaenaphthone, 3, allowed a symmetric halogenated decacyclene derivative to be constructed in a head-to-tail Lewis-acid catalyzed aldol cyclization. Prior work in Scotts group showed the addition of halogens facilitated a significant increase in yield through FVP and this was observed with halogenated decacyclene 4.

To overcome the overwhelmingly low yield, chlorines were added to interior carbons of decacyclene (Scheme 1.5). The addition of halogens for directing bond formation has been proven to be a reliable method to increase FVP yields.\(^{26}\) Unfortunately, the synthesis of decacyclene historically has relied on oxidative trimerization of acenaphthylene, which lacks the regioselective control needed when installing halogens in specific conditions to direct bond closures in FVP.\(^{27}\) To get around the problem of regioselectivity, Scott and coworkers designed acenaphthenone derivative 3, that they theorized could assemble in a head-to-tail manner in a Lewis-acid catalyzed aldol cyclization. After extensive screening of conditions, they reported that the


halogenated decacyclene derivative 4 could be produced in 25% yield through the slow addition of 3 dissolved in o-dichlorobenzene to a refluxing solution of TiCl₄ in o-dichlorobenzene.¹⁹b They were able to fully characterize 4 through NMR, UV-Vis absorption and X-ray crystal studies. FVP of 4 provided circumtrindene in 24-27% yield, a major increase over the prior method.

**1.2.3 Fragments of Higher Fullerenes and Large Buckybowls**

The bulk of fullerene research has centered around C₆₀ because of its large-scale production and isolation as outlined in Section 1.1. The next most prevalent fullerene is C₇₀, (Figure 1.3) which can be isolated from Johnson’s synthesis of C₆₀.⁵ Surprisingly, when compared to C₆₀, C₇₀ and larger analogues of fullerenes have not attracted as much

![Figure 1.3: Fullerene C₇₀, the next largest fullerene takes on a more ellipsoid shape as a result of the addition of 10 equatorial belt carbons. When compared to C₆₀, C₇₀ contains 8 unique bonds (a-h, blue) as measured by bond length and reactivity.](image)
interest. Structurally, C\textsubscript{70} is very similar to C\textsubscript{60} and can be regarded as two C\textsubscript{60} hemispheres joined with an equatorial belt of 10 carbons. Unlike C\textsubscript{60}, C\textsubscript{70} displays a very different bonding pattern and contains eight different types of C–C bonds (a-h, Figure 1.3)! The multiple types of C–C bonds (defined through variations in bond length as obtained through X-ray crystal structures) found in C\textsubscript{70} added a new dimension of complexity to functionalization chemistry as there are more possible addition sites. Despite this limitation, C\textsubscript{70} has been subject to functionalization studies including the Bingel reaction, transition metal complexes, halogenations, and cycloadditions to name a few.

The synthesis of buckybowls that map to the surface of C\textsubscript{70} have proved to be even more elusive with only a few reports on their synthesis over the past few decades. In 2006 Scott and coworkers reported several pyrene derivatives that mapped the surface of C\textsubscript{70}. These derivatives were not expected to be as deeply bowl-shaped as prior buckybowls and unfortunately, they were unable to obtain X-ray crystal data to confirm this. The solubility of these PAHs was very limited and the addition of tert-butyl groups

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was necessary to make characterization easier (Figure 1.4). Theoretical studies supported the shallow bowl shape and the bowl-to-bowl inversion barrier was computed to be only 0.33 kcal/mol.

In 2013 Wu and coworkers reported the next iteration of a buckybowl that maps to the surface of $\text{C}_{70}$ (Scheme 1.6).\(^{35}\) Wu constructed this highly strained fragment

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Figure 1.4: Scott’s 2006 report of pyrene derivatives map the surface of $\text{C}_{70}$, but suffered from low yield. They were calculated to have very shallow bowls, with an inversion barrier of 0.33 kcal/mol\(^{-1}\).

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Scheme 1.6: Using a palladium catalyzed arylation as the final strain inducing step, Wu demonstrated a short synthesis to a fullerene fragment that mapped the framework of C\textsubscript{70}, C\textsubscript{76}, and C\textsubscript{84} through the use of palladium-catalyzed intramolecular arylation reactions.\textsuperscript{36} Crystals suitable for X-ray analysis were obtained and the structure was validated. Wu’s buckybowl was slightly less curved than C\textsubscript{70}, deviating from the curved surface by about 0.31Å. (i.e. the diameter of the rim of Wu’s fragment was 0.31 Å wider than the analogous part of C\textsubscript{70}) The depth of the bowl was measured to be 2.28 Å, slightly shallower than what was observed for circumtrindene. Unlike prior reported buckybowls Wu’s fragment undergoes bowl-to-bowl inversion through a different mechanism. The inversion of corannulene\textsuperscript{35a, 37} and sumanene\textsuperscript{38} all proceed through a planar transition state however, DFT at the B3LYP/cc-pVDZ level of theory suggested an s-shaped transition state for Wu’s fragment. Furthermore, the bowl-to-bowl inversion barrier was quite high (\(\Delta G^\dagger = 79.8 \text{ kcal mol}^{-1}\)) meaning that the bowl remained static at room temperature and any chiral derivatives synthesized could be expected to remain stable.


Despite exhibiting similar properties to the more popular C\textsubscript{60} fragments, buckybowls of larger fullerenes and larger bowl-shaped fragments remain less explored. While many higher fullerenes have been reported, including C\textsubscript{76}\textsuperscript{39}, C\textsubscript{78}\textsuperscript{40}, C\textsubscript{82}\textsuperscript{41}, C\textsubscript{84}\textsuperscript{42}, C\textsubscript{96}\textsuperscript{43} and C\textsubscript{104}\textsuperscript{44}, the complexity of isolation has limited their study. While C\textsubscript{60} has one structural isomer, this number increases with fullerene size. For example, C\textsubscript{84} is known to have 24 isomers and C\textsubscript{96} has 196\textsuperscript{46} Thus, determining the structure of a higher fullerene and mapping a fullerene fragment to it becomes a great deal more complex. And since these fullerenes are isolated through tedious chromatography as side products in the synthesis of C\textsubscript{60} through combustion of graphite, access is severely limited. At the time of this writing, 5mg of C\textsubscript{76} is available from Sigma Aldrich for $1,590 ($318/mg). The next higher fullerene, C\textsubscript{78} is discontinued and the last remaining stock of it is going for the same price as C\textsubscript{76}. For comparison, Sigma Aldrich offers C\textsubscript{60} for $0.21/mg. Therefore, access to higher fullerenes can be quite limiting to research groups due to cost and complexity of isolating pure isomers.

Figure 1.5: Mordkovich observed giant fullerenes after laser pyrolysis of carbon black. TEM imaging revealed these nanostructures and he was able to determine the fullerene onions formed to comprise C\textsubscript{60}, C\textsubscript{240} and C\textsubscript{560}. Image by Mordkovich\textsuperscript{49}

Larger fullerenes have also been observed as carbon nano-onions (CNOs), which are smaller fullerenes nested within larger fullerenes (Figure 1.5). In 1992 Ugarte obtained CNOs through intense irradiation of carbon soot.\textsuperscript{45} Typically, these materials can only be characterized through high-resolution transmission electron microscopy (HRTEM) and raman spectroscopy.\textsuperscript{46} The existence of these giant fullerenes was purely speculative until Mordkovich was able to obtain the first high resolution images of C\textsubscript{60}/C\textsubscript{240} and C\textsubscript{80}C\textsubscript{240}C\textsubscript{560} clusters after laser pyrolysis of carbon black (Figure 1.5).\textsuperscript{47} Transmission electron microscopy (TEM) of the materials collected after purification through sublimation showed a variety of CNOs as well as some C\textsubscript{60}. Mordkovich assigned these designations by estimating the size of the fullerene based on the diameter. Despite the evidence for the existence of these giant fullerenes, direct isolation and characterization has yet to be realized. Furthermore, synthesis of

buckybowls of giant fullerenes remains largely unexplored, with Wu’s and Scotts reports
the only reports in the literature of fragments of fullerenes larger than C_{60}.

1.3 Properties and Applications of Buckybowls

It was hoped that the curved π-surface of buckybowls would exhibit similar
characteristics to those observed in buckminsterfullerene. In fact, buckybowls have been
shown to exhibit nearly identical spectral properties and reactivity as C_{60}. The
characterization of circumtrindene revealed the UV-absorption spectrum to be nearly that
of C_{60}, leading to the conclusion that as the fullerene fragment gets larger, the electronic
character will become more like C_{60}.

Alan Balch and coworkers were able to validate the structure of circumtrindene
through single crystal X-ray diffraction.\textsuperscript{48} The bowl depth was measured at 3.107 Å and
the radius at 4.068 Å. Interestingly, crystal structure data showed that while
circumtrindene does superimpose over C_{60}, the bowl splays out slightly at the top, with
the peripheral carbons deviating from their counterparts on C_{60} by ~0.6 Å. Furthermore,
they discovered that the bond lengths in circumtrindene mirrored their counterparts in
C_{60}. Density functional theory (DFT) calculations of circumtrindene using the B3LYP/6-
31G* functional indicated that the LUMO of circumtrindene was doubly degenerate with
the largest LUMO coefficients located at the interior 6:6 bonds. Electrostatic potential
maps for circumtrindene showed that the inner curved surface was similar to that of
benzene and the exterior curved surface was very electron deficient, much like that of C_{60}

\textbf{1997}, \textit{119}, 5766–5767
Thus, when circumtrindene is exposed to conditions used to functionalize C\textsubscript{60}, it reacts in the same manner with chemical additions occurring on the 6:6 bonds located on the most strained part of the bowl, supporting the predicted sites of reactivity from the calculations (Scheme 1.9).\textsuperscript{49}

When corannulene was compared to C\textsubscript{60}, it exhibited the same remarkable ability to reversibly accept electrons. When exposed to lithium metal in d\textsubscript{8}-THF, NMR showed reduction to the tetra-anion.\textsuperscript{50} This was observed through a series of color changes—green to purple to brown-red—over several days. It was not until the final brown-red color that an NMR spectrum could be recorded (attributed to the presence of paramagnetic species at intermediate stages of reduction) and when compared to the neutral species it was quite different. \textsuperscript{13}C NMR showed a dramatic high field shift with the average deviation from neutral being ~36.1 ppm, consistent with theoretical

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme1.9.png}
\caption{Fullerene-like reactivity is confirmed through Prato and Bingel-Hirsch conditions to give the Prato product, (left) and Bingel-Hirsch product (right).}
\end{figure}

**Scheme 1.8:** Under the presence of raw lithium metal in d$_8$-THF corannulene is reduced to the tetra anion over the course of three days. $^1$H and $^{13}$C NMR experiments revealed spectra consistent with a tetra-reduced species and quenching experiments with water returned tetra-hydro corannulene.

calculations for the tetraanion.

Quenching the species with water returned tetrahydro-corannulene, which supported that the species observed was the tetra anion. The reduced corannulene appeared to be quite stable and it was theorized that the stability arose through an aromatic cyclopentadienyl core suspended by 5 radial bonds within the hole of an exterior 18-electron annulenyl trianion (Scheme 1.8). NMR experiments into the corannulene tetra anion show that it does not exist in solution as a solitary molecule but instead as a dimer with the lithium ions sandwiched between the convex surfaces of corannulene.$^{51}$ It is interesting to note that when corannulene is reduced to the tetra anion it actually becomes more electron rich than the C$_{60}$ hexa-anion (0.2 e$^-$/ C vs 0.1 e$^-$/C).$^{52}$ This ability of corannulene to coordinate with metals reversibly led to numerous publications of

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Petrukhina reported the first X-ray crystal structure of the corannulenetetranion. A) Through slow vapor diffusion of hexanes into THF they observed that five Li$^+$ ions sandwiched in-between each flanking corannulene with one Li$^+$ ion coordinating with each exterior surface. B) Under the presence of a strong chelating agent the corannulene dimer remains intact while the exterior Li$^+$ ions coordinate with the chelating ligands. Image by Petrukhina


Crystal structures of these complexes. However, it was not until 2011 that the tetra anion sandwich was characterized. Petrukhina and coworkers obtained crystals suitable for X-ray analysis through slow vapor diffusion of hexanes into a solution of the tetra anion in THF. The solid-state structure contained five Li$^+$ cations in the dimer complex almost perfectly eclipsed with all six membered rings involved in interactions with a Li$^+$ ion (Figure 1.6). The X-ray crystal structure also revealed significant flattening of corannulene with the bowl depth decreasing to 0.288(2) Å from 0.875(2) Å in the neutral molecule. Bond lengths within the tetra anion also support the “annulene within an
annulene” model proposed to explain the stability of the reduced species, with the bond lengths of the interior five-membered ring decreasing slightly and the perimeter bond lengths equalizing. These studies are important, argued Petrukhina, for the development of PAHs into supercapacitors and for their use as thin films based on electrostatic layer-by-layer deposition.

Additionally, Petrukhina was able to confirm the stability of these dimers in solution. When strong chelating agents (crown ethers) were introduced to the solution, X-ray crystal structures revealed the two exterior Li\(^{+}\) atoms chelated with the crown ether and the corannulene sandwich remaining intact, even in the presence of strongly coordinating oxygen-donor ligands.

Another interesting use for buckybowls is based on molecular receptors. Currently, the design of a stable host-guest complex remains challenging. The curved \(\pi\)-surface of buckybowls made them attractive candidates for coordination with a fullerene through host-guest complexes. Obtaining complexes, especially those with corannulene, historically has been difficult with the only reported observations happening in the gas phase.\(^{55}\) Sygula’s report of the “bucky catcher” in 2007 represented the first observation of corannulene coordinating with C\(_{60}\) in the solid state (Figure 1.7A).\(^{56}\) Slow evaporation of a 1:1 solution of C\(_{60}\) and the “buckycatcher” in toluene produced dark red X-ray quality crystals. Upon analysis, it was found that the distance between the fullerene and the corannulene surface was 3.128 Å, confirming that the complex was supported through van der waals interactions. They also showed that the complex exists in


Figure 1.7: A) Sygula’s report on “molecular tweezers” utilizes a modified tetraphenylene with two opposing corannulenes acting as pincers and crystallizing with \( \text{C}_{60} \). B) Synthesis of the buckycatcher.

solution, with the coordination observed through NMR titration experiments. Synthesis of the buckycatcher utilized a furan functionalized corannulene in a [4 + 2] Diels-Alder cycloaddition with a dibenzocyclooctadiyne, which proceeded in good yield. Aromatization of six membered rings formed in the cycloadditon with low valent titanium gave the buckycatcher in 55 % overall yield (Figure 1.7B).\(^{40}\)

Buckybowls have also been used in the synthesis of small CNT fragments.\(^{57}\) Direct chlorination of corannulene with iodine monochloride and five-fold Negishi coupling with 2,6 dichlorophenylzinc chloride followed by FVP produced a small CNT fragment with the corannulene serving as the cap (Figure 1.8). X-ray diffraction studies

Figure 1.8: Chlorination of corannulene, followed by Negishi coupling and FVP gives the first example of a buckybowls used in the synthesis of a fragment of a CNT. Though small, this demonstrated the utility in using a buckybowls to build nanotubes with the buckybowls as the end cap.

revealed a bowl depth of 5.16 Å with the nanotubes measured diameter of just less than 10 Å. This was a significant discovery in that it highlighted a few key aspects of the ground-up synthesis of carbon nanotubes. It demonstrated the synthesis of a fragment that contained a fully cylindrical wall, which is necessary if the fragment is to act as a template for nanotube synthesis. Additionally, it proved that the synthesis of these fragments is a rational method to take for designing synthetic methods towards fragments of nanotubes of varying sizes.
1.4 Use of Aldol cyclization in Fullerene Synthesis

The methods developed in the syntheses of buckybowls laid the groundwork for Scott’s chemical synthesis of $C_{60}$. The Lewis-acid mediated cyclization of 1-acenaphthenone used in the synthesis of circumtrindene made the chemical synthesis of $C_{60}$ a reality. Laser-induced cyclodehydrogenation with a 337nm laser of a expanded decacylene derivative produced trace amounts of $C_{60}$ (Scheme 1.9). The large PAH used in this synthesis contained all 60 carbons found in $C_{60}$ as well as 75 of the 90 carbon-carbon bonds and was prepared with a modified 1-acenaphthenone derivative. In addition to the observed $C_{60}$, smaller fullerenes $C_{58}$, $C_{50}$ and $C_{44}$ were also observed.

Scheme 1.9: Modification of the acenaphthenone precursor to circumtrindene allowed for construction of a PAH containing all 60 carbons found in $C_{60}$.

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These are common to observe in a mass spectrum of C₆₀ as these are thought to be decomposition products.

While this method demonstrated that C₆₀ could be produced in a directed manner rather than through combustion of graphite, it lacked the ability to produce any significant material that could be isolated. With the demonstrated use of chlorines to raise the yield of circumtrindene from ~0.2% to ~25%, it was the next logical step to take in the synthesis of C₆₀. FVP of a tri-chlorinated precursor gave C₆₀ in an estimated 1% yield (Scheme 1.9). The material collected was characterized through HPLC and UV-absorbance against commercial acquired samples of C₆₀ and was confirmed that the material collected was pure C₆₀. Furthermore, no evidence of fragmentation and recombination was observed, as this would have led to trace amounts of C₇₀—none of which was observed. While these methods used to produce C₆₀ will never compete with the large-scale production through the combustion of graphite, they illustrate that the directed synthesis of fullerenes is possible and if one were to desire a larger fullerene, this could be the method to make one.

Some attempts to utilize FVP to form higher fullerenes have appeared in the literature over the last 10 years, (Specifically, C₇₈ and C₈₄) and have been largely unsuccessful. The precursors are synthesized through the same Aldol cyclizations that were successful in the synthesis of circumtrindene and C₆₀. Design of the materials is

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Figure 1.9 Precursors to fullerenes $C_{78}$ (left) and $C_{84}$ (right) were synthesized using Aldol cyclizations and subject to FVP. Unfortunately, no isolatable fullerenes were produced.

again, done through modification of the indanone or acenaphthenone precursor to give a large, warped PAH derivative. (Figure 1.9).\textsuperscript{60} Unfortunately, when these materials were subject to the same FVP conditions that returned $C_{60}$ in only trace quantities and no useful amount of fullerenes could be recovered. They were able to observe the presence of the desired materials in the mass spectrum, but no further developments in these materials has been reported.

