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Robbins, Steven J.

Lethbridge, Alta. : University of Lethbridge, Deptartment of Chemistry and Biochemistry, 2009
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# CYCLOPHANES FROM KINETICALLY STABILIZED BIS(ISOBENZOFURAN)S 

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B.Sc., University of Lethbridge, 2007

A Thesis<br>Submitted to the School of Graduate Studies Of the University of Lethbridge<br>In Partial Fulfilment of the Requirements for the Degree

## MASTER OF SCIENCE

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LETHBRIDGE, ALERTA, CANADA
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#### Abstract

Isobenzofurans (IBF)s are interesting molecules with regards to their structure and reactivity. The properties of these compounds are investigated through the use of gas phase calculations and kinetic studies. This work provides insight into the aromatic character of IBF and how substituents affect IBF's reactivity.

Substituted derivatives of naphtho[1,2-c:5,6-c]difuran are synthesized and reacted with tethered bis(dienophile)s to form cyclophanes. Phenyl-substituted naphtho[1,2-c5,6-c]difuran forms only a single isomer when reacted with a tethered bis(acrylate) and a tert-butyldimethylsilyl-substituted derivative exhibits higher selectivity towards cyclophane formation rather than polymer formation. Evidence for strong intramolecular interactions within these cyclophanes is presented as well.

A five-step synthesis of anthra[1,2-c:7,8-c]difuran is developed, although with a poor overall yield. Similar reaction conditions could be applied to the synthesis of anthra[1,2-c:5,6$c]$ difuran. We also propose the synthesis of two different aromatic belts from these compounds.


## Acknowledgements

I would like to thank my supervisor, Dr. Peter Dibble, for his support and guidance. I would have difficulty finding a supervisor with the same knowledge, experience, and helpfulness. Special thanks to Dr. René Boeré for his support as my co-supervisor and his guidance through all the crystallography. I acknowledge Dr. Brent Selinger for his guidance throughout my thesis which was greatly appreciated. I would also like to thank Dr. Stacey Wetmore for her help with the computational chemistry and the use of her cluster for some of the calculations.

Thanks for the financial support provided by the University of Lethbridge and the Keith and Hope Ferguson Memorial Scholarship. Thanks to Dr. Dibble for his generous assistance as well.

For their friendship I would like to thank my lab mates Anton Beigler, Elizabeth Baker, Lindsay Wichers, and David Franz. They were always around to teach me new things, share a laugh or two, celebrate my successes, and make me feel better about my failures. The members of the Boeré lab are also thanked for their cooperation in sharing the lab over the years. Thanks to the Advanced Organic Chemistry class who obtained some of the kinetic data and members of the Wetmore lab for their help with some of the calculations.

I would also like to thank my family and Jerrah Sawatsky for their love and support.

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## List of Abbreviations

| Ac | acetyl |
| :--- | :--- |
| AM1 | Austin model 1 (a semi-empirical method in quantum chemistry) |
| AO | atomic orbital |
| ASE | aromatic stabilization energy |
| b.p. | boiling point |
| t-Bu | tert-butyl |
| C | Celsius |
| COSY | correlation spectroscopy |
| CRE | classical resonance energy |
| d | doublet (NMR) |
| d | day(s) |
| dd | doublet of doublets (NMR) |
| ddd | doublet of doublet of doublets (NMR) |
| dec | decomposed (m.p.) |
| DMAP | 4-dimethylaminopyridine |
| dipytet | 3,6 -di(2'-pyridyl)-s-tetrazine |
| DRE | Dewar resonance energy |
| dt | doublet of triplets |
| EI | electron impact (MS) |
| ESI | electron spray ionization (MS) |
| Et | ethyl |
| eV | electron volts |
| FMO | frontier molecular orbitals |
| FVT | flash vacuum thermolysis |
| g | gram(s) |
| HOMA | harmonic oscillator measure of aromaticity |
| HOMO | highest occupied molecular orbital |
| h | hour(s) |
| Hz | Hertz |
| IBF | isobenzofuran |
| IR | infrared |
| ISE | isomerization stabilization energy |
| IUPAC | International Union of Pure and Applied Chemists |
| K | Kelvin |
| kcal | kilocalorie(s) |
| kJ | kilojoule(s) |
| LDA | lithium diisopropylamide |
| LUMO | lowest unoccupied molecular orbital |
| M | molarity |
|  |  |


| m | multiplet (NMR) |
| :---: | :---: |
| MA | maleic anhydride |
| MD | molecular dynamics |
| Me | methyl |
| mg | milligrams |
| MHz | megahertz |
| min | minutes |
| mL | millilitre(s) |
| MM | molecular mechanics |
| mm | millimetre(s) |
| mmol | millimole(s) |
| MO | molecular orbital |
| mol | mole(s) |
| m.p. | melting point |
| MS | mass spectroscopy |
| NICS | nucleus-independent chemical shift |
| NMM | N -methylmaleimide |
| NMR | nuclear magnetic resonance |
| NOESY | nuclear overhauser effect spectroscopy |
| Ph | phenyl |
| ppm | parts per million |
| PPTS | pyridinium $p$-toluenesulfonate |
| RE | resonance energy |
| REPE | resonance energy per $\pi$-electron |
| RMSD | root-mean-square deviation |
| s | singlet (NMR) |
| s | second |
| $\mathrm{SC}_{\text {products }}$ | structure count of products |
| $\mathrm{SC}_{\text {reactants }}$ | structure count of reactants |
| $\mathrm{SC}_{\text {ratio }}$ | structure count ratio |
| t | triplet (NMR) |
| TBS | tert-butyldimethylsilyl |
| TCA | trichloroacetic acid |
| THF | tetrahydrofuran |
| TMS | tetramethylsilane |
| TRE | topological resonance energy |
| UV | ultraviolet |
| Vis | visible |

## List of Numbered Structures


1

7

12

2

8


13


3


9


4


10


11


16


17

X
a S
b $\mathrm{CH}_{2}$
c $\mathrm{CH}_{2}$
d $\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$
e quinoxaline-2,3-diyl
f quinoxaline-2,3-diyl $\mathrm{CH}_{2} \mathrm{OAc}$
g quinoxaline-2,3-diyl CH 2 OH
h quinoxaline-2,3-diyl $\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CHCH}_{2}$
i quinoxaline-2,3-diyl $\mathrm{CH}_{2} \mathrm{OEt}$
j quinoxaline-2,3-diyl $\mathrm{CH}_{3}$ k $\mathrm{CH}_{2} \mathrm{OCH}_{2} \quad \mathrm{CH}_{2} \mathrm{OAc}$

## 20a-k


x
$\begin{array}{ll}\text { a } & \text { NLL } \\ \text { b } & 0\end{array}$
21

18a-k
$N-N$
$N$
$N=N$
19


22


27


23
3


26



28


29


30


31


32


33


34


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42


43


44


45 45


46


51


47


48


49


54
50


55

56

57

58

59
xviii

$\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}$

60


61


62


63


64


65


66


67


68


69


70
xix


71


72


73


74


75


76

a R1, R2 $=H, H \quad n=3$
b R1,R2 $=\mathrm{H}, \mathrm{H} \quad \mathrm{n}=4$
c R1,R2 $=H, H \quad n=5$
d R1, R2 $=\mathrm{H}, \mathrm{H} \quad \mathrm{n}=6$
e $\mathrm{R} 1, \mathrm{R} 2=\mathrm{Ph}, \mathrm{H} \quad \mathrm{n}=3$
$R 1, R 2=T B S, T B S \quad n=3$
g R1, R2 $=\mathrm{Ph}, \mathrm{SiPh}_{3} \quad \mathrm{n}=3$
77

$X=\left(\mathrm{CH}_{2}\right) n$
78



$$
\mathrm{X}=\mathrm{a}\left(\mathrm{CH}_{2}\right)_{3}
$$

$$
\mathrm{b}\left(\mathrm{CH}_{2}\right)_{4}
$$ c ${ }_{\text {c }}\left(\mathrm{CH}_{2} \mathrm{CCCH}_{2}\right.$ d $\left(\mathrm{CH}_{2}\right)_{5}$