1.4.1 A Cyclic Tetramer

Throughout the synthesis of buckybowls utilizing the Lewis-acid catalyzed aldol cyclization there was a significant effort put forth to optimize the reaction. One of the major downsides of this methodology was the messy mixture of products during the cyclization. Scott’s 2000 synthesis of circumtrindene\textsuperscript{19b} produced the acenaphylene dimer 5 and a cyclic tetramer, 6 in addition to halogenated decacyclene 4. The cyclic tetramer was never fully characterized but Scott was able to observe it in mass spectral analysis and stated it was typically found in the darker column fractions after purification (Figure 1.10). Other than the confirmation of this material as a by-product in the cyclization, it was largely ignored, however, the presence of a cyclic tetramer persisted throughout investigations into these Aldol cyclizations. In addition to the synthesis of circumtrindene and buckminsterfullerene, Scott reported another cyclic tetramer, 7,

![Diagram of 5 and 6](image)

**Figure 1.10:** The Aldol cyclization conditions that Scott used in the synthesis of circumtrindene produced numerous by-products. The acenaphthene dimer 51 was isolated while the cyclic tetramer 6 was only observed in the mass spectrum of the crude reaction material.
isolated when investigating carbon nanotube growth.\textsuperscript{61} Wei and coworkers reported the most extensive characterization of cyclic tetramers 8 and 9 in their report in 2005.\textsuperscript{62} And finally, Jansen observed the fluorinated cyclic tetramer 10 in the mass spectrum of their crude reaction mixtures (Figure 1.11).

Wei’s synthesis was the result of truxene derivatives as these PAHs have also found a lot of use in the synthesis of larger polyarenes. They looked to develop a synthesis to flat PAHs that were soluble in common organic solvents. In this report, they used the same methodology employed by Scott in his synthesis of decacyclene derivatives—the TiCl\textsubscript{4} mediated Aldol cyclization in boiling \textit{o}-dichlorobenzene. They were the first group to report the synthesis and isolation of the cyclic tetramer in this reaction, and were able to provide NMR and UV-Vis absorbance spectra in addition to the mass spectrum.\textsuperscript{65} However, they never followed up on the synthesis of this material with structural data or applications into coordination and organometallic chemistry as indicated in their study.

\textsuperscript{61} Hill, T.J.; Hughes, R.K. and Scott, L.T. \textit{Tetrahedron} 2008, 64, 11360–11369
Figure 1.1: Literature reports of cyclic tetramers detected during Lewis-acid catalyzed aldol cyclizations. Often these are only observed in the mass spectrum of crude reaction mixtures, however Wei was able to obtain NMR and UV-Vis data of 8.

Our group became interested in this fragment due to the presence of the central eight-membered ring and the potentially interesting structural and electronic properties that may result from it. Despite these potential properties, significant research has gone into minimizing the occurrence of cyclic tetramers in Aldol cyclizations with Amick and Scott providing a detailed account of tailoring reaction conditions to eliminate its
We were also inspired by the abundance of this cyclic tetramer. While Scott never reported a yield, Wei’s report showed yields ranging from 14-21%.

### 1.5 Project design

Inspired by the apparent accessibility of the cyclic tetramers observed in the reaction mixtures of various buckybowls, we sought to isolate and optimize the reaction to produce the cyclic tetramer. Once a successful synthesis is identified, the structural and electronic properties could be explored, with the goal of utilizing this material as a precursor to a buckybowl containing a central eight-membered ring. This was inspired by Terrones and coworker’s computational investigation of large fullerenes (up to $C_{840}$). They presented evidence that the larger fullerenes, namely $C_{240}$ and $C_{540}$ can incorporate larger ring sizes into their framework. Building off of a theoretical report by Stone and Wales in which they investigated the possibility of multiple isomers of $C_{60}$ through photochemically allowed pericyclic reactions, Terrones theorized that the $O_h$ isomer of $C_{240}$ would contain 24 pentagonal rings, 92 hexagonal

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Figure 1.12: A) C\textsubscript{240} fullerene can contain the typical carbon framework composed of five and six-membered rings. B) Up to six octagonal rings can be incorporated into C\textsubscript{240} through Stone-Wales type transformations. C) Within the O\textsubscript{h} C\textsubscript{240} fragment, the cyclic tetramer observed in the Aldol-reactions can be seen as a building block to a fragment. D) Envisioned fragment of fullerene C\textsubscript{240}, 11, is a much shallower bowl than previously reported systems. This fragment would represent the first buckybowl to contain an eight-membered ring.

rings and 6 octagonal rings (Figure 1.12B). When comparing the O\textsubscript{h} isomer of C\textsubscript{240} to the reported cyclic tetramers it becomes immediately apparent that it is the precursor to a buckybowl that maps the surface with the eight-membered ring as the core, 11, (Figure 1.12C). DFT calculations of the fragment showed it to adopt a much shallower bowl
shape than known fragments, which was to be expected given the nature of the structure (Figure 1.12D). We envisioned that this methodology could be expanded upon through modifications of the acenaphthenone precursor to give larger fragments of this fullerene and even end-caps for large carbon nanotubes. Motivated by the giant body of research on fragments of C\textsubscript{60} and the diverse applications observed due to their ability to form supramolecular complexes and display chemical reactivity analogous to that of fullerenes, we sought to isolate the cyclic tetramer prevalent in the aforementioned aldol cyclizations, synthesize the buckybowl and begin exploring its properties.

1.6 Prior Work in the Whalley Group Towards Non-Planar PAHs

The synthesis of non-planar PAHs has been a primary focus of the Whalley research group. As detailed in the prior sections, the introduction of curvature into aromatic systems results in a host of interesting properties and applications towards materials science. The affinity of these warped PAHs to form columnar structures makes them particularly attractive for applications in organic photovoltaics. In addition to just the synthesis of these warped materials, the group has taken a special interest into inserting non-traditional ring sizes into these PAHs. As seen with fullerenes and buckybowls, the frameworks are typically made up of five and six membered rings. The[n]circulene family of PAHs is defined by a central ring flanked by \( n \) fused benzene rings. Circulene derivatives up to [7] circulene have all been prepared, with [8] circulene,
Figure 1.13: (Top) The Whalley group synthesized the stable [8]circulene derivative tetrabenzo[8]circulene, 13. (Bottom) Clar model of aromaticity indicates that the parent [8]circulene, 12, contains four reactive sites (arrows) while the tetrabenzo[8]circulene derives its stability from no localized double bonds.

(12), remaining elusive, despite several attempts at the synthesis. The problem lay with the stability of the naked [8] circulene. When viewing [8] circulene through the Clar model of aromaticity one can see the presence of four reactive double bonds (Figure 1.13). The Clar model defines stability of a molecule through the isolation of $\pi$ electrons into individual rings. (known as aromatic sextets) Keeping the Clar model in mind, the group successfully synthesized the desired circulene derivative, tetrabenzo[8]circulene, (13), and found the material to be remarkably stable as a result of the addition of four benzene rings (Figure 1.13). Further studies by the group and refinements to the

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synthesis allowed a variety of functionalized derivatives to be produced—a valuable trait when designing compounds for applications into organic materials. Structural analysis of tetrabenzo[8]circulene revealed some interesting characteristics unusual of PAHs of this nature. Typically, these types of PAHs stack in a herringbone or slipstacking fashion. However, the Whalley group observed a complex three-dimensional network of packing where the peripheral benzenoid rings π-stack with their analogous counterpart on a neighboring molecule (Figure 1.14). Additionally, the solid-state structure differed significantly from the predicted DFT structure, taking on a pinwheel like shape rather than the expected saddle-shape. The Whalley group determined this discrepancy was the result of crystal packing forces and that the likely structure in solution was closer to the one predicted through DFT. Harmonic oscillator model of aromaticity (HOMA) was used to determine the aromaticity of the rings in the solid-state structure. This model compares the deviation of the observed bond lengths in the desired ring from those in an ideal aromatic ring. A bond length of 1.388 Å, observed in benzene, has been calculated as the optimal bond length in an aromatic ring. HOMA values of -1, 0, and 1 indicate anti-aromaticity, non-aromaticity and aromaticity respectively. It was found that HOMA values for the solid-state structure strongly supported the Clar model of aromaticity, with each of the benzenoid rings with HOMA values correlating to an

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Figure 1.14: The Whalley group reported the synthesis of the highly contorted PAH tetrabenzo[8]circulene. DFT calculations A) predicted a saddle-shaped structure B) X-ray diffraction studies showed a pinwheel like structure. C) Instead of the expected columnar stacking, the group observed a broader 3D like structure with the only π- π stacking interactions observed on the exterior benzenoid rings.

aromatic sextet. Interestingly, the HOMA value for the central eight-membered ring showed a HOMA value correlating to a slight degree of anti-aromaticity. The success of this synthesis inspired the group to continue to incorporate eight-membered rings into
PAHs. With this in mind, our lab became interested in the synthesis of large fullerene fragments to augment the research in our group towards large, nonplanar PAHs.

1.7 Concluding Remarks

A great body of work exists on the synthesis of fullerene fragments and the unique properties observed as a result of the curved π-systems. Research has only recently begun exploring materials that deviate from fragments of C_{60}. As a result, there is a great opportunity to begin exploring materials to expand this research. Herein we describe the isolation and full characterization of the cyclic tetramer of 1-acenaphthenone, which we have named tridecacyclene, the observed structural, electronic, supramolecular properties, synthesis of derivatives and synthetic efforts towards the bowl-shaped fragment of a fullerene C_{240}. 

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CHAPTER TWO: TRIDECACYCLENE

2.1 Introduction

The most common Lewis-acid catalyzed aldol cyclization conditions that result in the formation of the cyclic tetramer of acenaphthenone or indenone monomer is the slow addition of the into refluxing TiCl₄ in o-dichlorobenzene. Although all reported cyclic tetramers have been derived from substituted 1-acenaphthenone derivatives, we initially focused on 1-acenaphthenone due to its commercial and synthetic availability. Because the cyclic trimer is desired product out of these reactions, we felt decacyclene, the cyclic trimer of 1-acenaphthenone and the precursor to circumtrindene would be a good benchmark to compare our observed structural and electrochemical properties against. Decacyclene has been well studied since its synthesis in 1903 and in addition to its use in buckybowls has found a utility in a range of disciplines including surface modification, organometallic complexes, and liquid crystals. We were further inspired as decacyclene has been studied for use as an n-type semiconductor thanks to its ability to reversibly accept four electrons. With the wealth of information available on decacyclene, we began our investigations to fill the void on the characterization of the cyclic tetramer of 1-acenaphthenone and explore it’s utility against decacyclene.

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70 Dziewoński, K.; Chem. Ber. 1903, 36, 962–971
74 Saji, T. and Aoyagi, S. J. Electroanal. Chem. 1979, 102, 139–141
2.2 Synthesis of Tridecacyclene

Acenaphthene, (14), was dissolved in glacial acetic acid, and treated with one equivalent of sodium dichromate for 48 hours at room temperature. After quenching with NaHCO₃ and extraction of organic material with DCM, the crude residue was purified by flash column chromatography to give ketone 15 in 30% yield. Ketone 15 was dissolved in o-dichlorobenzene and slowly added to a refluxing solution of TiCl₄ in an equal amount of o-dichlorobenzene. Initially, we followed prior methods which called for a slow addition over the course of two hours with a syringe pump. We found that addition over the course of 5–10 minutes had no negative effects on final yield and carried out subsequent cyclizations without the syringe pump. Thin layer chromatography (TLC) of the crude reaction mixture revealed two distinct products—a yellow fluorescent spot with spectroscopic data matching that of decacyclene, (1), and a brown spot of similar polarity that we identified as the cyclic tetramer, 1,2;3,4;5,6;7.8-tetra[(1.8)-naphthylene]-1,3,5,7-cyclooctatetraene 16. Following the nomenclature used for decacyclene (ten cycles) we

![Scheme 2.1: Preparation of cyclotetramer 16, tridecacyclene, from 1-acenaphthenone](image)

75 Material from this chapter appears in the following form: Sumy, D.P.; Dodge, N.J.; Harrison, C.M.; Finke, A.D. and Whalley, A.C. Chem. Eur. J. 2016, 22, 4709–4712
have appropriately named 16 tridecacyclene (thirteen cycles). Unlike all prior observations though, 16 was recovered as the major product in 21% yield and not just a byproduct (Scheme 2.1).

Tetramer 16 is a stable brown solid that readily dissolves in a wide variety of organic solvents, unlike the poor solubility observed for decacyclene. The $^1$H NMR spectrum of 16 in CDCl$_3$ at 25 °C contains three peaks of equal integration at $\delta = 7.87$, 7.67, and 7.56 ppm. The $^{13}$C NMR spectrum contains seven unique chemical environments for the 48 carbon atoms in the structure, indicating a high degree of symmetry. In comparison, decacyclene, which is known to adopt a propeller-like shape due to steric interactions of the interior “bay region” hydrogens, exhibits a significant downfield resonance at $\delta = 8.83$ in the $^1$H NMR spectrum.\(^7\) This resonance is a result of the proton in the aforementioned bay region interacting with the ring current of both the ring it is attached to and the adjacentacenaphthyl subunit. The observed $^1$H NMR of 16 supports the anticipated boat shape, with the analogous bay-region proton found about 1 ppm further up field, indicating much less of a contribution from the adjacent ring and therefore a strong indication that 16 adopts a non-planar topology.

Dark brown cubic crystals of 16•1,2-DCE, grown from the slow diffusion of n-hexanes into a saturated solution of 1,2-dichloroethane, were used to validate the structure through single crystal X-ray diffraction (SC-XRD) studies.\(^7\) The solid-state structure

\(^7\) CCDC 1440430 (16) and 1440429 (2•2(C$_{60}$)•3(C$_6$H$_5$Cl)) contain the supplementary crystallographic data for the structures described in this chapter. This data is provided free of charge by the Cambridge Crystallographic Data Centre. Crystallographic data: 16: triclinic, C$_{48}$H$_{24}$, $M_r = 600.67$, $a = 11.361(3)$, $b = 11.595(3)$, $c = 15.309(4)$ Å, $V = 1822.1(8)$ Å$^3$, $T = 100$ K, space group $P-1$, $Z = 4$, $\lambda = 0.71073$ Å, $\rho = 1.095$ g cm$^{-3}$, $\mu = 0.062$ mm$^{-1}$, $R_I = 0.0540$, $wR$_{2} = 0.1582 for $I > 2\sigma(I)$. C$_{60}$ Complex: monoclinic, C$_{136}$H$_{39}$Cl$_3$, $M_r$
(Figure 2.1A) matched that predicted from density functional theory (DFT) calculations. The structure distorts significantly from planarity, with the average atom in the eight-membered ring deviating from the mean plane of the ring by 0.37 Å, producing an alternating up-down-up-down arrangement of the acenaphthylene subunits. Bond lengths obtained from the X-ray structure are consistent with those of acenaphthylene, with substantial bond alternation observed in the naphthalene subunits. Significant double bond character is observed in the bond shared by the five-and-eight membered ring, with the bonds connecting the acenaphthylene subunits displaying significantly more single bond character than what has been observed in decacyclene, in which the bond alteration places the shorter bonds between the acenaphthylene units (Figure 2.1B). The solid-state packing of 16 is unique, with two orthogonal naphthalene subunits of each molecule exhibiting π-stacking interactions with two adjacent molecules, resulting in a zigzag pattern throughout the crystal. Abundant C–H/π-interactions stabilize the crystal structure further (Figure 2.1 C).

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78 DFT calculations (B3LYP/6–31G**) were performed using the Jaguar (see Jaguar: Version 8.3 Maestro: Version 9.8, Schrödinger, LLC, New York, USA, 2014) software package.
Figure 2.1: A) The solid-state structure of tridecacyclene, 16; hydrogen atoms have been omitted for clarity and ellipsoids are shown at 80% probability. B) Representative bond lengths (Å) calculated from the solid-state structure; a full list of bond lengths is provided in the last chapter. C) Crystal packing of 16, illustrating the π-stacking interactions between adjacent molecules.

Aromaticity of each of the rings in 16 were calculated using the harmonic oscillator model of aromaticity (HOMA),\(^1\) and the results were consistent with those in decacyclene, 1. In both cases, the six-membered rings in the naphthylene units are highly aromatic (HOMA values of 0.89 and 0.90 for 16 and 0.84 and 0.90 for 1) and the five-membered
rings are predominately non-aromatic (HOMA values of 0.11 and -0.07 for 16 and 1, respectively), although 1 exhibits a small amount of anti-aromaticity.

2.3 Optoelectronic properties

The optoelectronic properties of 16 are considerably different than those of 1, despite having similar bonding patterns. In the UV/Vis spectra (Figure 2.2A) we observed that the $\lambda_{\text{max}}$ undergoes a hypsochromic shift when comparing 1 (377 nm) to 16 (360 nm) with a slight reduction in molar absorptivity. This is likely a result of the more efficient orbital overlap found in the more planar 1. Surprisingly, the opposite trend is observed in the solution-based optical gaps as judged by the absorption onsets. The absorption onset of 16 is considerably lower in energy than what is observed in 1. Cyclic voltammograms (Figure 2.2B) support these observations with 16 considerably easier to reduce than 1 by about 0.4 eV. This is primarily a result of the significant decrease in the energy of the lowest unoccupied molecular orbital (LUMO) of 16 when compared to 1. This observation can be related directly to the central eight-membered ring, as aromaticity is known to develop in cyclooctatetraene and derivatives through two electron reduction processes.79 Interestingly, this occurs through two one-electron reductions rather than a single two...