## 83

## 79

$$
\begin{array}{r}
\mathrm{H}_{2} \mathrm{~N}-\mathrm{X}-\mathrm{NH}_{2} \\
\mathrm{X}=\mathbf{a}\left(\mathrm{CH}_{2}\right)_{3} \\
\mathbf{b}\left(\mathrm{CH}_{2}\right)_{5} \\
\mathbf{c}\left(\mathrm{CH}_{2}\right)_{7} \\
\mathrm{~d}\left(\mathrm{CH}_{2}\right)_{9}
\end{array}
$$

80



$$
\begin{array}{r}
\mathrm{X}=\mathbf{a}\left(\mathrm{CH}_{2}\right)_{3} \\
\mathbf{b}\left(\mathrm{CH}_{2}\right)_{5} \\
\mathbf{c}\left(\mathrm{CH}_{2}\right)_{7} \\
\mathbf{d}\left(\mathrm{CH}_{2}\right)_{9}
\end{array}
$$

81
$\mathrm{HO}-\mathrm{X}-\mathrm{OH}$
$X=\mathbf{a}\left(\mathrm{CH}_{2}\right)_{3}$ b $\left(\mathrm{CH}_{2}\right)_{4}$
c $\mathrm{CH}_{2} \mathrm{CCH}_{2}$ d $\left(\mathrm{CH}_{2}\right)_{5}$

82


b

87

$\begin{aligned} \mathrm{X}= & \mathbf{a}\left(\mathrm{CH}_{2}\right)_{3} \\ & \mathbf{b}\left(\mathrm{CH}_{2}\right)_{4} \\ & \mathbf{c} \mathrm{CH}_{2} \mathrm{CCCH}_{2}\end{aligned}$
88


89



90


91


92

93


97


98


99


100


101


102





104

103


.


105


106


107


108


109


110


111

## Introduction

This thesis will discuss the use of both substituted and non-substituted
bis(isobenzofuran)s for the synthesis of cyclophanes. The purpose of this research is to generate novel materials that might find practical application in a variety of fields. Cyclophanes have been used in surface chemistry, material science, catalysis, and medicine.

Isobenzofuran chemistry is reviewed in Chapter 1 including its structure, aromaticity, and reactivity. Methods used to generate and isolate it will also be discussed in detail. A review of bis(isobenzofuran)s will also be presented including novel compounds synthesized in the Dibble research group.

Novel resonance calculations regarding the aromaticity of IBF will be presented in Chapter 2. The X-ray crystal structure of 1,3,6,8-tetrakis(t-butyldimethylsilyl)naphtho[1,2-c:5,6c]difuran will also be presented and the structural properties of this compound discussed.

Substituted derivatives of isobenzofuran will be discussed in Chapter 3. Various ways for generating these compounds will be reviewed and a number of examples presented. Novel calculations regarding the effect of substituents on isobenzofuran's molecular orbitals will be shown here as well. Kinetic measurements were performed on a variety of substituted isobenzofuran derivatives and the implications of this data are discussed.

Cyclophane chemistry will be the focus of Chapter 4 . Work done by several key researchers that is related to this study will be reviewed. The synthesis of two types of tethered bis(dienophile)s will be shown here as well. Two previously synthesized cyclophanes have been subject to rigorous structural analysis and the results will be shown here. Cyclophanes synthesized from tethered bis(acrylate)s have particularly interesting structures which will be analyzed based on NMR and computational data. The regiospecific directing effects of phenyl substituents will be discussed with regards to cyclophane formation as well. A proposal for the synthesis of a molecular belt will also be discussed here.

This thesis will conclude with the discussion of the synthesis of a new compound anthra[1,2-c:7,8-c]difuran in Chapter 5 and directions that might be pursued in the future. Here will be presented a proposed synthesis of an aromatic belts and a route towards the formation of a molecular capsule.

## 1 Isobenzofurans and Bis(isobenzofuran)s

### 1.1 Introduction

Isobenzofuran (IBF) 1, otherwise known as benzo[c]furan, is a fundamentally interesting molecule that has been studied extensively. ${ }^{1-5}$ It exhibits unusual electronic properties ${ }^{6}$ and undergoes rapid Diels-Alder cycloaddition with a variety of dienophiles. ${ }^{7,8}$ IBF has found use in a variety of fields including natural product synthesis ${ }^{1,3}$ polymer synthesis ${ }^{9}$ and open fullerene formation. ${ }^{10-12}$ Rickborn identified IBF as being "the most reactive isolable diene known." ${ }^{1}$ In recent years it has lost that title to its benzologue phenanthro[2,3-c]furan (2) which is an even more reactive diene. ${ }^{13}$ Herein will be described the synthesis, characterization, computational analysis, and kinetic details of IBF derivatives. These will include IBF, substituted IBF derivatives, bis(IBF)s (two IBF moieties linked together), and cyclophanes generated from bis(IBF)s.


1


Figure 1-1. Isobenzofuran (Left), Phenanthro[2,3-c]furan (Right)

### 1.2 Structure and Aromaticity

### 1.2.1 Evaluating Aromaticity

The concept of aromaticity was first introduced by Kekulé in $1865 .{ }^{14}$ The extra stability that was characteristic of certain unsaturated cyclic structures was attributed to the delocalization of the $\pi$-electrons. The best example of this is benzene in which the $\pi$-electrons are considered completely delocalized. IBF is a bicyclic compound consisting of a furan ring fused onto a
benzene ring. It is a planar $10 \pi$-electron system and should be aromatic by Hückel's rules for aromaticity. However, the molecule does not exhibit the stability typically associated with aromatic compounds. Evaluation of IBF's aromaticity can be useful for rationalizing reactivity which will be discussed in detail later.

Aromaticity continues to be a controversial topic and as a result many different methods for determining the aromatic character of unsaturated cyclic compounds have been developed. ${ }^{15,16}$ Several of these methods have been applied to IBF, some of which will be discussed here. The stability of an aromatic molecule can be quantified in terms of its resonance energy (RE). Prior to 1969 classical resonance energy (CRE) was commonly used to calculated the RE of aromatic compounds. CRE was based on comparing the energy of a molecule to a reference molecule with localized double bonds and $\pi$-electron energy based on ethylene. ${ }^{17}$ Palmer calculated the RE for a variety of aromatic compounds using this definition. ${ }^{18,19}$ However, this method was found to fail in many cases. Many molecules (including IBF) were predicted to have a large RE, but this was not representative of their reactivity. Dewar introduced the concept of Dewar resonance energy (DRE) which uses both an acyclic polyene reference molecule ${ }^{20}$ and an explicit treatment of the molecular orbitals (MOs). ${ }^{21}$ Using this method he calculated RE values for benzene, furan, and IBF which are summarized in Table 1-1. ${ }^{22}$

Hess et al. ${ }^{23}$ agreed with Dewar's choice of reference molecule, but not his deviation from simple Hückel MO theory and performed similar calculations using Hückel's definition. ${ }^{24}$ They chose to report their findings in terms of resonance energy per $\pi$-electron (REPE). Molecules with values of $\beta^{i}$ greater than 0.01 are considered aromatic, less than -0.01 are considered antiaromatic, and between 0.01 and -0.01 considered nonaromatic. Trinajstić ${ }^{25}$ suggested that the method for calculating DRE could be improved upon by reducing its

[^0]dependence on parameters. This was accomplished by simply formalizing DRE with different mathematical analysis. The resulting topological resonance energies (TRE) calculated for over 100 sample molecules showed good correlation relative to the molecule's stability.

Table 1-1. Resonance Energy for Aromatic Compounds Calculated by Multiple Methods

| Method | Benzene | Furan | Isobenzofuran |
| :---: | :---: | :---: | :---: |
| Palmer $(\mathrm{kcal} / \mathrm{mol})$ | -50.6 | -21.2 | -35.1 |
| Dewar $(\mathrm{kcal} / \mathrm{mol})$ | -20 | -1.6 | -2.4 |
| Trinajstić $(\beta)$ | 0.046 | 0.007 | 0.011 |
| Hess $(\beta)$ | 0.065 | 0.007 | 0.002 |

Magnetic susceptibility anisotropies were introduced as another means of evaluating aromaticity. ${ }^{26,27}$ In nuclear magnetic resonance (NMR) spectroscopy aromatic compounds exhibit a ring current which can have either shielding or deshielding effects on nuclei depending on their location relative to the ring. Jursic ${ }^{27}$ calculated the magnetic susceptibility anisotropies for a variety of compounds and found excellent correlation with experimental combustion data for five-membered heterocycles. Unfortunately the magnetic susceptibility anisotropies are also dependent upon ring size, ${ }^{26}$ therefore a comparison of IBF to furan or benzene is not particularly useful.