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Figure 2.2: A) Absorption spectra of decacyclene, 1, (red) and Tridecacyclene, 16 (blue) in CH$_2$Cl$_2$. B) Cyclic voltammetry of 1 (red) and 16 (blue) in 0.05M tetrabutylammonium hexafluorophosphate in MeCN with a Pt working electrode, Pt counter electrode, and a Ag/AgCl reference electrode. Scan rate: 50 mVs$^{-1}$. Ferrocene was added as an internal standard and referenced to 0 V.
electron process, indicating that the radical anion generated in the first reduction is a stable species under the experimental conditions. Further investigations into the reduction of 16 will be reported in Chapter 3. The highest occupied molecular orbitals (HOMO) between the two molecules are similar in energy, with 16 only 0.16 eV higher in energy than 1. A comparison of the optoelectronic properties between 16 and 1 is summarized in Table 1.1.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<td>–5.37</td>
</tr>
<tr>
<td>LUMO [eV]</td>
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<td>–3.26</td>
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<td>( E_{\text{-chem gap}} ) [eV]</td>
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<td>2.11</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} ) [nm]</td>
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<td>360</td>
</tr>
<tr>
<td>Optical gap [eV]</td>
<td>2.57</td>
<td>1.84</td>
</tr>
</tbody>
</table>

[a] Measurements taken at sample concentrations of 0.2 mM and potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard. (Figure 22B) \( E_{\text{ox/onset}} \) is the onset of the oxidation potential and \( E_{\text{red/onset}} \) is the onset of the reduction potential. HOMO and LUMO values were calculated on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV).
2.4 Solid-state structure with $C_{60}$

In view of the opposing convex surfaces of 16, we were interested to see if the compound would form supramolecular interactions with the convex surface of buckminsterfullerene ($C_{60}$). Although such interactions are prevalent in the literature, as detailed in Chapter One, the ability to complex a fullerene on two opposing concave surfaces is quite unique and have only appeared in the literature two times.\(^8\) It is important to note, however, that in the previous two examples of such complexes the host molecules were much more difficult to prepare than 16.

When saturated chlorobenzene solutions of 22 and $C_{60}$ were combined in a small scintillation vial and left to slowly evaporate, crystals of the supramolecular assembly (Figure 23) suitable for SC-XRD were produced after two days. The crystal is composed of $C_{60}$, 16, and chlorobenzene (asymmetric unit ratio of 2:1:3, respectively), wherein 16 and $C_{60}$ form a repeating zig-zag pattern throughout the solid-state structure. As predicted, each molecule of 16 interacts (“interaction” here means the atom-atom contacts less than the sum of their van der Waals radii) with two symmetry-related $C_{60}$ molecules, one on each of its opposing concave faces. On the other hand, the two molecules of 16 in one hemisphere, whereas the other hemisphere interacts with the second $C_{60}$ unit. The other $C_{60}$

unit (green) interacts with one acenaphtylene moiety of two different molecules of \textbf{16}, three molecules of the first \textit{C}_{60} unit and two molecules of chlorobenzene. The complexes

\textbf{Figure 23}: A) The solid-state cocrystalline supramolecular assembly of \textbf{16} (red) and \textit{C}_{60} (blue). Hydrogen atoms and solvent molecules have been omitted for clarity and ellipsoids are shown at 80\% probability. The \textit{C}_{60} molecule on the left is related to the \textit{C}_{60} molecule on the right by the symmetry operation ($-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$) B) The crystal packing of \textbf{16} and two separate units of \textit{C}_{60} (blue and green), illustrating the zig-zag arrangement of components as well as the $\pi$-stacking interactions that exist between \textbf{16} and one of the \textit{C}_{60} two \textit{C}_{60} molecules occupy two distinct environments. One \textit{C}_{60} (blue) interacts with half of units (blue) and the C–H/ $\pi$-interactions that between adjacent molecules of \textbf{16}. Unit cell is depicted with a blue dotted line.

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between 22 and C\textsubscript{60} exhibit strong $\pi$- $\pi$ interactions wherein the shortest distance from an atom of C\textsubscript{60} to the plane of an interacting naphthalene is 3.00 Å. This distance is nearly identical to those observed in the previously reported systems.

Despite the remarkable solid-state structure between 16 and C\textsubscript{60}, a solution based complex remained elusive. We looked to study the solution based complex through Job’s method and obtain the equilibrium constant of binding. The concentration of the 16/C\textsubscript{60} solution in chlorobenzene was kept constant with the mole fractions of the respective compounds varied. Starting with a solution of pure 16 and slowly adding C\textsubscript{60} while decreasing the ratio of 16, UV-absorbance spectra was collected. Unfortunately, this only resulted in a smooth transition in the UV-absorbance from the spectra of 16 to that of C\textsubscript{60} and no evidence of complexation was observed. NMR titration experiments also produced the same results. As a result, a binding constant could not be determined, and the likely reason was the lack of sufficient $\pi$- $\pi$ interactions to overcome the forces of entropy in solution. To overcome this, the $\pi$-surface of tridecacyclene would need to be expanded further to facilitate greater $\pi$- $\pi$ interactions between the acenaphthyl subunits and the surface of C\textsubscript{60}.
2.4 Concluding remarks

The TiCl$_4$ mediated Adol cyclization of 1-acenaphthenone produced almost exclusively the cyclic tetramer, rather than the cyclic trimer commonly observed. This compound exhibits a range of beneficial properties when compared to its trimeric analog including increased solubility, a significant decrease in reduction potential (and a decrease in the corresponding optically and electrochemically measured HOMO-LUMO gap) and the ability to form supramolecular assemblies with fullerenes. In addition to serving as the precursor towards a fragment of the fullerene C$_{240}$, tridecacyclene has wide potential for applications in supramolecular chemistry with fullerenes and carbon nanotubes.
CHAPTER 3: THE REDUCTIVE AROMATIZATION OF TRIDECACYCLENE

3.1 Introduction

The electrochemical properties observed with tridecacylene, 16, were quite unique in that the reductions observed proceeded through two independent one electron reductions, rather than a single two-electron process.\(^8^1\) In particular, PAHs containing five-membered rings have been the subject of multiple reduction studies due to their ability to reversibly accept electrons with little structural change.\(^8^2\) 1,3,5,7-Cyclooctatetraene (COT) is an eight \(\pi\)-electron carbocycle that adopts a tub-like shape in order to avoid the anti-aromatic character that would develop upon planarization of its 8-membered ring. Like 16, COT readily accepts two electrons upon reduction and the prevailing accepted explanation has been the adoption of Hückel aromaticity from the addition of two electrons. In addition, this is also expected to induce a conformational change, with the 8-membered ring flattening to maximize \(\pi\)-electron delocalization. This concept was first investigated by Katz in the 1960s, where NMR evidence suggested planarization of the reduced radical

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\(^8^1\) Material from this chapter appears in the following form: Sumy, D. P.; Finke, A.D. and Whalley, A.C. *Chem. Commun.* 2016, 52, 12368–12371

anion and dianion species of COT.\textsuperscript{78} Subsequently, planarization was observed in the solid-state structure of a reduced tetramethylated COT derivative providing further support for the theory of reductive aromatization.\textsuperscript{83} In the 1990s, Komatsu extended these studies to encompass a more highly substituted bicycle-[2,2,2]octane-fused COT derivative. Although calculations determined this structure was sterically prohibited from planarization by $>24$ kcal mol\textsuperscript{-1} it was concluded from NMR evidence that this also flattened upon reduction.\textsuperscript{78b} These conclusions are unfortunately brought into question as subsequent studies of an analogous dicationic COT species (also Hückel aromatic) appeared to planarize at room temperature but was ultimately found to be interconverting through two tub-shaped conformations on the NMR timescale.\textsuperscript{84} More recently, the relationship between planarity and aromaticity was investigated using 47 crystal structures of known COT–metal complexes and it was found that planarization was much more the result of the efficiency of the metal center-COT interaction than the aromaticity of the ring itself.\textsuperscript{85} This inconsistency with Hückel theory is also prevalent in the theoretical community where there is still significant discussion about the aromaticity of these reduced systems through what appears to be a lack of a clear definition of aromaticity.\textsuperscript{86} With the observed ease of reduction of 16 and the resistance the compound would have towards

\begin{thebibliography}{99}
\end{thebibliography}
planarization due to steric interactions with protons in the “bay region”, we felt this was a model compound to further study the relationship between planarization and aromaticity in COT-based systems.

3.2 Reduction with Potassium Metal

As described in Chapter 2, 16 undergoes two one-electron reductions at −1.54 V and −1.85 V to the radical anion and dianionic species, respectively. These states can also be accessed chemically. When 16 is exposed to excess metallic potassium in anhydrous THF in a glove-box under an atmosphere of nitrogen (Scheme 3.1) we observe the immediate formation of a green solution, indicative of a one-electron reduction to the radical anion 17. After several more minutes, the solution turns deep purple indicating further reduction to the dianion, 18. ¹H NMR spectra of each of these species in d₈-THF confirms these observations. As noted prior, 16 exhibits three well-defined proton resonances of equal integration at δ = 7.87, 7.67 and 7.56 ppm. Once this species is reduced to the radical anion 17, these signals are extinguished due to the presence of an unpaired electron. Upon further reduction to the dianion, 18, these resonances reappear as a triplet at δ = 8.26 ppm and a singlet at δ = 6.70 ppm (integrating to a total of three protons) (Figure 3.1).

Interestingly, when these reductions are closely monitored by ¹H NMR we observe an immediate broadening of the peaks upon exposure to potassium metal. Sharp peaks do not re-appear until the dianion, 18, is formed. This indicates that a high concentration of
Scheme 3.1: The reversible transformation of 16 into its radical anion (17) and dianion (18) through reduction with potassium metal in THF under an inert atmosphere.

the paramagnetic species, 17, is a major component of the reaction mixture as the reduction progresses. This is in stark contrast to Katz’s observations of the reduction of unsubstituted COT where the COT proton resonance persists throughout much of the reduction process. This is thought to arise from the large geometric change that occurs when the tub-shaped COT is converted to the planar reduced species. Because this flattening is more energetically demanding than the coulombic barrier associated with the addition of a second electron, the radical anion is thought to disproportionate, thereby minimizing its
Figure 3.1: A) $^1$H NMR of tridecacylene, 16, in d$_8$-THF at 25 °C. B) Upon immediate exposure to potassium metal we observe a broadening of the peaks in the $^1$H NMR C) Reduction to the radical anion, 17, results in an extinguished signal, due to the generated paramagnetic species. D) Proton resonances return upon further reduction to the dianion, 18, and appear as a triplet at $\delta = 8.26$ ppm and a doublet at $\delta = 6.70$ ppm (integrating to a total of three protons)

The fact that this is not observed in the reduction of 18 is an indication that, as expected, the molecule does not undergo a large geometric change upon reduction, and as a result, the increased coulombic energy associated with the introduction of a second electron has a much larger effect. This explains why we observe two separate reduction peaks by cyclic voltammetry (CV) and why disproportionation of 17 is not
observed. Calculations support these observations, indicating that less than 1% of the radical anion disproportionates in solution.\(^87\)

The optoelectronic properties of the reduced species are consistent with previously explored systems. With each subsequent reduction, we observe a bathochromic shift of the \(\lambda_{\text{max}}\) in the UV-Vis absorption spectrum as well as an increase of the molar absorptivity of the low energy transitions (Figure 3.2).

**Figure 3.2:** UV-Vis absorption spectra of tridecacyclene 16 (blue), the radical anion 17 (green) and dianion 18 (purple) in THF at 25°C showing an increase in molar absorptivity of the low-energy transitions with each subsequent reduction.

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\(^{87}\) For this system calculations show \(K_{\text{disp}} = 10^{-6}\) as referenced in: Lam, K. and Geiger, W.E., in *Organic Electrochemistry*, ed. Hammerich, O. and Speiser, B., CRC Press, Boca Raton, 5th ed, 2016, ch. 11, 397–398
3.3 Solid-state characterization

A variety of crystallization techniques were explored to obtain crystals of the radical anion 17 and dianion 18. The radical anion proved elusive as slow diffusion of a variety of solvents into a saturated solution of 17 in THF resulted in only amorphous powders. Additionally, vapor diffusion and crystallization attempts under reduced temperatures (0 °C) all provided material unsuitable for SC-XRD. Fortunately, dark brown, equant crystals of the dipotassium adduct C_{48}H_{24}K\cdot5.5(C_8H_8O)\cdot2K of 18 were grown from the slow diffusion of n-hexanes into a THF solution of freshly prepared 18 at 25 °C and were used to validate the structure through SC-XRD studies.\(^88\) The crystal structure of the dianion displays some unusual positional disorder of one of the potassium cations and one of the THF ligands as displayed in Figure 3.3. One of the potassium cations, K1, occupies a single position on one side of the tridecacyclene saddle where it bonds with the \(\pi\)-bonds of the tridecacyclene and three THF molecules. The second potassium, which is located the opposite side of the saddle, is disordered about two positions K2 and K3 in a ratio of 1:1 as determined by occupancy refinement. These potassium atoms are on opposite sides of K1 when looking down the axis orthogonal to the plane of the tridecacyclene, indicating the coordination spheres of K2 and K3 are similar to K1. Interestingly, K2 binds to three THF ligands to fill its coordination sphere whereas K3 is bound to only two of the THF

\(^88\) CCDC 1489304 contains the supplementary crystallographic data for the structure described in this chapter. This data is provided free of charge by the Cambridge Crystallographic Data Centre. Crystallographic data for 18: triclinic, C_{180}H_{136}K_4O_{11}, \(M_r = 2150.88\), \(a = 13.3928(13)\), \(b = 15.4263(15)\), \(c = 15.9182(15)\) Å, \(V = 2792.2(5)\) Å\(^3\), \(T = 140\) K, space group \(P-\bar{1}\), \(Z = 1\), \(\lambda = 0.71073\) Å, \(p = 1.279\) g cm\(^{-3}\), \(\mu = 0.224\) mm\(^{-1}\), \(R_f = 0.0524\), \(wR_2 = 0.1424\)
**Figure 3.3:** The solid-state structure of the dipotassium adduct of 18. Carbon, oxygen, and potassium atoms are depicted as grey, red and blue atoms, respectively. Alternate positions of disordered THF molecules and hydrogen atoms have been omitted for clarity. A) The asymmetric unit of C_{48}H_{24}•6(C_4H_8O)•K1•K2  B) The asymmetric unit of C_{48}H_{24}•(C_4H_8O)•K1•K3  C) Alternating positions of C_{48}H_{24}•6(C_4H_8O)•K1•K2 and C_{48}H_{24}•(C_4H_8O)•K1•K3 along the c-axis.
ligands that bind to K2. The oxygen of one of the THF ligands binds only to K2 and lies on an inversion center.

This, in conjunction with the 50% occupancy of K2, means that the ligand’s orientation is dependent on the occupancy of K2. The relative positions of K2 and K3, and the partial occupancy THF, force a particular orientation in the crystal: one molecule of C_{48}H_{24}\cdot6(C_4H_8O)\cdotK1\cdotK2 (Figure 3.3A) must be adjacent to one molecule of C_{48}H_{24}\cdot4(C_4H_8O)\cdotK1\cdotK3 (Figure 3.3B), where the positions of K2/K3 alternate along the c-axis (Figure 3.3C). The alternate position is related by inversion symmetry. Three of the five THF ligands are disordered in a manner independent of the positional disorder of the potassium atoms and they appear to be disordered due to thermal motion.

As expected, the dianion 18 maintains a tub-like shape much like its neutral counterpart. Although not immediately apparent, the eight-membered ring of 18 demonstrates a higher degree of planarity than that of neutral tridecacyclene. This is demonstrated by measuring the angle between the opposing faces of the central COT ring (Table 2.1B) which increases by 10° (from 102° in neutral tridecacyclene to 112°) upon two-electron reduction. While prior convention held that the flattening of a COT ring upon reduction is tied with the adoption of aromatic character it’s also possible this feature is a result of strong interactions between the potassium ions and the π-bonds of the COT ring.

A stronger case for the development of aromaticity in the COT ring arises from the change in bond lengths (Table 2.1) that are observed upon reduction. It is generally accepted that aromaticity is associated with an equalization of bond lengths as this is
indicative of a de-localized π-system.\textsuperscript{89} As described in Chapter 2, tridecacyclene clearly exhibits bond alteration in the COT ring with a variation in bond lengths of \textit{ca.} 0.1 Å. The

\begin{table}[h]
\centering
\caption{Structural comparison of neutral 16 and dianion 18.}
\begin{tabular}{|c|c|c|}
\hline
 & Neutral, 16 & Dianion, 18 \\
\hline
\hline
Bond Length\textsuperscript{a} (Å) & 1.470 & 1.432 \\
 & 1.369 & 1.427 \\
 & 1.478 & 1.481 \\
 & 1.373 & 1.389 \\
\hline
Splay Angle,\textsuperscript{b} θ & 102° & 112° \\
A & 0.09 & 0.48 \\
B & 0.13 & – 0.06 \\
C & 0.89 & 0.85 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Representative bond lengths obtained from single crystal x-ray diffraction data. A complete list of bond lengths is provided in Chapter 5. \textsuperscript{b}The splay angle, θ, is defined as the angle between the best-fit-planes calculated through opposing 4 carbon segments of the central 8-membered ring. \textsuperscript{c}HOMA indices of rings A, B, and C were calculated using a normalization constant, α, of 257.7 and optimal C–C bond length, $R_{opt}$, of 1.388 Å.

bond lengths of the dianion, however, are significantly closer in length, varying by ±0.01 Å. This is particularly remarkable, as to our knowledge, this variance is smaller than observed for any previously reported metal-COT complexes despite the fact that these COT rings remain significantly distorted from planarity.

The changes in bond lengths throughout the molecule also indicate that the primary site of reduction is the central COT ring. While the 5-membered rings are also known to undergo reductions in the presence of alkali metals, it is apparent that the bonds external to the 8-membered ring change very little in comparison to those within it. Furthermore, if the 5-membered rings did play a larger role in the reduction process we would expect to see more than two accessible reductions through CV.

Finally, HOMA indices were calculated for the neutral tridecacyclene, 16, and the dianion, 18, and these values are reported in Table 2.1. This model compares the bond lengths from the X-ray structure to an optimal bond length for an aromatic ring; where a calculated value of 1 indicates aromaticity, 0 non-aromaticity and -1 antiaromaticity. While the 5- and 6-membered rings undergo rather insignificant changes in their HOMA indices, the value for the 8-membered ring increases considerably from 0.09 to 0.48. While these values alone should not be used as a quantification of aromaticity, the fact that a large increase is observed for the COT ring provides additional support that this ring is increasing in aromatic character and that it is the primary site of reduction in the molecule.
3.4 Concluding Remarks

The cyclic tetramer ofacenaphthylene, tridecacyclene, 16, is reduced to the radical anion, 17, and dianion, 18, upon exposure to fresh-cut potassium metal. The solid-state structure indicates that there is an increase in the aromaticity of the central 8-membered ring despite steric interactions preventing planarization of the molecule. This evidence supports prior discussion that aromaticity is not inherently tied to the planarity of COT-based systems.