The next question that was posed regarding IBF questioned where the aromatic character resides? ${ }^{28-30}$ Sardella ${ }^{28}$ posed this question with regards to a variety of benzo[ $\left.c\right]$ heterocycles including IBF. Based on the analysis of bond averaging, NMR coupling constants, and RE calculations it was concluded that the best representation of IBF is as a molecule consisting of two non-interacting $\pi$-systems with an aromatic five-membered ring adjacent to a non-aromatic butadiene fragment as shown in Figure 1-1.


1

Figure 1-2. Representation of IBF with aromatic furan portion fused to a butadiene fragment

Von Ragué Schleyer ${ }^{6,29}$ investigated each ring in IBF using nucleus-independent chemical shift (NICS) calculations. As with magnetic susceptibility anisotropies, NICS relates aromaticity to the compounds NMR properties. Compounds that are more aromatic will have more ring current which will correspond to greater shielding effects in the center of the ring. By calculating the NICS at the center of a ring its aromaticity can be evaluated. Von Ragué Schleyer reported that in benzo $[b]$ heterocycles both rings share the aromaticity while in benzo[ $c$ ]heterocycles (including isobenzofuran) the five-membered ring was found to be aromatic and the six-membered ring was found to be weakly aromatic. This further supported the representation of IBF as shown in Figure 1-2.

Martinez ${ }^{30}$ performed NICS calculations on a similar set of compounds to von Ragué Schleyer ${ }^{29}$ with some surprising results. For the benzo[b]heterocycles Martinez obtained similar results to Schleyer with both rings exhibiting strong aromaticity. However, for the benzo[c]heterocycles it was found that the five-membered ring was weakly aromatic and the sixmembered ring was strongly aromatic. This result is confusing since this is the exact opposite result von Ragué Schleyer obtained.

Further experimental evidence exists for the depiction of IBF as in Figure 1-2. One of the methods for generating IBF, which will be discussed in more detail later, involves the decomposition of intermediate 3 shown in Scheme 1-1. ${ }^{31}$ The rate constant for the decomposition of this compound is $10^{5}$ times faster than the analogous methylene bridged compound $4{ }^{32}$ Wege postulates that the formation of IBF is more favorable than 5 because of the aromaticity that is gained by the formation of the furan ring. Compound 5 is analogous to $o$-xylylene (Figure 1-3)
which is non-aromatic and very reactive ${ }^{1, \text { iii }}$. If the furan ring was not significantly aromatic we would not expect to see such a disparity between these rate constants.


Figure 1-3. o-xylylene


## Scheme 1-1

### 1.3 Reactivity

As discussed in previous sections IBF does not exhibit a large amount of RE. However, when it reacts in a Diels-Alder cycloaddition with a dienophile a benzene ring is generated. This represents a large gain in resonance energy making this reaction very thermodynamically favorable and is one of the primary reasons for the high reactivity of IBF. ${ }^{1}$


## Scheme 1-2

By analogy benzannulated IBF derivatives will gain different amounts of resonance energy when they react with a dienophile. In the case of naphtho[2,3-c]furan (6) a naphthalene

[^1]ring is generated in the product resulting in a significantly larger gain in resonance energy than seen with IBF. Not surprisingly 6 is predicted to be much more reactive than IBF. ${ }^{8}$


6

## Scheme 1-3

The most recent study on IBF reactivity was done by Wege in $1990 .{ }^{8}$ Wege was able to determine the second-order rate constants for the reaction of a series of benzannulated IBF's with maleic anhydride (MA). The rate constants that Wege collected were rationalized using Structure Count Ratio ( $\mathrm{SC}_{\text {ratio }}$ ) theory developed by Herndon. ${ }^{38,39}$ The $\mathrm{SC}_{\text {ratio }}$ is a measure of resonance energy change associated with a reaction based on the number of possible Kekulé structures that can be drawn for the reactants and products. The $\mathrm{SC}_{\text {ratio }}$ is calculated using Equation 1.

Equation 1. $\mathrm{SC}_{\text {ratio }}=\left(\mathrm{SC}_{\text {reactants }}+\mathrm{SC}_{\text {products }}\right) / \mathrm{SC}_{\text {reactants }}$

Higher structure count ratios represent a larger gain in resonance energy and therefore a more facile reaction. The molecules that Wege studied ranged from the most reactive (IBF) with a $\mathrm{SC}_{\text {ratio }}$ of 3 and rate constant of $\mathrm{k}=75.8 \mathrm{M}^{-1} \mathrm{~s}^{-1}$, to the least reactive (pyreno[4,5-c]furan) with a $\mathrm{SC}_{\text {ratio }}$ of 2.2 and rate constant of $\mathrm{k}=0.22 \mathrm{M}^{-1} \mathrm{~s}^{-1}$. Wege plotted this data ${ }^{\text {iii }}$ and by extrapolating the trend line to a $\mathrm{SC}_{\text {ratio }}$ of 4 predicted the rate constant of the more reactive benzannulated IBF, 6, to be approximately 415 times more reactive than IBF.

The only other comprehensive kinetic study of IBF derivatives was done by Rickborn ${ }^{7}$ on a variety of substituted IBFs. This data will be discussed in Section 3.3.

[^2]
### 1.4 Generation and Isolation

IBF was first identified by Fieser and Haddidin ${ }^{40}$ in 1964 when adduct $\mathbf{9}$ formed from 1,4-dihydronaphthalene-1,4-endo-oxide (7) and tetraphenylcyclopentadienone (8) decomposed not into the expected anthracene derivative, but into 1,2,3,4-tetraphenylbenzene (10) and a reactive intermediate. This intermediate was trapped with additional $\mathbf{7}$ to generate 11. This led them to postulate that the reactive intermediate they had generated was in fact IBF.



Scheme 1-4

Wittig ${ }^{41}$ had previously generated polymeric IBF via the decomposition of a similar compound in the presence of copper powder, but this was the first time that it had been trapped in a monomeric form. This method of generating IBF is still used today although substitutes for tetraphenylcyclopentadienone are often employed including pyrone (12) and 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (dipytet) (13) (Scheme 1-5).


7



12



Scheme 1-5

Shortly after IBF was successfully trapped, several groups isolated IBF via pyrolysis techniques. Wege ${ }^{31}$ generated the adduct of $\mathbf{7}$ and $\mathbf{1 2}$ then subjected it to heat under reduced pressure. Under these conditions the compound decomposed resulting in a white crystalline solid which proved to be IBF. Wege discovered that IBF could be stored as a dilute solution $\left(<10^{-4} \mathrm{M}\right)$, but found concentrated solutions polymerized. Warrener ${ }^{42}$ used a similar technique except using the adduct formed from 7 and 13. Attempts to heat solutions of this adduct resulted in polymerization, however using vacuum pyrolysis it was possible to isolate pure IBF. Wiersum ${ }^{43}$ suggested that better results might be obtained by minimizing the time IBF is exposed to high temperatures. Using 7 as a precursor and hydrogenating the double bond (Scheme 1-6), he arrived at compound 14 which was subjected to flash vacuum thermolysis (FVT). Unlike vacuum pyrolysis, FVT quickly heats the sample to a high temperature $\left(650^{\circ} \mathrm{C}\right)$. Ethylene gas was expelled and a high yield of IBF collected in a cold trap.


Scheme 1-6

IBF can also be generated in solution under either acidic or basic conditions from the same protected aldehyde (15). Smith ${ }^{44}$ found that if this precursor was treated with hot acetic acid it was converted into 1-hydroxyphthalan (16) which subsequently underwent dehydration to generate IBF. Under these conditions IBF could be trapped with an appropriate dienophile. However, the lifetime of IBF under such conditions would be expected to be short and thus IBF could not be isolated. The same precursor (15) when stirred in methanol or ethanol in the presence of an acid catalyst (Dowex resin) forms the corresponding 1-alkoxyphthalan (17). These precursors have been demonstrated to undergo elimination of an alcohol in the presence of either heat ${ }^{45}$ or base ${ }^{46}$ to generate IBF. Other methods exist for generating IBF, ${ }^{47}$ but will not be discussed here.


17
Scheme 1-7

### 1.5 Bis(Isobenzofuran)s

### 1.5.1 Bis(IBF)s from Rubin, Watson, and Wege

Bis(isobenzofuran)s (bis(IBF)s) have two IBF moieties intrinsic to their structure and can undergo two Diels-Alder cycloadditions. Relatively few examples of bis(IBF)s exist in the literature and a large number of these were recently synthesized by Rubin ${ }^{12}$ for the use of generating open fullerenes. Rubin generated a variety of bis(dihydrepoxynaphthalene)
compounds (18a-k) connected by multiple tethers. Reaction of these compounds with 1,2,4,5tetrazine (19) generated the corresponding bis(IBF)s (20a-k) with the IBF moieties connected through the 1 position. These compounds were then reacted with $\mathrm{C}_{60}$ to form an open fullerene adduct.


18


R
$\mathrm{CH}_{2} \mathrm{OAc}$
H
$\mathrm{CO}_{2} \mathrm{Me}$
H
H
$\mathrm{CH}_{2} \mathrm{OAc}$
CH 2 OH
$\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CHCH}_{2}$
$\mathrm{CH}_{2} \mathrm{OEt}$
$\mathrm{CH}_{3}$
$\mathrm{CH}_{2} \mathrm{OAc}$

## Scheme 1-8

Another practical application of bis(IBF)s was utilized by Watson ${ }^{9}$ in the formation of polymers. Two stable phenyl-substituted bis(IBF)s 21a-b were generated from biphenyl and diphenyl ether backbones. These compounds exhibited similar stability to the parent compound 1,3-diphenylisobenzofuran and could be stored for many months in solid state although Watson acknowledges that they are highly sensitive to both oxygen and light. When 21a-b are reacted with a bis(dienophile) a polymer is generated.


21
X
$\begin{array}{ll}\text { a } & \mathrm{NIL} \\ \mathrm{b} & \mathrm{O}\end{array}$
Figure 1-4. Bis(IBF)s synthesized by Watson

Wege ${ }^{48}$ has isolated three compounds 22, 23 and $\mathbf{2 4}$ which can be classified as bis or tris(IBF)s. These compounds are intrinsically different than the bis(IBF)s that have been previously mentioned in that the furan moieties are fused to the same carbocyclic ring. They were isolated from precursors analogous to $\mathbf{1 4}$ using the FVT technique shown in Scheme 1-6. Although reactivity of IBF derivatives will be discussed later, it is worth mentioning an interesting property that is intrinsic to these particular compounds. After they undergo an initial Diels-Alder cycloaddition, the second furan moiety becomes more reactive and subsequent cycloadditions are faster than the first. The reason for this can be related to an increase in $\mathrm{SC}_{\text {ratio }}$ for subsequent reactions.


22


23


24

Figure 1-5. Bis(IBF)s synthesized by Wege

### 1.5.2 Bis(IBF)s from Dibble et al.

Dibble has synthesized a collection of bis(IBF)s from a wide variety of aromatic backbones. ${ }^{49,50}$ These compounds are typically reacted with a bis(dienophile), not for the intention of forming polymers like Watson, but to form cyclophanes.


25a




29



30

Figure 1-6. Bis(IBF)s synthesized in the Dibble research group

A bis(IBF) based on a naphthalene backbone (25a) was the first synthesized by Dibble. ${ }^{51}$ It was generated from 2,6-dimethylnaphthalene using the base catalyzed approach (Scheme 1-9). In this study attempts were made to optimize the synthesis by eliminating the oxidation step (step 4, Scheme 1-9). Our attempts were met with little success, therefore $\mathbf{2 5 a}$ was synthesized using Scheme 1-9 with no changes. ${ }^{52}$



Scheme 1-9

Another bis(IBF), synthesized in the Dibble research group by Thibault, based on a stilbene backbone (26) was made via both the based catalyzed approach (Scheme 1-10) and reaction of the corresponding bis(dihydroepoxynaphthalene) with dipytet (Scheme 1-11). ${ }^{50} \mathrm{~A}$ solution of the product formed by the base catalyzed approach was found to decompose via
hydrolysis and polymerization routes when stored at $-20^{\circ} \mathrm{C}$ indicating similar stability to IBF. When this bis(IBF) was generated using dipytet it was simply trapped using $N$-methylmaleimide (NMM) and the adduct analyzed. The first step in Scheme 1-10 was newly developed in this study. Previously the stilbene moiety was synthesized using reaction conditions similar to those used in the first step of Scheme 1-11. The development of this synthesis replaced four synthetic steps with a single reaction, a significant simplification to this reaction scheme. A crystal structure was obtained of $(E)$-1,2-bis(3-bromo-4-methylphenyl)ethene confirming the transorientation about the double bond. ${ }^{53}$


Scheme 1-10



$\left\lvert\, \begin{aligned} & \mathrm{NaNH}_{2} \\ & \mathrm{t}-\mathrm{BuOH}\end{aligned}\right.$
furan/THF

26



Scheme 1-11

A bis(IBF) based on a biphenyl backbone (27) has also been synthesized in the Dibble research group by Fischer (Scheme 1-12). ${ }^{49}$ This compound is essentially two IBF moieties linked by a carbon-carbon bond. For this reason it would be expected that this compound would exhibit similar reactivity to IBF itself. As expected, solutions of this compound polymerized at room temperature in a matter of hours.


Scheme 1-12

The acetylenic bis(IBF) (28) was generated from a bis(acetal) precursor via the base catalyzed mechanism by Fischer as well (Scheme 1-13). ${ }^{49}$ The compound is made by the coupling of two IBF precursors through a bromine substituent. Unfortunately, a very small amount of this compound was obtained therefore few experiments were performed on it. A bis(adduct) was obtained with NMM and the compound was characterized as an adduct.


Scheme 1-13

Another bis(IBF), 2,7-di(t-butyl)pyreno[4,5-c:9,10-c]difuran (29), has been recently synthesized in the Dibble research group by Franz (Scheme 1-14). A crystal structure has been obtained of this compound showing bond averaging distributed across four aromatic subunits. This compound is significantly less reactive than IBF and can be stored as a solid for weeks. This compound does exhibit significant light sensitivity and is typically stored under cool dark conditions.


29
Scheme 1-14


Scheme 1-15
Progress towards the synthesis of anthra[1,2-c:7,8-c]difuran (30, Scheme 1-15) has recently been made which will be discussed in greater detail in Section 5.2. This compound is expected to be less reactive than IBF and could prove isolable.

### 1.6 Summary

Isobenzofuran is a fundamentally important compound and has been given attention from several fields of chemistry ranging from natural product synthesis to material science. The question of its aromaticity is of interest and a definitive answer still has not been reached. This compound can be generated under acidic, basic and neutral conditions which makes it a convenient synthon. It is a very reactive substrate towards Diels-Alder cycloaddition and is one of the most reactive dienes known.

Calculations suggest that IBF does not have a large amount of aromatic character. It has resonance energy more comparable to a weakly aromatic molecule such as furan rather than a strongly aromatic compound such as benzene. A variety of bis(IBF)s have been made and several different aromatic systems have been used as a backbone for these compounds.

## 2 Novel Investigations into the Structure and Aromaticity of Isobenzofuran

### 2.1 Novel Calculations Towards Determining the Aromaticity of Isobenzofuran

There are several methods for evaluating aromaticity that have not been applied to IBF prior to this study. In recent years von Ragué Schleyer has introduced several concepts for evaluating aromaticity. ${ }^{6,33,34}$ Aromatic stabilization energy (ASE) can be calculated by utilizing a homodesmotic reaction scheme (Scheme 2-1). ${ }^{34}$ Such an equation is completely balanced for both bond and atom types with the difference in energy between products and reactants being attributed to any aromaticity associated with the molecule in question.


Scheme 2-1. Homodesmotic Reaction Scheme for Benzene (ASE $=-30.5 \mathrm{kcal} / \mathrm{mol})$

Von Ragué Schleyer ${ }^{34}$ applied this concept to over 50 five-membered heterocycles and found good correlation with other measures of aromaticity (NICS and HOMA). We applied this method to IBF and obtained an ASE of $-19.9 \mathrm{kcal} / \mathrm{mol}$ (Table 2-1).