3.5 Future directions

Throughout the course of these studies, the remarkable stability of the dianion became apparent. While 18 proved to be sensitive to water and oxygen, under inert atmospheres the material persists with little degradation. In fact, $^1$H NMR of the dianion after 24 hours showed no evidence of decomposition. To investigate this further, solutions of 18 were prepared in fresh THF and sealed in a glass tube under vacuum. After a month, the solutions were quenched and reverted back to neutral tridecacyclene (as evident by $^1$H NMR). Further quenching experiments with water and TMS-acetylene returned neutral 16. Quenching experiments have been utilized in the past to confirm the presence of the corannulene tetra-anion through the addition of protons to the site of reduction. While the protonated or alkylated quenched species were never recovered, it was likely the result of the tendency of the acenaphtylene bridge towards oxidation in the open atmosphere. The dianion was also noted to be quite soluble in THF, and with these reversible reductions and
the stability of the dianion, 18, presents itself as an attractive candidate for a non-aqueous redox flow cell battery.

Redox flow cell batteries typically utilize heavy metals, with the vanadium flow-cell battery the subject of the bulk of research since it was first constructed in the 1970s. One of the problems in the pursuit of green energy is the ability to store the energy for future use. These flow batteries have been gaining attention due to their ability to store energy in liquid form on a large scale and release it on demand by having the two liquids exchange ions through a selective membrane. Redox flow batteries utilizing aqueous media suffer some drawbacks, namely the use of heavy metals, the narrow electrochemical window of water, and restrictions to more temperate climates to prevent the freezing of the aqueous media. Redox flow batteries utilizing non-aqueous media, however, remain less studied. Recently, Aziz and coworkers have explored the use of small quinones incorporating organic molecules into redox flow batteries. Exploiting the stability gained from aromaticity gained upon reduction as the driving force for reduction, Aziz has produced a small number of functional batteries in aqueous media. In contrast, non-aqueous media allows a wider electrochemical window with the ability to incorporate a wide variety of organic molecules reducing the toxicity concerns of heavy metals. Furthermore, the depressed freezing points of organic solvents make a battery constructed

90 Thaller, L.H. The 9th Intersociety Energy Conversion Engineering Conference Proceedings 1974, 924–928
from them applicable to multiple climates. The electrochemical reversibility of tridecacyclene, in addition to the simple preparation from readily available starting materials make the dianion an ideal candidate for a redox flow battery. These investigations will be continued in the Whalley lab with the support of the University of Vermont’s Green Energy Fund.
CHAPTER 4: SYNTHETIC ATTEMPTS TOWARDS A FRAGMENT OF FULLERENE C\textsubscript{240}

4.1 Introduction

The synthesis of tridecacyclene, 16, revealed a host of unique properties due to the nature of the central eight-membered ring and has spawned multiple projects in the Whalley lab. However, the wealth of research demonstrated on small buckybowls (ie: corannulene) outlined in Chapter 1 motivated us to pursue this material as a new class of buckybowl. Specifically, tridecacyclene offers access to the precursor of the O\textsubscript{h} isomer of fullerene C\textsubscript{240} (Figure 1.13). We were especially interested in the prospect of flattening the central eight-membered ring as it would result in a Hückel anti-aromatic core. The anticipated success of this synthesis was supported with precedence as anti-aromatic COT derivatives are known in the literature.\textsuperscript{93}

While the prevailing method for synthesis of these fragments has been FVP, we were looking to avoid this method as several disadvantages including lack of functional group tolerance and scale-up to multi-gram reactions made the process significantly less attractive when compared to solution based chemistry. Additionally, it has been observed that extreme conditions can facilitate the ejection of a monomer.\textsuperscript{61} (ie, subjecting

tridecacylene to FVP conditions could produce circumtrindene rather than the $C_{240}$ fragment) Herein we present the synthetic efforts towards a fragment of the fullerene $C_{240}$ from tridecacylene using solution chemistry. Once the synthesis was optimized, we envisioned a thorough investigation of its structural, electronic, and supramolecular properties with $C_{60}$.

### 4.2 First Generation Synthesis

A recent report by Mao and coworkers of a large, warped PAH containing two heptagons utilized an oxidative cyclodehydrogenation, more commonly referred to as the Scholl reaction, in the final step of the synthesis. First reported over 100 years ago by Roland Scholl, the Scholl reaction utilizes a Lewis acid, often $\text{AlCl}_3$, to facilitate a coupling between two arene compounds. It is only recently that the Scholl reaction has

![Scheme 4.1: Proposed reaction to afford the fullerene $C_{240}$ fragment utilizing the Scholl reaction.](image)

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been demonstrated to induce strain into PAHs with the aforementioned Mao report and our labs second generation synthesis of tetrabenzo[8]circulene.69

Inspired by the literature precedents and in-house success, we looked to apply these methods to the synthesis of the C_{240} fullerene fragment (Scheme 4.1). Table 3.1 contains a summary of coupling conditions attempted. Conditions were initially modeled off those used by Miao in the synthesis of their large, saddle-shaped PAH. Freshly prepared tridecaetylence was dissolved into anhydrous dichloromethane and cooled to 0 °C. DDQ served as the oxidant and was added in one portion under nitrogen atmosphere, followed by slow addition of triflic acid (TfOH). The solution immediately adopted a deep blue color and was allowed to stir for five hours at 0 °C. TLC of the crude reaction mixture showed only starting material, and subsequent workup and \(^1\)H NMR of the crude reaction mixture confirmed this. Repeating the experimental conditions and allowing the material to slowly warm to room temperature overnight returned the same results. While the Scholl conditions used by Mao and our lab synthesizing tetrabenzo[8]circulene were done at 0 °C, historically Scholls have been shown to be effective at both low and elevated temperatures.96 We looked to apply these more vigorous conditions to tridecaetylence to facilitate bond closure. Solvent was changed from dichloromethane (due to the low boiling point of 39.6 °C) to 1,2-dichloroethane (bp = 83.4 °C). The initial reaction conditions were performed analogous to those using DCM, with the reaction mixture cooled to 0 °C and reagents added under an atmosphere of nitrogen. After slowly warming to room temperature the deep blue reaction mixture was heated to 50 °C and allowed to stir

overnight. TLC of the crude reaction mixture showed no observable product formation and starting materials dominated the solution. The reaction mixture was quenched with sodium bicarbonate over ice and $^1$H NMR of the crude reaction mixture confirmed the TLC observations. We felt it was necessary to explore stronger conditions, and the experiment was repeated with heating to reflux (95 °C). Unfortunately, as observed with the reaction at 50 °C, consumption of the starting materials could not be observed by TLC and $^1$H NMR of the crude reaction mixture showed clean tridecacyclene. With the apparent lack of reactivity under these conditions we concluded they could be abandoned. Fortunately, a number of Scholl conditions are known and could be applied to tridecacyclene.

$\text{AlCl}_3$ is one of the most common Lewis acids used in Scholl couplings. After screening conditions, we applied those reported in the synthesis of dibenzo[\textit{j,l}]fluoroanthenes.\textsuperscript{97} Tridecacyclene was dissolved in carbon disulfide, followed by addition of excess amounts of $\text{AlCl}_3$ and $\text{CuCl}_2$ and allowed to stir at room temperature overnight. TLC of the crude reaction mixture again showed no consumption of starting materials, which was confirmed by $^1$H NMR. We decided to again slowly raise the reaction temperature, and subsequent trials were run at reflux (60 °C). Under these conditions, we observed the complete consumption of tridecacyclene by TLC after about one hour. TLC of the crude reaction mixture showed a new product of slightly less polarity, which was isolated after workup and column chromatography. $^1$H NMR analysis of this product remained inconclusive, as the spectrum displayed multiple peaks in the aromatic region and not the paired doublets we were expecting. The material was submitted for mass

\textsuperscript{97} Dyker, G.; Merz, K. and Oppel, I.R. Synlett \textit{2007}, \textit{6}, 897–900
spectral analysis to help elucidate the products that were formed. No peaks of the desired molecular weight of the fragment (593 m/z) were observed. The observed peaks in the mass spectrum supported multiple chlorinations of tridecacyclene. In light of these results, we concluded that these conditions would not afford our desired buckybowl.

One of the most commonly used Lewis acids used in the synthesis of hexabenzocoronene and Suzuki’s synthesis of tetrabeno[8]circulene is FeCl₃. Tridecacyclene was dissolved in a mixture of dichloromethane and nitromethane and

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Product recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>TfOH, DDQ</td>
<td>DCM</td>
<td>0</td>
<td>starting material</td>
</tr>
<tr>
<td>TfOH, DDQ</td>
<td>DCM</td>
<td>25</td>
<td>starting material</td>
</tr>
<tr>
<td>TfOH, DDQ</td>
<td>1,2-DCE</td>
<td>50</td>
<td>starting material</td>
</tr>
<tr>
<td>TfOH, DDQ</td>
<td>1,2-DCE</td>
<td>95</td>
<td>starting material</td>
</tr>
<tr>
<td>AlCl₃, CuCl₂</td>
<td>CS₂</td>
<td>25</td>
<td>starting material</td>
</tr>
<tr>
<td>AlCl₃, CuCl₂</td>
<td>CS₂</td>
<td>60</td>
<td>multiple chlorinations</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>DCM/MeNO₂</td>
<td>–20</td>
<td>starting material</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>DCM/MeNO₂</td>
<td>25</td>
<td>starting material</td>
</tr>
</tbody>
</table>

*Reactions were conducted under a nitrogen atmosphere using oven-dried glassware and anhydrous solvents.

cooled to –20°C, followed by the addition of 10 equivalents FeCl₃. The resulting brown mixture was allowed to stir at –20°C for four hours and monitored by TLC. No consumption of tridecacyclene was observed and upon workup with MeOH and ether, tridecacyclene was recovered (confirmed by ¹H NMR). Allowing the reaction to warm to room temperature also showed no signs of reactivity on behalf of the tridecacyclene. We decided to let the reaction continue stirring, and it was monitored over the course of the next 72 hours. Despite the lengthy reaction time, no evidence of the fragment was able to be determined through all means of characterization. At this point, we came to the conclusion that we would need to devise a new synthetic plan, as the reactivity of the parent tridecacyclene was minimal under a broad range of Scholl conditions.

4.3 Second Generation Synthesis

Our initial results substantiated the need for a more reactive compound if the Scholl reaction was to be effective. It is known that methoxy groups promote and direct Scholl reactions. While the optimal position for activation places the methoxy para to the intended site of bond formation, this is simply not possible on 16. It was observed in our lab during the Scholl couplings on tetrabenzo[8]circulene that the position of the methoxy group—whether it was para or meta to the C–C bond being formed—had little effect on the yield. But when compared to the yield of the un-functionalized derivative the yield was substantially higher (ca. 20%). We hoped the addition of activating groups on the ring

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would facilitate some reactivity and we could recover our fragment. The synthesis of 5,6-dimethoxyacenaphthene, 19, was recently reported and looked to provide an excellent precursor to a modified 1-acenaphthenone.\textsuperscript{101} 5,6-dimethoxyacenaphthene, 19, was prepared from 5,6-dibromoacenaphthene, with sodium methoxide and CuI in 90% yield. Initial attempts to oxidize 19 to the monoketone with potassium dichromate were unsuccessful as 19 easily over-oxidized, returning a mixture of 19 and the quinone. To resolve this issue, we looked at the preparation of aryl ketones with DDQ in acetic acid as reported by Lee and Harvey.\textsuperscript{102} These conditions showed minimal propensity for oxidation beyond the mono-carbonyl. Dissolving 19 in acetic acid followed by addition of three equivalents DDQ afforded the monoketone 20 after thirty minutes of reaction time. Slow addition of 20 in refluxing o-dichlorobenzene with TiCl\textsubscript{4} produced the octa-methoxy tridecacyclene 21 in 5% yield (Scheme 4.2). Like tridecacyclene 16, 21 is a stable brown solid with exceptional solubility in all common organic solvents. It was noted a significantly higher portion of 20 was converted into the decacyclene, 22, than was observed with 16. Yield of 21 was also noticeably lower than tridecacyclene due to the difficulty in purification. The trimer exhibited nearly identical polarity, and extensive preparative chromatography was necessary to isolate 21 pure enough for analysis and Scholl coupling experiments. The \textsuperscript{1}H NMR of 21 in CDCl\textsubscript{3} at 25 °C exhibited two doublets of equal integration at $\delta = 7.57$ and 6.84. Like what was observed with 16, the “bay region” proton of 21 was about one ppm up-field from the analogous proton in the methoxy trimer 22. With 21 in hand we began exploring Scholl coupling reactions. DDQ was added to 21

Scheme 4.2: Preparation of octa-methoxy-tridecacyclene, 21, through cyclization of 5,6-dimethoxyacenaphtheneone 21.

Dissolved in anhydrous DCM at 0 °C, followed by slow addition of TfOH and the deep blue reaction mixture was allowed to stir for five hours. TLC of the crude material showed no visible 21, however upon quenching and workup a significant amount of starting material was recovered and characterized by $^1$H NMR. Repeated trials all produced the same results. Scholl couplings were again attempted at room temperature, 50 °C and reflux and returned unreacted starting materials. Observing the apparent stability of 21 under these conditions we elected to pursue other reagents. 21 was stirred with AlCl$_3$ and CuCl$_2$ under a nitrogen atmosphere in CS$_2$ overnight. TLC of the crude reaction mixture showed no evidence of product formation. The reaction mixture was quenched with 10% HCl and the organic material extracted with DCM. $^1$H NMR of the crude reaction material did not
exhibit any proton signals consistent with an aromatic molecule. After repeated trials of Scholl conditions with no promising results and the diminished yield in preparing the methoxylated tridecacyclene, we concluded that these conditions were unlikely to produce the desired fullerene fragment.

4.3 Third Generation Synthesis

With the stability of 16 and 21 observed under Scholl conditions, we next considered a stronger means to form the four necessary C–C bonds in the C_{240} fragment 11. As reported in the preparation of circumtrindene, a cyclic tetramer was observed in the mass spectrum of the crude reaction mixture. This cyclic tetramer, 6, contains chlorines in the necessary positions for the synthesis of our buckybow through arylation conditions. Our synthetic pathway began by replicating Scott’s synthesis of chlorinated acenaphthenone, 3, and isolating the chloro-tetramer from the crude reaction mixture. Because this material has never been isolated and characterized, optimization of the reaction conditions and purification conditions to maximize recovery have not been reported and would need to be explored. With 6 in hand, we envisioned the palladium catalyzed arylation conditions utilized in a wide variety of buckybow syntheses and the original syntheses of tetrabenzo[8]circulene would close the four C-C bonds giving the C_{240} fragment 11 (Scheme 4.3).

Preparation of 3 began with Friedel crafts acylation of 2-chloronaphthalene, 23, at -78° C in anhydrous dichloromethane. After warming to room temperature overnight and quenching with 10% HCl, the crude material was subject to flash column chromatography
Scheme 4.3: Revised synthesis towards the acenaphthenone precursor 3. Silver nitrate and iodine in refluxing methanol with trimethylorthofomrate produced the desire ester in 90% yield. These conditions avoided the use of thallium nitrate, alleviating concerns of toxicity.

giving the desired isomer 24 in 82% yield as an off-white powder. Transposition of the carbonyl functionality to the acetic ester 25 was initially reported with Thallium(III) nitrate supported on K10 clay in refluxing 1,2-dichloroethane. Unfortunately, attempts to perform this transformation failed to provide the desired ester. After trouble shooting technique and the reaction conditions, it was concluded that the issue likely lay with the thallium reagent. Additionally, the toxicity of the thallium was a concern, requiring excessive PPE and
special waste removal. Therefore, we felt an alternative method for this transformation was necessary. Higgins and Thomas reported the conversion of acetophenone to methyl phenyl acetate with I\(_2\) and AgNO\(_3\) in refluxing methanol with trimethylorthofomate.\(^{103}\) Applying these conditions to 24 provided 25 in 90\% yield as a clear oil that slowly crystallized and needed no further purification. Sodium hydroxide in THF at 50 °C overnight saponified the ester to carboxylic acid 26 in quantitative yield. Finally, an intramolecular Friedel-crafts reaction gave the chlorinated acenaphthenone, 3, in an 80\% yield after column chromatography. While we had observed the synthesis of tridecacyclene was complete after about 5-10 minutes stirring with TiCl\(_4\), we felt it was prudent to follow the experimental procedures as they were written in order to more effectively replicate Scott’s results. Addition of 3 into a refluxing solution of \(\text{o-dichlorobenzene}\) containing 6 equivalents of TiCl\(_4\) over the course of two hours via syringe pump produced a dark solution and complete consumption of starting materials was observed through TLC. The solution was quenched hot over crushed ice and concentrated HCl. After extraction with dichloromethane and removal of solvent, we observed a complicated reaction mixture with TLC revealing multiple products, including the distinct green fluorescence of the cyclic trimer. However, there were no spots with the characteristic brown color of tridecacyclene, unlike what was observed in our prior syntheses. Each spot visible in the TLC was isolated through column chromatography and characterized through \(^1\text{H NMR}\). We expected the \(^1\text{H}\) of the chlorinated tetramer 6 to be relatively simple to identify, exhibiting the five protons of the acenaphthyl subunit in the \(^1\text{H}\) in a very similar manner to the cyclic trimer. However,

Figure 4.1: $^1$H NMR in CDCl$_3$ at 25 °C of major byproduct isolated out of TiCl$_4$ mediated aldol cyclization. We were unable to identify any peaks that would correspond to what we expected from the cyclotetramer. Interestingly, the mass spectrum of this material was consistent with what was expected for the cyclotetramer, including the correct isotope ratio for four chlorines.