Scheme 2-2. Homosdesmotic Reaction Scheme for IBF (ASE = -19.9 kcal/mol)

Table 2-1. ASE and ISE for Furan, Benzene, and IBF

| Calculation | Furan | Benzene | IBF |
| :---: | :---: | :---: | :---: |
| ASE $(\mathrm{kcal} / \mathrm{mol})$ | -14.8 | -30.5 | -19.9 |
| ISE $(\mathrm{kcal} / \mathrm{mol})$ | -14.7 | -33.2 | -27.4 |

The method of isomerization stabilization energy (ISE) has also been introduced as a measure of RE. ${ }^{33}$ The difference in energy between a methyl substituted aromatic hydrocarbon and a non-aromatic prototropic tautomer (Scheme 2-3) gives the ISE. This method has been found useful in the determination of the RE of polycyclic aromatic hydrocarbons, heterocycles, and strained systems.


Scheme 2-3 . ISE energies shown in kcal/mol

Von Ragué Schleyer applied this method to toluene and in an analogous manner we calculated ISE values for methylisobenzofuran and methylfuran (Scheme 2-3). The results (Table 2-1) seem to suggest that IBF has slightly less RE than benzene itself. However, if we consider these values in terms of REPE we find that furan and IBF have very similar aromatic character $(\operatorname{REPE}=2.45$ and $2.76 \mathrm{kcal} / \mathrm{mol}$ respectively) with benzene being significantly more aromatic $($ REPE $=5.53 \mathrm{kcal} / \mathrm{mol})$.

Good correlation was found between the ASE and the ISE for furan and benzene, but not for IBF. Although qualitatively both methods agree that IBF has a larger RE than furan and
smaller than benzene, quantitatively there is significant disparity between these values. However, given that homodesmotic reaction schemes have not been previously applied to fused ring systems there could potentially be error intrinsic to the ASE calculation.

Analysis of bond lengths about an aromatic ring is perhaps one of the best qualitative indications of aromaticity. ${ }^{35}$ When electron density is delocalized about an aromatic ring bond averaging occurs. By contrast a non-aromatic compound will exhibit polyene character. This measure has been quantified by Krygowski into what he calls the Harmonic Oscillator Measure of Aromaticity (HOMA) shown in Equation 2. . $^{35-37}$

Equation 2. HOMA $=1-\alpha / \mathrm{n} \sum\left(\mathrm{R}_{\text {opt }}-\mathrm{R}_{\mathrm{ij}}\right)^{2}$

The HOMA sums the deviations from an optimal bond length $\left(\mathrm{R}_{\text {opt }}\right)$ and averages it over all bonds $(\mathrm{n})$. This number is then scaled by a factor $(\alpha)$ such that for a system where all bonds are equal to $\mathrm{R}_{\text {opt }}$ the HOMA is equal to 1 and for a system that represents a perfect Kekulé structure with localized bonds the HOMA is equal to 0 . The HOMA can be used to measure the aromaticity of entire molecules as well as only parts. Although the HOMA has not previously been applied to IBF, it has been applied to benzene $(\mathrm{HOMA}=1)^{36}$ and furan $(\mathrm{HOMA}=0.298$ ( 0.778 for the three $\mathrm{C}-\mathrm{C}$ bonds) ). ${ }^{34}$

In this study HOMA calculations were performed on optimized structures of IBF and furan using the same level of computational theory (B3LYP/6-31G(d). The values for $\alpha$ and $\mathrm{R}_{\text {opt }}$ were taken from Krygowski. ${ }^{37}$ The data that was obtained for several different molecular fragments is summarized in Table 2-2. Foremost it is observed that the HOMA is higher for IBF compared to furan overall, but perhaps more striking is the evidence that the furan ring in IBF has a higher HOMA than furan itself. This effect, which is primarily due to shorter $\mathrm{C}-\mathrm{O}$ bonds in IBF, suggests that the furan ring in IBF is more aromatic than furan itself. However, the HOMA for both IBF's benzenoid ring and the butadiene fragment are high relative to the furan ring. This
might suggest that IBF possesses aromatic character that is not accounted for in the furan ring. If we compare these values to other polycyclic aromatic hydrocarbons, such as naphthalene, it can be seen that IBF's benzenoid fragment is much less aromatic.

Table 2-2. Results from HOMA Calculations on Furan, IBF, and Naphthalene

|  | Molecule |  |  |
| :---: | :---: | :---: | :---: |
| Fragment | Furan | IBF | Naphthalene |
| full molecule | 0.186 | 0.432 | 0.777 |
| furan ring | 0.186 | 0.205 | - |
| furan carbons | 0.608 | 0.584 | - |
| benzenoid ring | - | 0.521 | 0.769 |
| butadiene | - | 0.717 | 0.906 |

The HOMA was applied to the crystal structure of 1,3-diphenylisobenzofuran, but was found to be significantly lower for all fragments than the calculated model. The same phenomenon was found when the HOMA was applied to the crystal structure of furan. The HOMA seems to suggest that the calculated structures overestimate the bond averaging in these compounds.

### 2.2 Naphtho[1,2-c:5,6-c]difuran and Derivatives



|  | $\mathbf{R}_{1}$ | $\mathbf{R}_{\mathbf{2}}$ |
| :--- | :--- | :--- |
|  |  | H |
| a | H | Ph |
| b | H | TBS |
| c | TBS |  |
| d | $\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{15}$ | $\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{15}$ |
| e | $\mathrm{SiPh}_{3}$ | Ph |

Figure 2-1. Naphtho[1,2-c:5,6-c]difuran and substituted derivatives of it (25a-d)

Naphtho[1,2-c:5,6-c]difuran (25a) was first isolated via a base catalyzed approach. ${ }^{54}$ This compound was found to be significantly more stable than IBF and survived purification by chromatography (while IBF has not survived purification by this method). ${ }^{52}$ Evidence suggested that hydrolysis of the furan ring was the primary decomposition route rather than polymerization.

Working with such reactive compounds can be problematic. In situ generation of 25a can result in less than perfect stoiciometry and purification of this compound can result in low yields.

Rickborn ${ }^{7}$ found that IBF could be stabilized significantly through the addition of substituents to IBF with larger substituents having a more significant effect. Analogously derivatives of 25a were synthesized and it was expected that the substituents would provide enough kinetic stabilization that they could be isolated in the solid state. This proved to be the case and crystals were grown of both $\mathbf{2 5} \mathbf{c}$ and $\mathbf{2 5 d}$ which were of high enough quality to collect an X-ray crystal structure. Unfortunately the bulky thexyl (2,3-dimethylisobutyl) groups of 25d were badly disordered and could not be modeled. The overall quality of this structure was poor as can be seen by the partial representation of it is shown in Figure 2-2. The crystal structure of 25c (Figure 2-3) was of much higher quality, bond lengths reported in Table 2-3.


Figure 2-2. Partial crystal structure of 25d with disordered alkyl substituents removed. Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.


Figure 2-3. Crystal structure of 25c. Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.

The crystal structures that have been obtained of IBF derivatives ${ }^{55-58}$ have substituents that stabilize the parent compound sufficiently for it to crystallize. In the "tortured aromatic", iv (32), discovered by Lu, ${ }^{56}$ and commercially available 1,3-diphenylisobenzofuran (33), characterized by Boeré, ${ }^{57}$ the substituents exert both a significant electronic effect on the IBF moiety as well as a considerable amount of steric protection. The compounds made by Rodrigo ${ }^{55}$ (31) and Lynch ${ }^{58}$ (34) are primarily stabilized by stereo-electronic factors, although the nature of stabilization provided by methoxy substituents on the butadiene fragment is not entirely clear. By

[^3]contrast $\mathbf{2 5 c}$ is stabilized primarily through steric interactions since silyl substituents have been shown to exhibit only minor electronic effects. ${ }^{59,60}$


31


32


33


34

Figure 2-4. IBF derivatives for which X-ray crystal structures have been obtained.