$^1$H NMR of all the additional products isolated out of the reaction did not produce the anticipated spectrum. Scott noted that the cyclic tetramer was typically found within the darker portions of the column fractions and the $^1$H NMR spectrum of those showed multiple peaks in the aromatic region, suggesting oligomers (Figure 4.1). This material was a deep red powder and repeat cyclizations with TiCl$_4$ varying addition speed and length of reaction time produced the same dark red powder consistently. Unable to characterize the material through $^1$H NMR, we submitted it for mass spectral analysis. Much to our surprise, the mass spectrum matched the expected mass at 738 m/z of the desired cyclotetramer (Appendix II, Figure A11, 12) and showed the correct isotope ratio expected for a material containing four chlorines. With this information, we looked to rule out any potential contaminants in the $^1$H NMR. Despite numerous preparative columns of
the material, we were unable to clean the \(^1\)H NMR up to anything discernable. Attempts to
grow crystals to validate the structure through SC-XRD studies also failed. When saturated
solutions of \(6\) in 1,2-DCE were layered with a variety of solvents to facilitate crystal growth
\((n\text{-hexanes, MeOH, EtOH, etc})\) we were only able to produce an amorphous powder.
Nuckolls demonstrated SC-XRD quality crystallization of hexabenzocorones with a
vacuum crystal oven.\(^{80b}\) With the precedence of growing crystals through this method, we
applied it to \(6\). When \(6\) was placed in our vacuum crystal oven, we began using high
vacuum and lower temperatures (\textit{ca} 200 °C) with a steady stream of nitrogen acting as the
carrier gas. No crystals were observed forming at the cooler end of the crystal oven and we
slowly increased the temperature. After increasing the temperatures to 300 °C we began to
observe a red powder collecting at the far end of the crystal oven and decomposition of the
starting material in the hot end of the oven. Based on these results we concluded that
obtaining a crystal for characterization was unlikely to be successful. Despite this, we were
confident that the material we isolated was our desired cyclotetramer. High resolution mass
spectrometry (HRMS) validated the initial mass spectral results we received and with a
tentative assessment that the red powder isolated from the cyclization was cyclotetramer \(6\),
we determined the yield to be approximately 13%—consistent with Wei’s observations.\(^{67}\)

We theorize that the \(^1\)H NMR does not reflect what we expect due to the nature of
the center 8-membered ring. The ring itself will contort into a boat shape to avoid anti-
aromaticity resulting in four possible structural conformations (Figure 4.2). One
conformer contains a C\(_4\) rotational axis corresponding to five unique proton signals in the
\(^1\)H NMR. A second conformer contains a C\(_2\) rotational axis results in 10 proton signals.
Figure 4.2: Four proposed conformations of 6. A & B) Two conformations containing no symmetry. C) Conformation with C\textsubscript{2} rotation axis. D) Conformation with C\textsubscript{4} rotation axis. Combined, all four conformations would result in 55 unique proton signals in an NMR spectrum.

Finally, two conformers contain no symmetry with all protons in a unique chemical environment. As a result of these conformers, a total of 55 unique proton signals could be observed in a \textsuperscript{1}H NMR. We do not know the extent of the percentage of each isomer, however any mixture would complicate a \textsuperscript{1}H NMR beyond analysis. We theorized heating the mixture of conformers could allow 6 to relax to the lowest energy conformation, giving a cleaner NMR. Heating 6 for several hours in o-dichlorobenzene at 200 °C and slowly cooling to room temperature returned the same NMR spectrum observed prior to the heating. Despite these issues obtaining cleaner NMR spectrums of the cyclotetramer, we felt confident in the mass spectral results that we were producing the desired compound.
With the cyclotetramer 6 in hand, explorations into closing the four C-C bonds utilizing palladium arylation chemistry could begin.

We began our investigations with the microwave assisted arylation conditions that worked smoothly for tetrabenzo[8]circulene. 6 was dissolved in de-oxygenated DMA and DBU with 40 mol% of Pd(PC\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} in a microwave tube and sealed under a nitrogen atmosphere. Heating for one hour at 160 °C for one hour in the microwave reactor (CEM Discover 909150) produced a deep black solution consistent with what was seen in the synthesis of tetrabenzo[8]circulene (Scheme 4.4). TLC of the crude reaction mixture (SiO\textsubscript{2}, 20% DCM, 80% Hexanes) showed complete consumption of the starting materials. A small fluorescent spot was observed at a slightly higher polarity than 6 and a dark baseline spot. Workup with water to remove the DMA and extraction with dichloromethane gave a black solid. Further TLC analysis however did not reveal any additional spots. The observed green fluorescent spot was isolated through preparative chromatography and characterized with \textsuperscript{1}H NMR. Much to our surprise, the \textsuperscript{1}H NMR matched the published spectrum reported for circumtrindene. We determined that the production of circumtrindene was likely a result of trace amounts of the cyclic trimer present in the starting material. Despite the evidence of a small amount of trimer impurity, we were encouraged as this result suggested we would be successful as the arylation conditions were sufficient to make the considerably more strained circumtrindene.
Scheme 4.4: Subjecting cyclic tetramer 6 to the palladium arylation conditions used in the synthesis of tetrabenzo[8]circulene did not produce any products that could be identified as the C_{240} fragment by \(^1\)H NMR.

A follow-up report to Wu’s C\(_{70}\) fragment examined the optimal reaction conditions for synthesizing buckybowls through palladium arylation.\(^{104}\) Wu found that high temperatures could lead to de-halogenation of the starting materials. They also reported that the base stoichiometry was important—decreasing the base loading from eight equivalents to four had a noticeable effect on the yield. Yields of the fullerene fragments were most effected, however, by the concentration of the starting materials. Concentrated solutions (0.1 M) or dilute solutions (5 x 10\(^{-3}\) M) all returned trace amounts of material. A concentration of 0.02 M was determined to be the optimal concentration, returning a 40% yield. With this new information in mind, we began to explore reaction concentrations, temperature and time to determine the optimal conditions for forming the C\(_{240}\) fragment. A summary of reaction conditions applied to 6 is shown in Table 3.2. Investigations began with milder conditions, progressing to those that were more forcing. 6 was dissolved in DMA (concentration of 0.02 M) under an atmosphere of nitrogen in a microwave reaction tube, followed by addition of the catalyst and heated in the microwave reactor for 20

minutes. TLC of the crude reaction mixture revealed remaining unreacted starting materials. Extending the reaction time to one hour showed consumption of 6 by TLC and trace amounts of circumtrindene. Extending the reaction time to 2 hours and increasing the temperature to 160 °C returned the same results as seen with the initial attempts. Further attempts varying the amounts of catalyst and base used all failed to return any isolatable material by TLC. Wu also reported successful syntheses of C_{70} fragments and in the interest of being thorough, 6 was dissolved in DMF under an atmosphere of nitrogen, followed by addition of the palladium catalyst and base in a pressure reaction vessel and stirred for 36 hours at 160 °C. Unfortunately, the results of these conditions mirrored those that were seen with the microwave arylation. We consistently observed a trace amount of circumtrindene produced and heavy baseline product.

Troubleshooting the reaction conditions proved to be quite challenging, as we were unable to obtain any products. We saw no evidence of single bond closure or dehalogenation of 6. One of the major issues encountered in the synthesis of 6 were the low yields encountered with the cyclization step. 2-chloronaphthalene proved to be moderately expensive with long shipping times, and an in-house synthesis of a halogenated naphthalene from the more widely available 2-naphthol would allow larger scale reactions to be prepared. Research into the preparation of 2-chloro naphthalene from 2-naphthol did not provide an attractive route as syntheses required expensive reagents or suffered from low yields. Fortunately, preparation of 2-bromonaphthalene from 2-naphthol is known to proceed in moderate yield.\textsuperscript{105} With precedent by Wang and Shevlin in the use of triflates

and bromines preparing benzo[ghi]fluoranthenes through palladium catalyzed arylations.\textsuperscript{106} We theorized the addition of bromines to our cyclic tetramer would facilitate

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>mol%</th>
<th>base</th>
<th>solvent</th>
<th>[M]</th>
<th>type</th>
<th>°C</th>
<th>time</th>
<th>results</th>
</tr>
</thead>
<tbody>
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<td>8 eq</td>
<td>DMA</td>
<td>0.01</td>
<td>(\mu)-wave</td>
<td>140</td>
<td>1hr</td>
<td>NR</td>
</tr>
<tr>
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<td>8 eq</td>
<td>DMA</td>
<td>0.02</td>
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<td>36hr</td>
<td>NR</td>
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<td>20</td>
<td>8 eq</td>
<td>DMA</td>
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<td>(\mu)-wave</td>
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<td>DMA</td>
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<td>(\mu)-wave</td>
<td>160</td>
<td>2hr</td>
<td>NR</td>
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\*p.v. = pressure vessel \ DMA = dimethyacetamide \ DMF = dimethylformamide \ base = 1,8-Diazabicyclo[5.4.0]undec-7-ene \ NR = no recovery of 57 by \(^1\text{H NMR}\), \(\mu\)-wave experiments were conducted on a CEM Discover model 909150 with 10 mL microwave tubes.

improved yields of the C-C coupling through easier insertion of the palladium catalyst into the weaker C-Br bond. With those two things in mind, we envisioned a synthesis of a brominated acenaphthenone, followed by aldol cyclization to a brominated tetramer.

4.3 Fourth Generation Synthesis

Preparation of the tetra-brominated tridecacyclene derivative began with the synthesis of 2-bromonaphthalene from 2 naphthol. 2-naphthol, 27, was added into a cooled solution of triphenylphosphine and bromine in acetonitrile and heated to 70 °C for thirty minutes. Distillation of excess acetonitrile and heating to 340 °C gave 2-bromonaphthalene, 28, in 70% yield. Friedel-crafts acylation of 28 with AlCl₃ and acetyl chloride gave 29 in comparable yields to the chlorinated derivative. Ester 30 was prepared with AgNO₃ and I₂ in 90% yield, and subsequent saponification to 31 and intra-molecular Friedel-crafts afforded the brominated acenaphthenone 32 in a similar overall yield as 3. Slow addition of 3 into a refluxing solution of TiCl₄ in o-dichlorobenzene produced the cyclic tetramer, 33, in 6% yield as an orange solid (Scheme 4.5). ¹H NMR of the brominated tetramer unfortunately was very similar to 6 with numerous peaks in the aromatic region of the spectrum that could not be assigned to any individual proton. Mass spectral analysis supported the presence of the brominated cyclic tetramer, with the purified material producing only one peak in the mass spectrum corresponding to the protonated molecular ion at 917 m/z (Appendix II, Figure A23, A24). Furthermore, like 6 the correct
Scheme 4.5: Preparation of tetra-brominated tridecacylene, 33.

isotope ratio was observed for four bromines, and we felt confident that we had made the desired material. Attempts to validate the structure through SC-XRD were unsuccessful, as no crystals suitable for analysis could be grown. Applying the crystallization conditions used on 6 returned similar amorphous powders. Attempts to grow crystals in a vacuum crystal oven also failed, with most of the material decomposing. Based on these observations, it is reasonable to conclude that the brominated tetramer 33 shares similar conformations as 6.
Scheme 4.6: Microwave assisted palladium arylations on 33 failed to return any recoverable 11.

With scalable access to 33, explorations into palladium arylations could begin. Dissolving 33 in anaerobic DMA with DBU and Pd(PCy$_3$)$_2$Cl$_2$ and heating at 160 °C in the microwave reactor for one hour unfortunately produced the same results as was observed for 6 (Scheme 4.6). Repeating the microwave arylation conditions screened for 6 returned similar results. Extensive TLC analysis of the crude material was unable to reveal any spots which could correspond to the product however trace amounts of de-halogenated material was observed. Staining the TLC plates with iodine and permanganate also failed to provide any products. $^1$H NMR of the crude reaction mixture in CDCl$_3$ showed no evidence in the aromatic region of any products, with only aliphatic peaks observed from residual catalyst.

The observed de-halogenation of our material, while small, prompted us to relax conditions to prevent this from happening. 33 was dissolved in anaerobic DMF with Pd(PCy$_3$)$_2$Cl$_2$ and DBU and sealed in a reaction pressure vessel. The resultant dark mixture was allowed to stir for 36 hours at 140 °C. TLC of the crude reaction mixture again showed evidence of dehalogenation. Further TLC analysis of the crude reaction mixture again failed to provide an isolatable material that could be identified as the C$_{240}$ fragment. A recent report by Shinokubo and coworkers reported mild arylation conditions in the
synthesis of a nitrogen-embedded buckybowl.\textsuperscript{107} We had hoped that a new catalyst under different conditions might improve our results and that perhaps alleviate the dehalogenation observed with \textbf{33}. Pd(OAc)\textsubscript{2} and PCy\textsubscript{3}•HBF\textsubscript{4} was the catalyst and ligand of choice for the final curvature inducing step of their nitrogen-embedded buckybowl. The appropriate catalyst and ligand were obtained, and test reactions on \textbf{33} were explored. \textbf{33} was dissolved into de-oxygenated DMA in a 2-neck round-bottomed flask followed by the Pd(OAc)\textsubscript{2} catalyst and PCy\textsubscript{3}•HBF\textsubscript{4} with K\textsubscript{2}CO\textsubscript{3} as the base (\textbf{Scheme 4.7}). The mixture was stirred for 36 hours at 130 °C and worked up according to the published procedure. Disappointingly, dehalogenated material was recovered and these reactions failed to return any isolatable trace of \textbf{11}.

\textbf{Scheme 4.7:} Trace amounts of dehalogenation were observed when arylation was attempted with reaction pressure vessels.

While initially disappointing, this result was encouraging as it demonstrated that of the issues we were observing, insertion of the catalyst into the C–Br bond was not one of

them. After exhausting arylations using microwave reactors and pressure vessels, we concluded, based on the consistent results, that these conditions were not going to give us the C$_{240}$ fragment.

**4.4 Fifth Generation Synthesis**

Zweig and Henderson reported a photolytic cyclodehydrogenation of 1-o-chlorophenyl-naphthalene in the synthesis of fluoranthene in 1967. Subsequent studies found similar success with the most recent work reported by Scott Hartley and coworkers. With the reactivity observed for chlorinated substrates and the irreversibility of the reaction due to the expulsion of HCl, this method warranted a closer look. 6 was dissolved into benzene under bubbling nitrogen in a 1L Ace Glass photoreactor equipped with a 450W Hg lamp. Propylene oxide was added to the solution to neutralize the anticipated HCl produced in the cyclization and 6 was irradiated overnight. After irradiation, the organic solvent was removed under reduced pressure. Unlike prior attempts to form the fragment, TLC analysis showed multiple products forming. Of most interest was a fluorescent blue spot of significant less polarity than the starting material. The products were isolated through preparative chromatography and $^1$H NMR collected. Unfortunately, we were unable to identify the fragment through NMR. The NMRs

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Scheme 4.8: Irradiation of 6 and 16 resulted in decomposition of materials and no recovered 11.

suggested decomposition products of the starting material. The predominate blue spot isolated was identified as biphenyl and came from small amounts of the solvent dimerizing under irradiation with the photo lamp. Based on these observations we concluded that 6 decomposed under the reaction conditions. Having some amount of tridecacyclene on hand, we applied the more standard photocyclization conditions to see if we could form the C–C bonds without the directing effect observed with halogens. Tridecacyclene was dissolved under a stream of nitrogen bubbling in benzene. I₂ was added as an oxidant with propylene oxide and the reaction mixture was irradiated overnight. After removal of the solvent, similar products to 6 were observed with significant decomposition of starting materials along with the recovery of a small amount of biphenyl (Scheme 4.8). To confirm proper operation of the photoreactor lamp and technique, a series of control experiments were run. Cis-stilbene was dissolved in benzene under a stream of nitrogen and irradiated with propylene oxide and I₂. After removal of the benzene under reduced pressure, ¹H NMR of the crude material showed complete conversion to phenanthrene. After repeating
the photocyclization conditions on 6 and tridecacyclene and observing the same decomposition products, we felt that this method warranted no further exploration.

4.5 Mechanistic Insights to Aldol Cyclization

One of the major disadvantages to the synthetic attempts of the fullerene fragment were the low yields of the halogenated cyclotetramers 6 and 33. Specifically, aldol cyclizations are known to suffer greatly with a halogen in the 2 position. Further adding to the complexity of determining how to improve conditions is the unknown mechanism by which the cyclotetramer forms. While investigations into forming the C240 fragment were ongoing, we directed a significant effort to optimize the syntheses of 6 and 33 to alleviate some of the extensive chromatography that was required to obtain cyclotetramers that were free of impurities. Furthermore, while we could run larger aldol reactions (ca 1g), the yield was still unsatisfactory and a directed, efficient synthesis would have been beneficial.

It is well known that the trimer synthesis is initiated by the reaction of two acenaphthenone monomers to form a dimer, which then reacts with an additional monomer to form an acyclic trimer. This molecule then undergoes a 6π-electrocyclization giving the fully cyclized trimer species. In the case of the tetramer it is unclear whether the mechanism proceeds through the reaction of two dimers in solution or through the acyclic trimer reacting with an additional monomer, giving an acyclic tetramer (Scheme 4.9). The former case seemed to be more likely, as we expected the intramolecular cyclization of the acyclic trimer to occur much more rapidly than the intermolecular reaction with an additional
Scheme 4.9: The assembly of decacyclene (top) proceeds through the acyclic trimerization of 1-acenaphthenone followed by electrocyclization and loss of water. It is unclear whether the assembly of tridecacyclene (bottom) proceeds through the assembly of two acenaphthenone dimers or the addition of an additional monomer to the acyclic trimer.

monomer. With the observed stability of 16 to Scholl and photocyclizations in addition to the relative ease of synthesis and purification we focused our efforts on the halogenated cyclotetramer 6. We theorized that this could be confirmed through the synthesis of the dimer of 6, which could then be subjected to the TiCl₄ cyclization conditions. By converting all the monomer into the dimer, the synthesis of the trimer could be avoided with the absence of monomer in the reaction conditions (Scheme 4.10). The presence of the dimer of 6 has been noted as one of the byproducts in the synthesis of circumtrindene, however the structure has never been fully characterized. Dimerization of 1-acenaphthenones has been shown to occur under the presence of a Lewis acid and mild
Scheme 4.10: Proposed route to cyclotetramer 6 to circumvent the Lewis-aldol cyclization.