Table 2-3. Bond lengths ( $\AA$ ) of IBF derivatives crystal structures.

| Bond | $\mathbf{2 5 c}$ | $\mathbf{3 1}$ | $\mathbf{3 2}$ | $\mathbf{3 3}$ | $\mathbf{3 4}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C1-C2 | $1.368(3)$ | 1.355 | $1.388(3)$ | $1.373(3)$ | $1.358(3)$ |
| C2-C3 | $1.442(2)$ | 1.436 | $1.444(3)$ | $1.435(3)$ | $1.441(2)$ |
| C3-C4 | $1.387(3)$ | 1.372 | $1.389(3)$ | $1.372(3)$ | $1.360(3)$ |
| O1-C4 | $1.387(2)$ | 1.355 | $1.376(3)$ | $1.369(2)$ | $1.362(3)$ |
| O1-C1 | $1.374(2)$ | 1.374 | $1.374(3)$ | $1.366(2)$ | $1.364(2)$ |
| C2-C7A | $1.426(3)$ | 1.431 | $1.434(3)$ | $1.425(3)$ | $1.431(3)$ |
| C6-C7 | $1.345(3)$ | 1.353 | $1.381(3)$ | $1.351(3)$ | $1.350(3)$ |
| C6-C5 | $1.439(3)$ | 1.454 | $1.470(3)$ | $1.435(3)$ | $1.445(3)$ |
| C5-C5A | $1.393(4)$ | 1.353 | $1.386(3)$ | $1.346(3)$ | $1.349(3)$ |
| C3-C5 | $1.443(2)$ | 1.462 | $1.438(3)$ | $1.427(3)$ | $1.432(3)$ |

Difuran $\mathbf{2 5} \mathbf{c}$ is planar as expected for the parent compound (25a). The silyl substituents likely add a certain amount of strain to the molecule, although analysis of the bonds about the aromatic rings show that $\mathbf{2 5 c}$ has only a few bonds that differ from $\mathbf{3 1 - 3 4}$. The $\mathrm{C} 1-\mathrm{C} 2, \mathrm{O} 1-\mathrm{C} 2$, and C3-C4 bonds are all slightly longer in $\mathbf{2 5 c}$ than in the other IBF derivatives. However, these are probably a result of strain placed on the molecule by the bulky substituents. Looking at bond angles it is clear that the silyl substituents are forced away from the aromatic portion. The C2-C1-Sil bond angle, which represents the non-bay region angle, is $137.95(14)^{\circ}$ which deviates
significantly from the expected $126^{\circ}$ for a $\mathrm{sp}^{2}$ center about a five membered ring. Even more significant is the C3-C4-Si2 bond angle, which represents the bay region angle, at $143.18(14)^{\circ}$. It can be seen that the more sterically hindered bay region forces the silyl substituent even further away from the $\pi$-system. This correlates well with the increased C3-C4 bond length. These distortions were consistent with the calculated gas phase model therefore we do not believe this is an artifact of crystal packing. Despite the strain introduced by the silyl substituents the structure of $\mathbf{2 5 c}$ is still very comparable to that of the other IBF derivatives.

The double bonds in 31-34 exhibit polyene character. As mentioned in Section 2.2, aromatic compounds exhibit bond averaging. Bond localization in 31-34 indicate that they are not strongly aromatic. The same type of bond arrangement is found in $\mathbf{2 5 c}$ which suggests that it too has low aromatic character. This effect is most prominent in the C $6-\mathrm{C} 7$ bond $(1.345(3) \AA)$ which is significantly shorter than the analogous bond in naphthalene $(1.377 \AA)^{\mathrm{v}}$.

The calculated gas phase model of 25c (B3LYP/6-31G(d)) correlated well (especially the aromatic portion) with the crystal structure. This basis set's ability to correctly predict the geometry of $\mathbf{2 5} \mathbf{c}$ suggests that it may be generally useful for calculating the geometry of other IBF derivatives. The conformation found in the crystal structure was not found to be the global minimum as the silyl substituents are not in the most favorable orientation. The substituents most likely adopt the conformation they do to better satisfy crystal packing forces.

### 2.3 Summary

The aromaticity of IBF has been evaluated using several different methods. The resonance energy of IBF has been determined using both ASE and ISE calculations and determined to be more aromatic than furan. The aromaticity of IBF has also been evaluated using the HOMA

[^4]method which is based on bond averaging. This method suggests that IBF exhibits polyenic character. This is consistent across all crystal structures of IBF derivatives including the newly acquired structure of $\mathbf{2 5 c}$.

### 2.3.1 Computational Details

### 2.3.1.1 Optimization and single point calculations for ISEs

Molecules were built and optimized using AM1 level of theory with HyperChem 7.5. ${ }^{61}$ Higher level optimization and single point calculations were done using the Gaussian 03 program package. ${ }^{62}$ These calculations were done using the popular hybrid density functional B3LYP, which has been used successfully for a variety of calculation types. ${ }^{63}$ This functional was coupled with an appropriate Pople basis set for both optimization and single point calculations for a final B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory for which frequency scale factors are available. ${ }^{64}$ Zero point vibrational energies, scaled by the correction factors developed by Moran and Radom, ${ }^{64}$ were used to correct the final energies. Orbitals were viewed using the Gaussview 4.1 program package. ${ }^{65}$

### 2.3.1.2 Optimizations for ASEs

Molecules were built and optimized uing AM1 level of theory with HyperChem 7.5. ${ }^{61}$
Higher level optimization and single point calculations were done using the Gaussian 03 program package. ${ }^{62}$ These calculations were done using MP2/6-311+G(d,p) level of theory and corrected with unscaled zero point vibrational energies.

### 2.3.2 $\quad$-ray Data Collection Details

### 2.3.2.1 1,3,6,8-tetrakis(tert-butyldimethylsilyl)naphtho[1,2-c:5,6-c]difuran, 25c.

From ethyl acetate were obtained X-ray quality crystals by slow cooling of $\mathbf{2 5 c}$ as yellow plates. One such crystal was coated with paraffin oil and mounted on a glass fibre. The data set was collected ${ }^{66}$ on a Bruker ApexII CCD area detector diffractometer using graphite
monochromated Mo K $\alpha$ radiation. The data was corrected for absorption and Lorentz polarization using a multi-scan method. ${ }^{67}$ The structure was solved by direct methods and refined using SHELXTL. ${ }^{68}$ Aliphatic hydrogen atoms were constrained to ideal tetrahedral geometries with optimal $\mathrm{C}-\mathrm{H}$ bond lengths and refined using a riding model. Methyl groups were allowed to rotate and align with optimal electron density. Aromatic hydrogen atoms were fixed at ideal bond lengths and refined using a riding model and non-hydrogen atoms were refined anisotropically. The compound crystallized in the triclinic $\mathrm{P}-1$ space group on a special Wyckoff site resulting in one molecule per unit cell. Agreement factors of $R=0.0391$ ( $\mathrm{I}>2 \sigma$ ) and $w R=0.0960$ (all data) were obtained after the final least-squares cycle. Additional crystallographic details can be found in Appendix 1.

Table 2-4. Crystal data and structure refinement for $\mathbf{2 5 c}$.

| Identification code | 25c |
| :---: | :---: |
| Empirical formula | C38 H64 O2 Si4 |
| Formula weight | 665.25 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=6.8355(5) \AA \quad \alpha=72.0720(10)^{\circ}$. |
|  | $b=11.3386(8) \AA \quad \beta=88.2660(10)^{\circ}$. |
|  |  |
| Volume | 1025.84(13) $\AA^{3}$ |
| Z | 1 |
| Density (calculated) | $1.077 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.174 \mathrm{~mm}^{-1}$ |
| F(000) | 364 |
| Crystal size | $0.22 \times 0.09 \times 0.04 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.92 to $25.03^{\circ}$. |
| Index ranges | $-8<=\mathrm{h}<=8,-13<=\mathrm{k}<=13,-16<=\mathrm{l}<=16$ |
| Reflections collected | 9931 |
| Independent reflections | $3604[\mathrm{R}(\mathrm{int})=0.0300]$ |
| Completeness to theta $=25.03^{\circ}$ | 99.7 \% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9933 and 0.9626 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3604 / 0 / 209 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.024 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0391, \mathrm{wR} 2=0.0893$ |
| R indices (all data) | $\mathrm{R} 1=0.0526, \mathrm{wR} 2=0.0960$ |
| Largest diff. peak and hole | 0.333 and -0.188 e. $\AA^{-3}$ |

2.3.2.2 1,3,6,8-tetrakis(dimethylthexysilyl)naphtho[1,2-c:5,6-c]difuran, 25 d.

From hexanes were obtained X-ray quality crystals by slow cooling of 25d as yellow plates. One such crystal was coated with paraffin oil and mounted on a glass fibre. The data set was collected ${ }^{66}$ on a Bruker ApexII CCD area detector diffractometer using graphite monochromated Mo K $\alpha$ radiation. The data was corrected for absorption and Lorentz polarization using a multiscan method. ${ }^{67}$ The structure was solved by direct methods and refined using SHELXTL. ${ }^{68}$ Carbon atoms that were not part of the aromatic ring or directly attached to a silicon atom were found to be badly disordered. Aliphatic hydrogen atoms were constrained to ideal tetrahedral geometries with optimal C-H bond lengths and refined using a riding model. Methyl groups were allowed to rotate and align with optimal electron density. Aromatic hydrogen atoms were fixed at ideal bond lengths and refined using a riding model and non-hydrogen atoms were refined anisotropically. The compound crystallized in the triclinic $\mathrm{P}-1$ space group on a special Wyckoff site resulting in one molecule per unit cell. Agreement factors of $R=0.2122$ (I $>2 \sigma$ ) and $w R=0.5741$ (all data) were obtained after the final least-squares cycle. Additional crystallographic details can be found in Appendix 1.

Table 2-5. Crystal data and structure refinement for 25d.

| Identification code | 25d |
| :---: | :---: |
| Empirical formula | C46 H80 O2 Si4 |
| Formula weight | 777.46 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{c}$ |
| Unit cell dimensions | $a=15.8079(18) \AA \quad \alpha=90^{\circ}$. |
|  | $b=11.5759(13) \AA \quad \beta=111.856(2)^{\circ}$. |
|  | $\mathrm{c}=14.0484(16) \AA \quad \gamma=90^{\circ}$. |
| Volume | $2385.9(5) \AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.082 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.158 \mathrm{~mm}^{-1}$ |
| F(000) | 856 |
| Crystal size | $0.28 \times 0.28 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.24 to $19.04^{\circ}$. |
| Index ranges | $-14<=\mathrm{h}<=14,-10<=\mathrm{k}<=10,-12<=1<=12$ |
| Reflections collected | 15324 |
| Independent reflections | $1936[\mathrm{R}(\mathrm{int})=0.0549]$ |
| Completeness to theta $=19.04^{\circ}$ | 99.9 \% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9838 and 0.9567 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 1936 / 12 / 163 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 2.624 |
| Final R indices [ $1>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.2122, \mathrm{wR} 2=0.5330$ |
| R indices (all data) | $\mathrm{R} 1=0.2589, \mathrm{wR} 2=0.5741$ |
| Largest diff. peak and hole | 1.568 and -0.487 e. $\AA^{-3}$ |

### 2.3.3 Experimental Details

Solvents were used without additional purification with the exception of diethyl ether and THF which were obtained from an MBraun solvent purification system. Melting points were performed in open capillaries and are uncorrected. NMR spectra were recorded on a Bruker Avance II 300 MHz NMR spectrometer at room temperature. ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ chemical shifts were referenced to TMS when in $\mathrm{CDCl}_{3}$ and the residual solvent peak when in other deuterated solvents. Infrared spectra were obtained using a Bruker Alpha FT-IR spectrometer. UV/Vis data were obtained using a Varian Cary-50 UV/Vis spectrophotometer and fluorescence spectra were obtained using a Varian Cary Eclipse Fluorescence spectrophotometer. Mass spectra were obtained from the University of Alberta Mass Spectrometry Laboratory and elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

### 2.3.3.1 1,3,6,8-Tetrakis(tert-butyldimethylsilyl)naphtho[1,2-c:5,6-c]difuran, 25c.

In 100 mL of dry THF was stirred $200 \mathrm{mg}(0.84 \mathrm{mmol})$ of 3,8-dimethoxy-1,3,6,7-tetrahydronaphtho[1,2-c:5,6-c]-difuran. Under $\mathrm{N}_{2}$ the solution was cooled to $-60^{\circ} \mathrm{C}$ before the addition of catalytic amounts of LDA $(0.40 \mathrm{~mL}, 2.0 \mathrm{M})$ and $6 \mathrm{~mL}(8.4 \mathrm{mmol})$ of $1.4 \mathrm{M} \mathrm{sec}-$ butyllithium. This solution was stirred for 10 min . before the addition of $0.63 \mathrm{~g}(4.2 \mathrm{mmol})$ of TBS chloride. The mixture was warmed to $20^{\circ} \mathrm{C}$ and stirred for 5 h . The reaction was quenched with 100 mL of water and the aqueous phase extracted with three 30 mL portions of methylene chloride. The solvent was dried with $\mathrm{MgSO}_{4}$ and filtered. The resulting solid was mixed with 10 mL of hexanes and placed atop a column of silica. The column was eluted with hexanes and recrystallized from hexanes to give 0.40 g of yellow crystals (yield $=72 \%$ ). mp 231-233; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 0.47(12 \mathrm{H}, \mathrm{s}), 0.56(12 \mathrm{H}, \mathrm{s}), 0.97(18 \mathrm{H}, \mathrm{s}), 1.03(18 \mathrm{H}, \mathrm{s}), 7.56$, $(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9.0 \mathrm{~Hz}), 7.74(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9.0 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm})-5.72,-3.83$, $17.82,18.61,26.48,26.92,118.85,123.49,123.67,132.59,133.34,156.70,156.85$; IR
(crystalline) 2951, 2927, 2882, 2855, 1470, 1462, 1360, 1248, 806, 772, 674, 434, $417 \mathrm{~cm}-1$;

UV/vis (c $1.052 \times 10^{-5}$, n-hexane) $\lambda_{\max } 256,266,276,291,349,369,389,411 \mathrm{~nm} ; \mathrm{MS}(E I) \mathrm{m} / \mathrm{e}$ calc'd for $\mathrm{C}_{38} \mathrm{H}_{64} \mathrm{O}_{2} \mathrm{Si}_{4}: 664.3966$, found 664.3977; $665\left(\mathrm{M}^{+}, 12\right), 664$ (21), 607 (15), 147 (15), 91 (15), 73 (70), 57 (22), 55 (100);

Anal. Calc. for $\mathrm{C}_{38} \mathrm{H}_{64} \mathrm{O}_{2} \mathrm{Si}_{4}$ : C, 68.61; H, 9.70. Found: C, $69.00 ; \mathrm{H}, 9.68$.

### 2.3.3.2 1,3,6,8-Tetrakis(dimethylthexysilyl)naphtho[1,2-c:5,6-c]difuran, $25 d$.

In 100 mL of dry THF was stirred $100 \mathrm{mg}(0.42 \mathrm{mmol})$ of 3,8-Dimethoxy-1,3,6,7-tetrahydronaphtho[1,2-c:5,6-c]-difuran. Under $\mathrm{N}_{2}$ the solution was cooled to $-60^{\circ} \mathrm{C}$ before addition of catalytic amounts of LDA ( $0.40 \mathrm{~mL}, 2.0 \mathrm{M}$ ) and $3 \mathrm{~mL}(4.2 \mathrm{mmol})$ of 1.4 M secbutyllithium. This solution was stirred for 10 min . before the addition of $0.66 \mathrm{~g}(3.36 \mathrm{mmol}) \mathrm{of}$ dimethylthexylsilyl chloride. The mixture was warmed to $20^{\circ} \mathrm{C}$ and stirred for 5 h . The reaction was quenched with 100 mL of water and the aqueous phase extracted with three 30 mL portions of methylene chloride. The solvent was dried with $\mathrm{MgSO}_{4}$ and filtered. The resulting oil was mixed with 10 mL of hexanes and placed atop a column of silica. The column was eluted with hexanes and removal of the eluant gave 149 mg of the product as a yellow solid (yield $=46 \%$ ). mp 148-150 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 0.52(12 \mathrm{H}, \mathrm{s}), 0.61(12 \mathrm{H}, \mathrm{s}), 0.83(12 \mathrm{H}, \mathrm{d}, \mathrm{J}$ $=7 \mathrm{~Hz}), 0.84(12 \mathrm{H}, \mathrm{d}, \mathrm{J}=7 \mathrm{~Hz}), 0.96(24 \mathrm{H}, \mathrm{s}), 1.00(24 \mathrm{H}, \mathrm{s}), 1.67(2 \mathrm{H}, \mathrm{p}, \mathrm{J}=7 \mathrm{~Hz}), 1.82(2 \mathrm{H}, \mathrm{p}$, $\mathrm{J}=7 \mathrm{~Hz}), 7.57(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 7.77(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm})$ $-3.40,-1.46,18.61,21.19,21.58,24.80,25.53,34.42,34.72,118.79,123.72,132.95,157.24$, 157.53; IR (KBr) 2957, 2926, 2867, 1465, 1391, 1251, 1123, 1102, 1059, 874, 836, 813, $774 \mathrm{~cm}-$ $1 ;$

Anal. Calc. for $\mathrm{C}_{46} \mathrm{H}_{80} \mathrm{O}_{2} \mathrm{Si}_{4}$ : C, $71.06 ; \mathrm{H}, 10.37$. Found: C, $71.17 ; \mathrm{H}, 10.18$.