Working concurrently with groupmate Nicholas Dodge, preparation of the dimer, 34, was achieved through dimerization of 3 with BBr₃ in toluene at 55 °C in 70% yield (Scheme 4.10). The structure of 34 was validated with ¹H, ¹³C and DEPT-135 NMR. The presence of the chlorine in the dimer favored the formation of α-γ unsaturated configuration due to the strain present between the chlorine atoms and the carbonyl oxygen in the α-β dimer. DEPT-135 NMR supported this conclusion with the presence of 12 C–H bound carbons. When 34 was added to refluxing TiCl₄ in o-dichlorobenzene, we were unable to recover any of 6 and only led to the presumed formation of long oligomers as evidenced by the recovery of insoluble materials. Propionic acid and p-toluenesulfonic acid were shown by Amick to produce decacyclene in high yields, and those were the next conditions explored. Under those conditions we observed complete consumption of the starting materials and two new products—one deep red in color, 35, and one purple, 36 (Scheme 4.11). Oxygen appears to be a vital component in this reaction as no 35 or 36 are observed when anaerobic solvents are used under an atmosphere of nitrogen.
**Scheme 4.10**: Preparation of the dimer of 2-chloroacenaphthenone was carried out by Nick Dodge to investigate the mechanism of formation of the cyclic tetramer.

$^1$H NMR and $^{13}$C spectrum of the material showed clear aromatic protons and carbons that were not consistent with what was observed for 6. The $^1$H NMR the red material, 35, in CDCl$_3$ exhibited 10 aromatic protons, suggesting the material produced contained a C$_2$ axis of symmetry. When we obtained the $^1$H NMR of purple material, 35 in CDCl$_3$ there was peak broadening on two of the protons, suggesting the motion of those protons were slow on the NMR timescale. When a solution of 36 in d$_6$-DMSO was gently heated to 75 °C the peaks resolved into a doublet and triplet with equal integration, providing a spectrum very similar to what was observed for 35. The $^{13}$C of the two compounds revealed the presence of a carbonyl carbon and this was supported by the mass spectrum of 35 and 36. The two compounds produced were identical in mass and they both were exactly two oxygens larger than 6 with a molecular weight of 769 m/z (For reference, the chlorotetramer, 6, returned a mass of 737 m/z). These results are consistent to those reported by Scott.$^{64}$ When the 1-acenaphthenone derivative used by Scott was added to TiCl$_4$ in hot o-dichlorobenzene a red material was isolated through preparative
Scheme 4.11: It was initially believed that reaction of 34 with a Brönsted acid produced two acyclic tetramers red and purple in color. SC-XRD of the material revealed that instead the reaction formed red cyclotetramer 35 and purple cyclotetramer 36.

chromatography. Mass spectrum of this material, like the material recovered by us, showed the presence of two additional oxygens. Scott tentatively assigned the as an acyclic tetramer with two ketones. Applying this to our observed results, we expected the structure of the red and purple material to be acyclic tetramers with two ketones (Scheme 4.11). Unlike what was observed for 6 and 33, these materials were very crystalline and we sought to validate the structure through SC-XRD. We were also unsure which compound (red or purple) corresponded to which potential configuration. Slow diffusion of hexanes into a saturated solution of 35 in chloroform produced deep red block-like crystals. Slow evaporation of a saturated solution of 36 in DMSO produced dark purple block-like
Figure 4.3: Exposing the acenaphthenone dimer 34 to a Brønsted acid did not result in the synthesis of 6 but deep red and purple material, 35 and 36. The solid-state structure of 35 (A) and 36 (B) revealed a cyclic tetramer with a central eight-membered ring with the orientation of the ketones trans in 35 and cis in 36. Hydrogen and solvent molecules have been omitted for clarity and thermal ellipsoids are shown at 70% probability. C) Crystal packing of 35. D) Crystal packing of 36.

To our surprise, the X-ray structure was not that of an acyclic tetramer, but that of a cyclic tetramer containing a central six-membered ring (Figure 4.3).

The structure of 35 distorts significantly from planarity and is composed of four acenaphthylene subunits flanking a central six-membered ring. Two of the acenaphthyl units comprise two sides of the six-membered ring and only deviate from planarity due to steric interactions between the adjacent hydrogens giving a propeller shape to one half of
the molecule (analogous to what is seen in decacyclene). The second pair of acenaphthyl units are oriented perpendicular to the previous two with the sp$^3$ hybridized carbons in the benzylic position of the acenaphthyl subunit serving as each “corner” of the ring. 35 positions the two ketones in a trans configuration (Figure 4.3A) and is likely dictated through the dipole moment between the two acenaphthenone units which minimizes steric and electronic repulsion. The structure of 36 is very similar to 35 only differing by the orientation of the carbonyl groups (Figure 4.3B). The positioning of the carbonyls trans in 35 is expected to result in a more favored structure. This is supported by the fact that we observe 35 to be the major product (43%) over 36 (6%) which orients the ketones in a cis configuration (Figure 4.3B), increasing the amount of steric and electronic strain between the carbonyl oxygens.$^{111}$

These surprising results allowed us to conclude that a direct synthesis of the cyclotetramer 6 could not be achieved. Furthermore, the mechanism of two dimers of 32 coming together in solution to form the cyclotetramer in the Lewis-acid catalyzed aldol reaction was not as straightforward as additionally believed, with the complex products isolated suggesting a more randomized arrangement of halogens, supporting the observations noted by Scott in the second synthesis of circumtrindene.$^{19b}$

$^{111}$ Crystallographic data for: 35, monoclinic, C$_{36}$H$_{26}$Cl$_{10}$O$_2$, $M_r = 1009.17$, $a = 30.948(3)$, $b = 13.2601(4)$, $c = 16.4381(17)$ Å, $V = 4274.8(14)$ Å$^3$, $T = 100$ K, space group C/2c, $Z = 4$, $\lambda = 0.71073$ Å, $p = 1.568$ g cm$^{-3}$, $\mu = 0.696$ mm$^{-1}$, $R_1 = 0.0381$, $wR_2 = 0.0987$ for $I > 2(I)$. 36, C$_{48}$H$_{30}$Cl$_{4}$O$_2$, $M_r = 770.44$, $a = 10.5055(4)$, $b = 11.9411(5)$, $c = 17.2568(7)$, $V = 2051.24(14)$ Å$^3$, $T = 100$ K, space group P -1, $Z = 2$, $\lambda = 0.71073$ Å, $p = 1.247$ g cm$^{-3}$, $\mu = 0.326$ mm$^{-1}$, $R_1 = 0.0495$, $wR_2 = 0.1366$.
4.6 Discussion

Throughout the course of these investigations, the difficulty of preparing the C_{240} fullerene fragment persisted, further complicated by either no reactivity of the starting materials or decomposition of the materials. We initially theorized that the $^1$H NMR observed (Figure 4.1) was the result of multiple atropisomers of 6 (Figure 4.2), but that the head-to-tail arrangement of the chlorines still remained. Based on the results observed for 6 we arrived at the same conclusions for the observed $^1$H NMR of 33. The results observed in Section 4.5, however, have cast doubt on those initial conclusions. The results indicate that when dimer 34 is produced in solution it can assemble into an acyclic tetramer which does not position the chlorines in the correct arrangement to facilitate bond closure through palladium catalyzed arylations. The observed presence of materials similar to 35 and 36 in TiCl$_4$ mediated aldol cyclizations further affirms that these materials are likely a major byproduct of the reaction, and their assembly does not support a full head-to-tail assemble of the cyclic tetramer. Thus, we can conclude that the observed $^1$H NMR spectrum is not the result of contortions of the central eight-membered ring, but is a result of multiple configurations of the tetramer with the chlorines dispersed randomly throughout. A direct consequence of this would be the inability to form the fragment through palladium arylations. With those results in mind we felt that the synthesis of the C_{240} fragment was unlikely to be successful, as we demonstrated increasingly more forcing
Figure 4.4: Tetracyclopenta[defjkl,pqr,vwx]tetraphenylene (TCPTP), was never successfully characterized with the only recorded instance that of a mass-spec hit of the di-cation.\textsuperscript{117} Recent attempts of the synthesis reveal extreme instability of the material. In this case, it was attributed to the presence of radicals.

conditions that led to the eventual breakdown of starting materials and the inability to assemble the necessary precursor for the palladium arylations.

During the duration of this project, reports published by other research groups further affirm that preparations of materials of this nature are not always successful. A PAH very similar to the fragment we were trying to prepare, Tetracyclopenta[defjkl,pqr,vwx]tetraphenylene (TCPTP) has been known for a few decades, however it has never been characterized beyond the mass spectrum of the dication (Figure 4.4).\textsuperscript{112} A more recent theoretical study shows that the material contains $28\pi$ electrons distributed over the molecule as a central anti-aromatic ring of $8\pi$ electrons and a peripheral ring of $20\pi$ electrons—also anti-aromatic.\textsuperscript{113} The theoretical calculations showed the material would exhibit di-radical and tetra-radical states. Further calculations of the electron densities on the structures placed the radicals in the five-membered rings,

\textsuperscript{112} Heimbach, H. and Hey, H. \textit{Angew. Chem. Int. Ed.} 1970, 9, 527–528
Scheme 29: Tobe’s recent report on Scholl couplings in the synthesis of planar COT derivatives found a propensity for skeletal re-arrangements over the formation of C-C bonds. This was supported with theoretical calculations, with the barrier of bond migration significantly lower in energy than that of the bond formation.

which resulted in the instability of the molecule. While this molecule does not exhibit directly the same electronic structure as our desired fragment 11, it does illustrate that despite the synthesis of some planar COT derivatives there still remains many situations where the structures are unable to be prepared.114

A more damning report to the instability of PAHs containing the central core we were trying to synthesize was reported very recently (Scheme 4.12).115 Subjecting a COT


derivative prepared by the group prior\textsuperscript{116} to Scholl conditions would have given almost an identical molecule to the one we have tried to prepare. When this COT derivative was subject to two different variations of Scholl conditions, skeletal re-arrangements of the core were observed. FeCl\textsubscript{3} in a mixture of nitromethane and dichloromethane gave exclusively a skeletal re-arrangement where the central eight-membered ring was transformed into a seven-membered ring. When subject to DDQ and Sc(OTf\textsubscript{3}) in chlorobenzene at 120 °C, the central eight-membered ring actually re-arranged into a hexabenzocoronene derivative. It was determined that the seven-membered ring was an intermediate step in the synthesis of the hexabenzocoronene product as treatment with DDQ and Sc(OTf\textsubscript{3}) facilitated the re-arrangement of the seven-membered ring to the six (Scheme 4.12). Calculations revealed that the skeletal re-arrangement was energetically preferable to the formation of a new C–C bond. We attempted to replicate the observed skeletal re-arrangement with 16. As we have previously reported, FeCl\textsubscript{3} had little effect on the material. When 16 was dissolved in chlorobenzene with DDQ and Sc(OTf\textsubscript{3}) and heated overnight at 120 °C, TLC of the crude reaction mixture showed only starting materials. After quench, workup and purification the \textsuperscript{1}H NMR was unable to confirm the presence of 16, only showing multiple peaks in the aromatic region, giving evidence to decomposition of materials. With the recent reports on the instability of similar structures and the difficulties in assembling 6 in a head-to-tail manner we concluded that the synthesis of 11 warranted no further attention and we should direct our efforts in expanding the utility of tridecacyclene.

\textsuperscript{116} Nobusue, S.; and Tobe, Y. Synlett. 2016, 27, 2140–2144
4.7 Conclusions and Future Work

A number of methods were attempted on tridecacyclene, 16, and other derivatives to form a fragment of the $O_h$ isomer of the fullerene $C_{240}$ which contains six octagonal rings in its carbon network in addition the more traditional five-and six-membered rings. Scholl couplings all returned unreacted starting materials or products with none of the necessary C–C bonds formed. Likewise, photolytic cyclodehydrogenation resulted in the decomposition of materials and none of the desired compound was recovered. Palladium arylations utilizing the chlorinated and brominated tetramers did show consumption of starting materials, however the high amount of insoluble material recovered suggested that the material was likely decomposing under the conditions. The growing body of evidence supporting the inherent instability of materials with this particular eight-membered ring flanked by four hexagonal rings and four pentagonal rings allows us to conclude that the synthesis of this fragment with its central anti-aromatic core is unlikely to be successful and research efforts can be directed elsewhere.

The precursor, tridecacyclene, has much brighter future directions. As detailed in Chapter 3, the electronic nature of tridecacyclene makes it an ideal candidate for investigations into non-aqueous flow-cell batteries and development of such batteries are currently under investigation in the Whalley research lab.
CHAPTER 5: EXPERIMENTAL PROCEDURES

5.1 General

Unless otherwise noted, all reagents were used as received and all reactions were carried out under a dry N\textsubscript{2} atmosphere using flame dried glassware and monitored by TLC (SiO\textsubscript{2}-60 F\textsubscript{254} pre-coated plates, Silicycle Inc., Québec, Canada). All commercially available starting materials were purchased from Acros, Fisher-Scientific, Sigma Aldrich or Oakwood Chemicals. Anaerobic and anhydrous solvents were obtained from purification columns (Pure Process Technology, Nashua, NH). Column chromatography was performed on a CombiFlash R\textsubscript{f} 200 with Redisep normal phase silica columns. (ISCO Inc., Lincoln NE) UV-visible absorption spectra were recorded on a Shimadzu 2450 UV-visible Spectrometer with UV Probe 2.33 software.

\textsuperscript{1}H NMR spectra were recorded on a Varian Unity Inova 500 (500 Mhz) or a Bruker ARX 500 (500 Mhz) spectrometer at room temperature. \textsuperscript{13}C NMR spectra were recorded on a Bruker ARX 500 (125 Mhz) spectrometer at room temperature. Chemical shifts are recorded in parts per million (ppm) and calibrated with an internal TMS standard. Data is reported as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet) coupling constant (Hz) and number of protons. Microwave experiments were conducted on a CEM Discover 909150 using 10 mL microwave tubes. (CEM Corporation, Matthews, NC) High-resolution mass spectra were collected on a Thermo-Fisher Scientific LTQ Orbitrap Discovery 3. SC-XRD data for Chapters Three and Four was collected on a Bruker Smart Apex II X-ray diffractometer.
5.2 Experimental procedures for Chapter 2

1-Acenaphthenone (15): Acenaphthene, 14, (5.0g, 32.4 mmol) was dissolved in 200 mL of glacial acetic acid in a 2-necked round-bottom flask equipped with a stir bar. Potassium dichromate (9.53g, 32.4 mmol) was added in portions to the solution with rapid stirring and reaction flask was cooled with ice. The reaction mixture was allowed to slowly come up to room temperature and stirred for 48hrs. The dark green reaction mixture was poured into water and the organic layer was extracted with DCM (3 x 15 mL). The organic fractions were combined and washed with saturated sodium bicarbonate, dried over MgSO₄ and solvent was removed under reduced pressure. Crude material was subject to flash column chromatography (SiO₂, 40g, 3:2 DCM/Hexanes) to provide 2.0g (37 % yield) of 14 as a light tan solid. ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.09 (d, J = 8 Hz, 1H), 7.96 (d, J = 7 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.71 (t, J = 15, 7 Hz, 1H), 7.6 (dd, J = 15, 8 Hz), 7.46 (d, J = 7 Hz, 1H), 3.82 (s, 2H) ¹³C NMR (125 MHz, CDCl₃, ppm) δ 202.9, 142.9, 135.0, 134.7, 131.4, 130.9, 128.3, 128.0, 123.9, 121.4, 121.0, 42.0 NMR shifts are in agreement with published spectra.
Tridecacyclene (16): This procedure was adapted from known Aldol cyclization conditions. A flame-dried 2-necked round-bottomed flask was equipped with a stir bar and reflux condenser and purged with an atmosphere of N₂. TiCl₄ (0.94 mL, 8.6 mmol) and o-dichlorobenzene (10.5 mL) were added to the flask and the reaction mixture was brought to reflux. 1-acenaphthenone, (0.241 g, 1.43 mmol) dissolved in o-dichlorobenzene (10.5 mL) was then added dropwise to the refluxing TiCl₄ mixture. The reaction was monitored by TLC until complete consumption of 1-acenaphthenone was observed. The reaction mixture was then poured (while hot) into a 250 mL Erlenmeyer flask containing crushed ice and conc. HCl(aq) (10 mL). The organic layer was extracted with dichloromethane (3 x 5 mL), the organic fractions were combined and the solvent was removed under reduced pressure. Crude material was subject to flash column chromatography (SiO₂, 12 g column, 1:4 DCM / cyclohexane, Rf = 0.38) to provide 45 mg (21% yield) of 16 as a brown solid. 

$^1$H NMR (500 MHz, CDCl₃, ppm) δ 7.87 (d, 1H, $J = 8.0$ Hz), 7.67 (d, 1H, $J = 6.9$ Hz), 7.56 (t, 1H, $J = 7.5$ Hz) $^{13}$C NMR (125 MHz, CDCl₃, ppm) δ 140.6, 137.7, 129.9, 128.2, 127.7, 127.4, 125.0 HRMS (M+1) Calcd for C₄₈H₂₅ 601.1956 m/z; Found 601.1951.
Also recovered from Aldol cyclization:

\[
\text{Decacyclene (1): Yellow solid, (<1\%) } ^1\text{H NMR (500 Mhz, CDCl}_3\text{, ppm) } \delta 8.83 \text{ (d, 1H, } J = 7.1 \text{ Hz) } 7.97 \text{ (d, 1H, } J = 8 \text{ Hz) } 7.81 \text{ (t, 1H, } J = 7.4 \text{ Hz) NMR shifts are in agreement with published spectra.}^{65}
\]

5.3 Experimental procedures for Chapter 3

\[
\text{Tridecacyclene radical anion (17): In a glove box under nitrogen atmosphere freshly cut potassium metal (excess) was added to tridecacyclene (10 mg, 0.016 mmol) dissolved in 0.5 mL THF in a scintillation vial with vigorous stirring. Reduction to the radical anion was observed as the solution adopted a dark green color, quickly followed by reduction to}
\]
the dianion indicated by a dark purple color. Excess potassium metal was removed through filtration and tridecacyclene (10mg, 0.016 mmol) in 0.5 mL THF was added to the reaction mixture to produce the dark green solution of the radical anion. $^1$H showed no identifiable peaks, consistent of a species with an unpaired electron.

**Tridecacyclene dianion (18):** In a glove box under nitrogen atmosphere freshly cut potassium metal (excess) was added to tridecacyclene (20mg, 0.032 mmol) dissolved in a 1 mL THF in a scintillation vial with vigorous stirring. Reduction to the dianion was observed as the reaction mixture adopted a dark purple color. Excess potassium metal was removed through filtration to yield the tridecacyclene dianion. $^1$H NMR (500 Mhz, d$_8$-THF, ppm) $\delta$ 8.21 (t, 1H, $J = 5$ Hz) 6.65 (d, 2H, $J = 5$ Hz) $^{13}$C NMR (125 Mhz, d$_8$-THF, ppm) $\delta$ 143.7, 133.9, 131.5, 126.7, 120.8, 118.3, 113.4
5.4 Experimental procedures for Chapter 4

5,6- dibromoacenaphthene: Acenaphthene (10g, 154.2 mmol) was dissolved in anaerobic DMF (65 mL) under an atmosphere of nitrogen in a 250 mL two-necked round-bottom flask. NBS (29.7g, 167.3 mmol) was added to the solution slowly and the reaction mixture was stirred at 40 °C overnight and precipitated a yellow material. Precipitate was collected through vacuum filtration, washed with water and cold methanol and air dried. Crude material was recrystallized from hot Hexanes/CHCl$_3$ (5:3) to give 3.8g of light brown crystals. (19% yield) $^1$H NMR (500 Mhz, CDCl$_3$, ppm) δ 7.80 (d, 1H, $J$ = 7.5 Hz), 7.10 (d, 1H, $J$ = 7 Hz), 3.31 (s, 2H) $^{13}$C NMR (125 Mhz, CDCl$_3$, ppm) δ 147.0, 141.9, 135.8, 127.8, 120.9, 114.4, 30.0 NMR shifts are in agreement with published spectra.$^{117}$

5,6-dimethoxyacenaphthene (19): Fresh cut sodium (1.5g, 65.38 mmol) was added to 30 mL of anhydrous methanol under an atmosphere of nitrogen in a flame dried 100 mL 2-neck round-bottomed flask equipped with a stir bar and reflux condenser. The raw sodium was stirred until fully dissolved. CuI (0.609g, 3.2 mmol) and 15 mL of anhydrous dioxane were added and the resulting orange solution was heated at reflux for 30 minutes. 5,6-
dibromoacenaphthene (1.99g, 6.4 mmol) was added to solution and refluxed for 4 hours, after which the excess methanol was distilled off and the brown solution was refluxed an additional 24-48 hours. After consumption of starting materials was observed by TLC, the solution was cooled to room temperature and washed with saturated ammonium chloride and organic layer was extracted with ethyl acetate (15mL x 3) Crude material was recrystallized from methanol to yield 1.1g (81%) of a light brown solid. $^1$H NMR (500 Mhz, CDCl$_3$, ppm) δ 7.13 (d, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 1H) 3.96 (s, 3H) $^{13}$C NMR (125 Mhz, CDCl$_3$, ppm) δ 153.9, 142.6, 137.5, 119.6, 115.6, 107.3, 56.6, 29.9 NMR shifts are in agreement with published spectra.$^{101}$

![Structure](https://example.com/structure.png)

5,6-dimethoxy-1(2H)-Acenaphthylene (20): In a 2-neck RBF equipped with a stir bar, 19 (0.610g, 2.85 mmol) was dissolved in 285 mL of glacial acetic acid and 57 mL of distilled water. DDQ (1.94g, 8.55 mmol) was added to the reaction mixture and solution immediately adopted a dark color. Upon consumption of starting materials by TLC, organic material was poured into water and extracted with CHCl$_3$ (5 mL x 6). Organic fractions were combined, washed with saturated sodium bicarbonate to quench remaining acid and then dried over MgSO$_4$. Solvent was removed under reduced pressure and crude material was subject to Flash Column Chromatography (SiO$_2$, 40g column, 2:3 EtOAc/Hexanes) to yield 144 mg (22%) of a light tan solid. $^1$H NMR (500 Mhz, CDCl$_3$, ppm) δ 7.93 (d, $J = 8$ Hz, 1H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 8$ Hz, 1H), 6.85 (d, $J = 7.5$ Hz, 1H), 4.08 (s,
1H, 4.00 (s, 3H), 3.69 (s, 2H) $^{13}$C NMR (125 Mhz, CDCl$_3$, ppm) δ 202.1, 161.6, 155.3, 146.5, 127.5, 126.1, 124.1, 122.2, 114.5, 107.3, 106.7, 56.6, 56.2, 41.9

1,6,7,12,13,18,19,24-octamethoxy-tridecacyclene (21): A flame-dried 2-necked round-bottomed flask was equipped with a stir bar and reflux condenser and purged with an atmosphere of N$_2$. TiCl$_4$ (0.44 mL, 4.0 mmol) and o-dichlorobenzene (9 mL) were added to the flask and the reaction mixture was brought to reflux. 20, (0.153 g, 0.67 mmol) dissolved in o-dichlorobenzene (9 mL) was then added dropwise to the refluxing TiCl$_4$ mixture. The reaction was monitored by TLC until complete consumption of 20 was observed. The reaction mixture was then poured (while hot) into a 250 mL Erlenmeyer flask containing crushed ice and conc. HCl$_{(aq)}$ (10 mL). The organic layer was extracted with dichloromethane (3 x 5 mL) and dried over MgSO$_4$. The organic fractions were combined and the solvent removed under reduced pressure. Crude material was subject to preparative thin layer chromatography (SiO$_2$, DCM) to provide 7 mg (5% yield) of 21 as a brown solid. $^1$H NMR (500 Mhz, CDCl$_3$, ppm) δ 7.57 (d, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 8$ Hz, 1H), 4.05 (s, 3H) $^{13}$C NMR (125 Mhz, CDCl$_3$, ppm) δ 158.1, 135.0, 133.3, 132.6,
126.2, 113.0, 106.3, 56.4 HRMS (M+) Calcd for C_{56}H_{40}O_{8} 840.2730 m/z found 840.2736 m/z

Also recovered from Aldol cyclization:

1,6,7,12,13,18-hexa-methoxydecacyclene (22): Orange solid (5%) $^1$H NMR (500 Mhz, CDCl$_3$, ppm) $\delta$ 8.66 (d, $J = 7.95$ Hz, 1H), 7.06 (d, $J = 8.05$ Hz, 1H), 4.15 (s, 3H)

1-(7-chloronaphthalen-1-yl)ethanone (23): was prepared according to a published procedure.$^{10b}$ In a flame dried 250 mL 3-neck round bottom flask equipped with a stir bar under an atmosphere of nitrogen was dissolved 2-chloronaphthalene, 23, (10.0g, 61.5 mmol) in 100 mL of anhydrous dichloromethane and cooled to -10 °C. AlCl$_3$ (25.33g 190 mmol) was added slowly in portions. The resulting red solution was allowed to stir for 10 minutes and then cooled to -78 °C. Acetyl chloride (9.06 mL, 127 mmol) was added drop-
wise and solution was allowed to stir for 5 hours at -78°C after which it was allowed to come up to room temperature overnight. Reaction mixture was quenched with 10% HCl in an ice bath and organic layer extracted with dichloromethane (3 x 10 mL). Solvent was removed under reduced pressure and crude material subject to Flash Column Chromatography (SiO₂, 1:1 DCM/Hexanes) to give 10.4g of a tan powder. (83%) ^1H NMR (500 Mhz, CDCl₃, ppm) δ 8.88 (d, J = 2.0 Hz, 1H), 7.99 (dd, J = 7.2, 1.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.49 (dd, J = 8.0, 7.2 Hz, 1H), 7.47 (dd, J = 8.4, 2.4 Hz, 1H), 2.73 (s, 3H); ^13C NMR (125 Mhz, CDCl₃, ppm) δ 201.17, 134.62, 134.17, 133.18, 132.34, 130.87, 130.15, 129.93, 127.59, 125.46, 124.74, 29.86.

**Methyl 2-(7-chloronaphthalen-1-yl)acetate (25):** In a flame dried 2-neck 500 mL round bottom flask equipped with a stir bar was added 1-(7-chloronaphthalen-1-yl)ethanone, 23, (12.0g 58.82 mmol) and 100 mL of anhydrous methanol under an atmosphere of nitrogen. Trimethylorthoformate (88 mL, 807.35 mmol) was added to the mixture, followed by AgNO₃ (19.98, 117.65 mmol). Finally, I₂ (14.92g, 58.82 mmol) was added and mixture was stirred at reflux for 24 hours. After consumption of 23 was observed on TLC, the reaction mixture was cooled to room temperature and silver salts were removed through gravity filtration. The filtrate was evaporated under reduced pressure to give 13.6g of a brown oil that slowly crystallized. (99%) ^1H NMR (500Mhz, CDCl₃, ppm) δ 7.97 (d, J = 1.6 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.77 (1H, X portion of ABX pattern), 7.46—7.41(2H,
AB portion of ABX pattern), 7.44 (dd, \( J = 8.4, 1.6 \) Hz, 1H), 4.03 (s, 2H), 3.71 (s, 3H); \(^{13}\text{C}\) (125Mhz, CDCl\(_3\), ppm) \( \delta \) 171.75, 132.92, 132.49, 132.16, 130.42, 129.95, 129.13, 128.03, 126.84, 125.87, 123.06, 52.38, 38.86

2-(7-chloronaphthalen-1-yl)acetic acid (26): Methyl 2-(7-chloronaphthalen-1-yl)acetate, 25, (13.4g, 57.26 mmol) was dissolved in a 1:1 solution of NaOH/THF in a 250 mL round bottom flask equipped with a stir bar. NaOH solution was prepared to be 1M with 3 equivalents of NaOH. Solution was heated for 24 hours at 50 °C. Reaction mixture was cooled to room temperature and washed with conc. HCl and organic layer was extracted with dichloromethane (3x 15 mL). Organic fractions were combined and solvent was removed under reduced pressure. Crude material was rinsed with cold dichloromethane to give 11.49g of a white powder (99%). \(^1\text{H}\) (500Mhz, DMSO-\( d_6\), ppm) \( \delta \) 12.51 (s, 1H), 8.01 (d, \( J = 2.4 \) Hz, 1H), 8.00 (d, \( J = 8.8 \) Hz, 1H), 7.90 (1H, X portion of ABX pattern), 7.55 (dd, \( J = 8.8, 2.2 \) Hz, 1H), 7.05 (2H, AB portion of ABX pattern), 4.06 (s, 2H); \(^1\text{H}\) (500Mhz, CDCl\(_3\), ppm) \( \delta \) 7.94 (d, 1H, \( J = 1.6 \) Hz), 7.80 (d, 1H, \( J = 8.8 \) Hz), 7.78 (1H, X portion of ABX pattern), 7.45—7.41 (2H, AB portion of ABX pattern), 4.06 (s, 2H); \(^{13}\text{C}\) (125Mhz, CDCl\(_3\), ppm) \( \delta \) 177.46, 132.92, 132.22, 130.53, 129.40, 129.22, 128.38, 127.03, 125.93, 123.02, 38.69.
8-chloroacenaphthylene-1(2H)-one (3): In a flamed dried 3 neck 1000 mL round bottom flask equipped with a stir bar, 2-(7-chloronaphthalen-1-yl) acetic acid, 26, (9.36g, 42.45 mmol) was dissolved in 70 mL of thionyl chloride under an atmosphere of nitrogen. The resulting red solution was heated at reflux for one hour and excess thionyl chloride was removed through distillation. The resultant acid chloride was dissolved in 500 mL of anhydrous dichloromethane and cooled to 0 °C in an ice bath. AlCl₃ (11.6g, 87.03 mmol) was added in portions and mixture was stirred for 1 hour at 0 °C and then heated to reflux for 15 minutes. After 15 minutes, the solution was cooled to room temperature and washed with KF (7.79g, 134.15 mmol) in 10% HCl. Organic layer was extracted with DCM (3 x 15mL), fractions combined and solvent removed under reduced pressure. Crude material was subject to flash column chromatography (SiO₂, 2.5:2.5 DCM/Hexanes) to yield 6.87g of 8-chloroacenaphthenone, 3, as a tan solid (80%). ¹H NMR (500Mhz, CDCl₃, ppm) δ 8.00 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.61 (dd, J = 8.4, 7.2 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.50 (dd, J = 7.2, 0.8 Hz, 1H), 3.86 (s, 2H); ¹³C (125Mhz, CDCl₃, ppm) δ 199.97, 143.82, 133.93, 132.77, 130.32, 130.01, 129.52, 129.25, 128.62, 124.20, 122.06, 42.52
**3,9,15,21-tetrachloro-tridecacyclene (6):** TiCl₄ (8.82 mL, 80.42 mmol) was added to 75 mL of o-dichlorobenzene in a flame dried 300 mL two-necked round-bottomed flask equipped with a reflux condenser and stir bar and the resultant yellow solution was heated to 180 °C. 8-chloroacenaphthylen-1(2H)-one, 3, (2.62g, 12.97 mmol) was dissolved in 75 mL of o-dichlorobenzene and added to the refluxing TiCl₄/o-dichlorobenzene mixture with a syringe pump over the course of one hour. After addition, the reaction mixture was allowed to stir an additional hour. TLC of the crude reaction material showed consumption of 3 and reaction mixture was poured hot over crushed ice and conc. HCl (20 mL). Organic layer was extracted with DCM (3 x 20mL), fractions combined, dried over MgSO₄ and evaporated under reduced pressure to give a black residue. Flash column chromatography (SiO₂ 1:4 DCM/Hexanes) gave 257 mg of a deep red powder (11%). NMR data unable to be obtained due to multiple atropisomers. HRMS (M⁺) Calcd for C₄₈H₂₀Cl₄ 737.0397 m/z; Found 737.0400 m/z.
2-bromonaphthalene (28): A 500ml 3-neck round bottom flask was equipped with a stir bar and addition funnel. Triphenylphosphine (144g 0.55 mol) was added to 125 mL acetonitrile. Solution was cooled to 0° C with an ice bath and bromine (28.3 mL, 0.55 mol) was added dropwise over 30 minutes with stirring at 0 °C. After addition of bromine, 2-naphthol, 27, (72g, 0.50 mol) in 100 mL acetonitrile was added and mixture was heated to 70 °C for 30 minutes. Acetonitrile was distilled off and round bottom flask was fitted with a large glass tube connected to a 500-mL round bottom flask half filled with water. Mixture was heated to 220 °C until all solid has melted and then heated to 340 °C until evolution of HBr ceased. Reaction melt was cooled to 100 °C and poured into a 1L beaker and cooled to room temperature. Crude residue was purified through column chromatography (SiO₂, hexanes) to give a 77g of a white crystalline solid (75%). ¹H NMR (500 Mhz, CDCl₃, ppm) δ 8.00 (d, J = 1.85 Hz, 1H), 7.80 (m, 1H), 7.75 (m, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.54 (dd, J = 8.7, 1.9 Hz), 7.49 (m, 2H) ¹³C (125 Mhz, CDCl₃, ppm) δ 134.4, 131.8, 129.9, 129.5, 129.2, 127.8, 126.9, 126.8, 126.2, 119.7

1-(7-bromonaphthalen-1-yl)ethanone (29): Prepared using the same procedure 23, white solid (73%). ¹H NMR (500 Mhz, CDCl₃, ppm) δ 9.03 (d, J = 2 Hz, 1H), 7.99 (dd, J = 7.5
Hz, $J = 1.5$ Hz, 1H), 7.97 (d, $J = 8$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.62 (dd, $J = 8.5$ Hz, $J = 1.5$ Hz, 1H), 7.52 (dd, $J = 8.5$, 7.5 Hz, 1H), 2.74 (s, 3H) $^{13}$C (125 Mhz, CDCl$_3$, ppm) 201.0, 134.1, 133.0, 132.4, 131.1, 130.0, 129.8, 128.5, 124.7, 123.0, 29.7 HRMS (M+) Calcd for C$_{12}$H$_9$BrO 248.9915 m/z; found 248.9925 m/z.

Methyl 2-(7-bromonaphthalen-1-yl)acetate (30): Prepared using the same procedure as 24, white solid, (99%). $^1$H NMR (500 Mhz, CDCl$_3$, ppm) δ 8.14 (d, $J = 1.5$ Hz, 1H), 7.75 (dd, $J = 7.5$, 2.5 Hz, 1H) 7.72 (d, $J = 8.5$ Hz, 1H), 7.56 (dd, $J = 8.5$ Hz, 1.5 Hz, 1H), 7.43 (m, 2H), 4.02 (s, 2H), 3.70 (s, 3H) $^{13}$C (125 Mhz, CDCl$_3$, ppm) δ 171.5, 133.2, 132.2, 130.3, 129.8, 129.2, 128.9, 127.9, 126.2, 125.9, 120.7, 52.2, 38.7 HRMS (M+) Calcd for C$_{13}$H$_{11}$BrO$_2$ 279.0021 m/z; found 279.0027 m/z.

2-(7-bromonaphthalen-1-yl)acetic acid (31): Prepared using the same procedure as 25, white solid (99%). $^1$H NMR (500 Mhz, CDCl$_3$, ppm) δ 8.12 (s, 1H) 7.75 (dd, $J = 6.85$, 2.6 Hz 1H), 7.73 (d, $J = 8.7$ Hz, 1H), 7.57 (dd, $J = 8.7$, 1.85 Hz, 1H ), 7.44 (m, 2H), 4.05 (s, 2H) $^{13}$C NMR (125 Mhz, CDCl$_3$, ppm) δ 177.2, 133.1, 132.2, 130.4, 129.3, 129.1, 128.9,
128.2, 126.1, 125.9, 120.9, 38.4 HRMS (Na+) Calcd for C\(_{12}H_9BrO_2\) 286.9678 \(m/z\); found 286.9695 \(m/z\).

![8-bromoacenaphthylene-1(2H)-one](image)

**8-bromoacenaphthylene-1(2H)-one**: Prepared using the same procedure as 8-chloroacenaphthylene-1(2H)-one Tan Solid. 63\% \(^1\)H NMR (500 Mhz, CDCl\(_3\), ppm) \(\delta\) 7.90 (d, \(J = 8.5\) Hz, 1H) 7.80 (d, \(J = 8\) Hz, 1H) 7.76 (d, \(J = 8.5\) Hz, 1H) 7.62 (dd, \(J = 8.5, J = 7\) Hz, 1H) 7.50 (dd, \(J = 7, 1\) Hz, 1H,) 3.86 (s, 2H) \(^{13}\)C NMR 200.1, 144.2, 133.5, 133.0, 132.4, 132.1, 129.7, 128.5, 124.1, 121.7, 116.9, 42.3 HRMS (M\(^+\)) Calcd for C\(_{12}H_7BrO\) 246.9759 \(m/z\); found 246.9769 \(m/z\).

![3,9,15,21-tetrabromo-tridecacyclene](image)

**3,9,15,21-tetrabromo-tridecacyclene (33)**: Prepared using the same procedure as 6. Red Powder (12\%) NMR data unable to be obtained due to multiple atropisomers. HRMS (M\(^+\)) Calcd for C\(_{48}H_{26}Br_4\) 916.8338 \(m/z\); Found 916.8350 \(m/z\).
(Z)-3,8'-dichloro-2H,2'H-[1,1'-biacenaphthylenylidene]-2-one (34): 3 (100 mg, 0.493 mmol) was dissolved in anhydrous toluene (7 mL) in a flame dried 50 mL round-bottom flask equipped with a stir bar and reflux condenser under an atmosphere of nitrogen. The solution was slowly heated to 55 °C and BBr₃ (1.35g, 5.43 mmol, 0.5 mL) was added dropwise to the warm reaction mixture slowly. After addition of BBr₃, the resultant red solution was stirred at 55 °C until consumption of starting materials was observed via TLC (~ 4 hours). Reaction mixture was cooled to room temperature and poured over crushed ice and conc. HCl (5 mL) and organic layer was extracted with DCM. Organic fractions were combined, dried over MgSO₄ and solvent removed under reduced pressure. The crude residue was purified via flash column chromatography (SiO₂ 2:3 DCM/Hexanes) to give 85 mg (90 %) of a yellow residue. 

\begin{align*}
\text{^1H NMR (500 Mhz, CDCl}_3, \text{ppm) } & \delta 8.05 (d, J = 8.5 \text{ Hz, 1H}), 7.85 (m, 1H), 7.74 (d, J = 8.1 \text{ Hz, 1H}), 7.78 (d, J = 8.3 \text{ Hz, 1H}), 7.64 (d, J = 8.5 \text{ Hz, 3H}), 7.54 (d, J = 8.7 \text{ Hz, 1H}), 7.46 (m, 2H), 6.52 (s, 1H), 5.97 (s, 1H) \\
\text{^13C NMR (125 Mhz, CDCl}_3, \text{ppm) } & \delta 198.8, 142.8, 139.1, 137.7, 137.6, 135.1, 132.7, 131.6, 130.4, 130.2, 130.0, 129.9, 129.5, 129.3, 128.8, 128.7, 127.8, 127.4, 127.0, 126.7, 124.8, 124.4, 122.6, 52.0
\end{align*}

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35 and 36: In a flame dried 2-neck round bottom flask equipped with a reflux condenser and stir bar was added tosyllic acid (0.22g, 1.16 mmol) and propionic acid (0.9 mL, 1.16 mmol) in 1 mL o-dichlorobenzene and heated to 140 °C. ((Z)-3,8'-dichloro-2H,2'H-[1,1'-biaacenaphthylenylidene]-2-one), 34, (90 mg, 0.23 mmol) was dissolved into 3 mL o-dichlorobenzene and added to the hot reaction mixture via syringe. Solution was monitored by TLC until consumption of starting materials was observed and quenched with 5M NaOH. Organic layer was extracted with DCM (5mL x 3). Organic fractions were combined and solvent was removed under reduced pressure. Crude material was purified via flash column chromatography (SiO2, 3:2 DCM/Hexanes) to give red (38mg) and purple (5.3 mg) compounds (35) and (36).
35: Dark red solid, (43%) \(^1\)H NMR (CDCl\(_3\), 500 Mhz, ppm) \(\delta\) 8.46 (d, \(J = 7\) Hz, 1H), 7.90 (d, \(J = 8.05\) Hz, 1H), 7.83 (d, \(J = 8.6\) Hz, 1H), 7.76 (dd, \(J = 8.15, 7.1\) Hz, 1H), 7.64 (dd, \(J = 8.5, 2.6\) Hz, 2H), 7.46 (d, \(J = 6.95\) Hz, 1H), 7.42 (d, \(J = 8.6\) Hz, 1H), 7.33 (dd, \(J = 8.3, 7.1\) Hz, 1H), 7.12 (d, \(J = 8.5\) Hz, 1H) \(^{13}\)C NMR (CDCl\(_3\), 125 Mhz, ppm) \(\delta\) 197.1, 142.9, 137.4, 136.1, 134.9, 134.4, 134.1, 132.3, 131.0, 130.9, 130.5, 129.5, 129.2, 129.1, 128.7, 128.3, 128.2, 127.3, 127.0, 126.1, 125.0, 123.9 HRMS (M+) Calcd for C\(_{48}\)H\(_{20}\)Cl\(_4\)O\(_2\) 769.0296 m/z; Found 769.0300 m/z.

36: Dark Purple Solid, (6%) \(^1\)H NMR (d\(_6\)-DMSO, 500 Mhz, ppm, 65\(^\circ\) C) \(\delta\) 8.57 (d, \(J = 7.05\) Hz, 1H), 8.12 (d, \(J = 8.0\) Hz), 8.09 (d, \(J = 8.65\) Hz), 7.93 (m, 2H), 7.82 (d, \(J = 8.25\) Hz, 1H), 7.54 (d, \(J = 8.6\) Hz, 1H), 7.25 (d, \(J = 8.5\) Hz, 1H), 7.13 (t, \(J = 15.45, 7.25\) Hz, 1H) 6.57 (d, \(J = 6.95\) Hz, 1H) \(^{13}\)C NMR (d\(_6\)-DMSO, 125 Mhz, ppm 65\(^\circ\) C) 197.7, 143.2, 138.2, 136.4, 134.4, 133.9, 133.3, 131.1, 130.7, 130.2, 129.9, 129.6, 129.2, 129.1, 128.7, 128.6, 128.1, 127.5, 127.3, 126.2, 123.2, 64.7 HRMS (M+) Calcd for C\(_{48}\)H\(_{20}\)Cl\(_4\)O\(_2\) 769.0296 m/z; Found 769.0300 m/z.
A crystal of compound 16 was measured on a Bruker D8 diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 100 K. A crystal of 16•2(C$_{60}$)•3(C$_6$H$_5$Cl) was measured with synchrotron radiation at beamline X10SA, Swiss Light Source ($\lambda = 0.6199$ Å). The structures were solved by direct methods with SHELXT$^{118}$ and refined by full-matrix least-squares analysis (SHELXL)$^{119}$ using the program package OLEX2.$^{120}$ Data for 2 were corrected for absorption effects using the multi-scan method (SADABS)$^{121}$ Data for 2•2(C$_{60}$)•3(C$_6$H$_5$Cl) were corrected for absorption using an empirical method (XDS)$^{122}$ All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters (in terms of a riding model). CCDC 1440430 (16) and 1440429 (16 • 2(C$_{60}$) • 3(C$_6$H$_5$Cl)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif.
A structural model consisting of the host plus 3 disordered 1,2-DCE solvate molecules was developed; however, positions for the idealized solvate molecules were poorly determined. Since positions for the solvate molecules were poorly determined a second structural model was refined with contributions from the solvate molecules removed from the diffraction data using the bypass procedure in PLATON. No positions for the host network differed by more than two su's between these two refined models. The electron count from the "squeeze" model converged in good agreement with the number of solvate molecules predicted by the complete refinement.

Crystal data at 100 K for C$_{48}$H$_{24}$, $D_c = 1.095$ mg/mm$^3$, $\mu$(MoK$\alpha$) = 0.062 mm$^{-1}$. Black block crystals (linear dimensions approx. 0.24 mm x 0.16 mm x 0.10 mm) were grown by slow vapor diffusion of hexane into a 1,2-dichloroethane solution at 25 °C. Number of measured and unique reflections 31405 and 8394, respectively ($R_{int} = 0.0467$). Final $R_1 = 0.0540$, $wR_2 = 0.1467$ for independent reflections with $I > 2\sigma(I)$, 433 parameters.
and $2.72 < \theta < 55.18^\circ$ (corresponding R values based on all 8394 reflections are 0.0814 and 0.1582, respectively).

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A structural model consisting of 2, 2 C\textsubscript{60}, and 3 C\textsubscript{6}H\textsubscript{5}Cl was developed. The structure as a 2-component twin (BASF 0.26). Twin law found with TwinRotMat function of PLATON\textsuperscript{123} Structure solution and refinement was done with a single domain, and the two-domain reflection list (HKLF 5) was used for the final refinement.

Crystal data at 100 K for C\textsubscript{186}H\textsubscript{39}Cl\textsubscript{3} \( D_c = 1.593 \text{ mg/mm}^3 \), \( \mu (0.6199 \text{ Å}) = 0.122 \text{ mm}^{-1} \). Black plate crystals (linear dimensions approx. 0.2 mm x 0.2 mm x 0.01 mm) were grown by mixing saturated solutions of 2 and C\textsubscript{60} in chlorobenzene at 25 °C and left for several days. Number of measured reflections 30180. Final \( R_1 = 0.0607 \), \( wR_2 = 0.1708 \) for independent reflections with \( I > 2\sigma(I) \), 1703 parameters and \( 2.146 < \theta < 52.562^\circ \) (corresponding R values based on all reflections are 0.0618 and 0.1714, respectively).
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X-Ray quality crystals were obtained from a freshly prepared solution of 3 in THF with hexanes layered on top. X-Ray diffraction data was collected at 140K on a Bruker APEX 2 CCD platform diffractometer (MoKα, \( \lambda = 0.71073 \) Å). Crystals were mounted under Paratone-N cryoprotectant oil onto a nylon loop. A structural model consisting of host, 5.5 THF solvent ligands, and 2 K atoms was developed. One potassium atom occupies two positions with a 50:50 ratio. H atoms were included as riding idealized contributors. H atom U values were assigned as 1.2 times the carrier \( U_{eq} \). Three of the
THF molecules had significantly larger thermal parameters; thus, these moieties were modeled as disordered over two discrete positions. Rigid-bond restraints (s.u. 0.01) were imposed on displacement parameters for all disordered sites and similar displacement amplitudes (s.u. 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The C-C bonds and C-O bonds for disordered positions were restrained to be similar (s.u. 0.01); the 1,4-distances were also restrained to be similar (s.u. 0.04). The displacement parameters of C60A and C60B were constrained to be equivalent. One THF molecule sits on an inversion center. The occupancies of the atoms of this molecule were set to 0.5 as befitting the special position. Bond lengths were fixed to idealized values. The C-C bonds for C71-C72 and C70-C69 were fixed at 1.535 Å, for C71-C70, 1.539 Å, for O6-C69 and O6-C72, 1.443 Å. In addition, Rigid-bond restraints (s.u. 0.01) and similar displacement amplitudes (s.u. 0.01) were imposed for these atoms.

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5.5 Crystallography for Chapter 4

Crystal Data for 35:

X-Ray quality crystals were obtained from a freshly prepared solution of 35 in CHCl₃ with hexanes layered on top. X-Ray diffraction data was collected at 140K on a Bruker APEX 2 CCD platform diffractometer (MoKα, λ = 0.71073 Å). Crystals were mounted under Paratone-N cryoprotectant oil onto a nylon loop. Data were measured using ω scans scans of n/a (d, scan_width)° per frame for n/a (d, scan_rate) s using MoKα radiation (fine-focus sealed X-ray tube, ? kV, ? mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent). The actually achieved resolution was Θ = 28.766.
Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 18819 reflections, 75 of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarisation. The final completeness is 100.00 out to 28.766 in \( \Theta \). The absorption coefficient (\( \mu \)) of this material is 0.696 and the minimum and maximum transmissions are 0.93280 and 1.00000. The structure was solved in the space group C2/c (# 15) by Direct Methods using the \textit{ShelXT} (Sheldrick, 2015) structure solution program and refined by Least Squares using version of \textit{ShelXL} (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of \( Z' \) is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

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5.7 Experimental References


121 G. M. Sheldrick, SADABS. Program for Empirical Absorption Correction of Area Detector Data. Univ. of Göttingen, Göttingen, Germany, **1996**.


LIST OF ABBREVIATIONS

$^1$H NMR ................................................................. Proton Nuclear Magnetic Resonance
6-31G** ................................................................. Polarized Basis Set
$^{13}$C NMR ................................................................. Carbon Nuclear Magnetic Resonance
AcOH ........................................................................ Acetic Acid
APCI ................................................................. Atmospheric-pressure Chemical Ionization
B3LYP ................................................................. Becke, three parameter, Lee-Yang Parr
cc-pVDZ ................................................................. Correlation-consistent Basis Set
CNO ........................................................................ Carbon Nano-onions
CNT ........................................................................ Carbon Nanotube
COT ........................................................................ Cyclooctatetraene
CS$_2$ ........................................................................ Carbon Disulfide
CV ........................................................................ Cyclic Voltammetry
DBU ........................................................................ 1,8-Diazabicyclo(5.4.0)undec-7-ene
DCE ........................................................................ Dichloroethane
DCM ........................................................................ Dichloromethane
DDQ ........................................................................ 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DFT ........................................................................ Density Functional Theory
DMA ........................................................................ Dimethylacetamide
DMF ........................................................................ Dimethylformamide
eq ........................................................................ equivalent
FVP ........................................................................ Flash Vacuum Pyrolysis
THF ............................................................. Tetrahydrofuran
TLC ............................................................ Thin-layer Chromatography
TMS ........................................................... Trimethylsilyl
TOFMS ........................................................ Time of Flight Mass Spectrometry
UV .............................................................. Ultraviolet
XRD ............................................................ X-ray Powder Diffraction
SC-XRD ...................................................... Single Crystal X-ray Diffraction


Chernichenko, K.Y.; Sumerin, V.V.; Shpanchenko, R.V.; Balentova, E.S. and Nenajdento V.G. Angew. Chem. Int. Ed. 2006, 45, 7367–7370


Dyker, G.; Merz, K. and Oppel, I.R. Synlett 2007, 6, 897–900


Howard, J.B.; Mckinnon, T.J.; Makarovsky, Y.; Lafleur, A.L.; and Johnson, M.E. Nature 1991, 139–141


Jiang, H.; See Lee, P.; and Li, C. Energy Environ. Sci. 2013, 6, 41–53


Nibusue, S.; and Tobe, Y. *Synlett.* **2016**, *27*, 2140–2144


Sakurai, H.; Daiko, T.; and Hirao, T. *Science*, 2003, 301, 1878


Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8


APPENDIX I: LIST OF BOND LENGTHS
Table A1: Complete list of bond lengths for compound 16.

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Table A2: Complete list of bond lengths for 16 $/C_{60}$ complex

Picture of asymmetric unit with residue suffixes.
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(C6F)-(C1F) | 1.382(3)
(C1F)-(Cl1F) | 1.742(2)
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C(6) C(7) 1.371(4)
C(7) C(8) 1.426(3)
C(8) C(9) 1.412(3)
C(8) C(13) 1.414(3)
C(9) C(10) 1.369(3)
C(10) C(11) 1.424(3)
C(11) C(12) 1.371(3)
C(12) C(13) 1.413(3)
C(14) C(24) 1.379(3)
C(14) C(15) 1.477(3)
C(15) C(16) 1.378(3)
C(15) C(25) 1.430(3)
C(16) C(17) 1.428(3)
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C(18) C(19) 1.414(3)
C(19) C(25) 1.398(3)
C(19) C(20) 1.422(3)
C(20) C(21) 1.368(4)
C(21) C(22) 1.418(3)
C(22) C(23) 1.386(3)
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Figure A1: $^1$H NMR of tridecacyclene, 16, in CDCl$_3$
Figure A2: $^{13}$C NMR of tridecacylene, 16, in CDCl$_3$
Figure A3: $^1$H NMR of decacyclene, 1, in CDCl$_3$.
Figure A4: $^1$H NMR of the Tridecacyclene dianion, 18, in d$_8$-THF
Figure A5: $^{13}$C NMR of the Tridecacyclene dianion, 18, in d$_8$-THF
Figure A6: $^1$H NMR of 20 in CDCl$_3$
Figure A7: $^{13}$C NMR of 20 in CDCl$_3$
Figure A8: $^1$H NMR of 21 in CDCl$_3$
Figure A9: $^{13}$C NMR of 21 in CDCl$_3$
Figure A10: $^1$H NMR of 22, in CDCl$_3$
Figure A11: Direct Infusion Positive APCI LCMS of 6
Figure A12: Direct Infusion Positive APCI LCMS of 6 (magnified around 737 m/z region)
Figure A13: $^1$H NMR of 28 in CDCl$_3$
Figure A14: $^{13}$C NMR of 28 in CDCl$_3$
Figure A15: $^1$H NMR of 29 in CDCl$_3$
Figure A16. $^{13}$C NMR of 29 in CDCl$_3$
Figure A17: $^1$H NMR of 30 in CDCl$_3$
Figure A18: $^1$H NMR of 30 in CDCl$_3$
Figure A19: $^1$H NMR of 31 in CDCl$_3$
Figure A20: $^{13}$C NMR of 31 in CDCl$_3$
Figure A21: $^1$H NMR of 32 in CDCl$_3$
Figure A22: $^{13}$C NMR of 32 in CDCl$_3$
Figure A23: Direct Infusion Positive APCI LCMS of 33
Figure A24: Direct Infusion Positive APCI LCMS of 33 (magnified around 916 m/z region)
Figure A25: $^1$H NMR of 31 in CDCl$_3$
Figure A26: $^{13}$C NMR of 31 in CDCl$_3$
Figure A27: DEPT-135 NMR of 34 in CDCl₃
Figure A28: $^1$H NMR of 35 in CDCl$_3$
Figure A29: $^{13}$C NMR of 35 in CDCl$_3$
Figure A30: $^1$H NMR of 36 in CDCl$_3$
Figure A31: $^1$H NMR of 36 in d$_6$-DMSO at 25 °C
Figure A32: $^1$H NMR of 36 in $d_6$-DMSO at 65 °C
Figure A33: $^{13}$C NMR of 36 in d$_6$-DMSO at 65 °C