## 3 Substituted Isobenzofuran Derivatives

### 3.1 Introduction

Friedrichsen reported 14 substituted IBF's in his 1980 review. ${ }^{5}$ By the time Rickborn published his IBF review ${ }^{1}$ in 1989 there had been over 80 substituted IBFs reported in the literature. The major portion of these IBF's are 1,3-substituted, due to either the chemistry used to form these compounds or greater interest in how these positions effect the IBF.


Figure 3-1. IUPAC numbering system for IBF

### 3.2 Synthesis of Substituted Isobenzofurans

Many 1,3-substituted IBF derivatives can be easily accessed from an acetal precursor (17) using the base induced mechanism to generate IBF in situ. In the presence of additional strong base, deprotonation will occur at the 1 and 3 positions, although the second proton is significantly less acidic than the first. The corresponding lithiated anion (35) can react with substrate $R X\left(R=M e, E t, S i M e_{3} \ldots\right.$ etc $)$ to form a substituted IBF.


## Scheme 3-1

Oxa-substituted IBFs are typically very reactive species due to the activating nature of the oxygen atom. ${ }^{1}$ In fact there has only been a single 1,3 -dioxaIBF ever isolated. ${ }^{69}$ While 1-oxa-substituted IBFs are not accessible under the conditions described previously, they are easily made from a corresponding phthalide (36). ${ }^{70}$ Treatment of the phthalide with LDA generates an anion (37) which can undergo substitution to generate an oxa-substituted IBF.


Scheme 3-2

Oxa-substituted IBFs can also be generated under acidic conditions using a method that was independently developed by two different groups. ${ }^{71,72}$ Treatment of $\mathbf{3 6}$ with an aklylating agent such as $\mathrm{Et}_{3} \mathrm{O}^{+} \mathrm{BF}_{4}^{-}$generates the phthalidium salt (38). This compound can then be reacted with an alkoxy ion to make the orthoester (39) which can be treated with LDA as in Scheme 3-3 to generate 1-ethoxyisobenzofuran (40).


## Scheme 3-3

Phthalide precursors can be useful for adding any substituent that can be derived from Grignard or alkyllithium reagent. Addition to the carbonyl and subsequent dehydration with acetic acid gives the corresponding 1 -substituted IBF. ${ }^{9}$ This method provides easy access to both phenyl and alkyl substituted IBFs. Methods exist for generating other IBF derivatives including amino, ${ }^{73,74}$ cyano, ${ }^{55}$ and acetoxy ${ }^{75}$ substituted examples.


Scheme 3-4

Although the majority of substituted IBFs are substituted at the 1 and/or 3 position many examples of substitution on the benzenoid ring exist as well. Besides the many examples of annulated IBFs ${ }^{8}$ there exist multiple alkyl, ${ }^{76}$ alkoxy, ${ }^{58}$ phenyl, ${ }^{56,69}$ and halide ${ }^{77}$ substituted IBF derivatives. The chemistry used to generate these compounds is generally similar to that already discussed.

### 3.3 Effects of Substituents on the Reactivity of Isobenzofurans

Rickborn ${ }^{7}$ analyzed the effect of substituents on the rate of reactivity of IBF derivatives. He synthesized a variety of 1 and 1,3-substituted IBF derivatives and subjected them to competition kinetics. By mixing an equimolar amount of two IBF derivatives and allowing them to vie for a limited amount of dienophile (NMM) he was able to obtain relative rate constants. This data suggests that the rate of reaction is highly dependent on both steric and electronic effects. The relative contribution of each of these components has not been studied for IBF, therefore we chose to investigate the electronic effects of substituents on IBF.


Scheme 3-5

Table 3-1. Relative Rate Constants for a Variety of Substituted IBFs Collected by Rickborn

| Substituent |  |  |
| :---: | :---: | :---: |
| $\mathbf{R}_{\mathbf{1}}$ | $\mathbf{R}_{\mathbf{2}}$ | $\mathbf{k}_{\text {rel }}$ |
| OEt | H | 3.8 |
| Me | H | 2.2 |
| $\mathrm{n}-\mathrm{Bu}$ | H | 1.8 |
| H | H | 1 |
| Ph | H | 0.77 |
| OEt | $\mathrm{SiMe}_{3}$ | 0.25 |
| Ph | Ph | 0.088 |
| $\mathrm{SiMe}_{3}$ | $\mathrm{SiMe}_{3}$ | 0.023 |

It is well known that, in normal-electron-demand Diels-Alder cycloadditions, electron donating groups activate dienes and conversely electron withdrawing groups deactivate dienes. It has been shown that for substituted 1,3-butadienes there is good correlation between the HOMO energy of the diene and its reactivity. ${ }^{78}$ This measure is imperfect because steric considerations are not accounted for. However, the HOMO energies, once coupled with reactivity information, can give insight into how sterically stabilizing substituents are.

Orbital energies were calculated for a variety of 1 and 1,3-substituted IBF derivatives for which kinetic data is available. ${ }^{7}$ Calculations were performed using the B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level of theory which has recently been used to investigate the stereo-electronic factors of both Diels-Alder reactions ${ }^{79,80}$ and IBF. ${ }^{81}$ As expected, the weakly donating methyl substituents raise the energy of the HOMO; therefore it is not surprising that 1methylIBF is 2.2 times more reactive toward cycloaddition with NMM than IBF (Table 3-1). From this we can infer that the steric effects of the methyl groups are small relative to their electronic activation. Silyl groups have both weak $\sigma$-donating and weak $\pi$-withdrawing effects ${ }^{59}$ and it can be seen in Figure 3-2 that silyl substituents exert very little net effect on the HOMO relative to the parent compound. Given that TBS-substituted IBF is approximately 100 times less reactive than IBF with NMM we can attribute this almost entirely to steric interactions.


Figure 3-2. Variations in the FMO energies (absolute values) and the gap between them for 1substituted IBF derivatives (Top) and 1,3-disubstituted IBF derivatives (Bottom)

The popular belief has been that phenyl groups stabilize IBF sterically as well as electronically. ${ }^{3}$ We can see from Figure 3-2 that phenyl groups exert a significant stereoelectronic effect on IBF, however, the effect should be activating. Not only do phenyl groups raise the energy of the HOMO, but they also reduce the energy gap between the frontier molecular orbitals (FMO) more so than any other substituent we tested. This suggests the steric bulk of the phenyl groups counteract their electronic activating ability. This effect can be seen in the case of 1-phenylbutadiene which is in fact more reactive than butadiene itself. ${ }^{78}$ Likewise, 1phenylisobenzofuran is 0.77 times as reactive as IBF which is only a small decrease in reactivity considering the size of the phenyl group. Further evidence for this can be seen in the reaction of

1,3-diphenylisobenzofuran with singlet oxygen. Rickborn described the apparent anomaly of 1,3diphenylisobenzofuran being 10 times more reactive than IBF with singlet oxygen, but less reactive than IBF with other dienophiles. ${ }^{82}$ The small size of this dienophile might reduce the impact of the bulky substituents. Therefore the reaction with singlet oxygen might then be more representative of the intrinsic reactivity of 1,3-diphenylisobenzofuran relative to IBF. This theory could potentially be tested by measuring the relative reactivity of these two compounds with dienophiles of varying sizes. Unfortunately the kinetics of 1-phenylisobenzofuran reacting with oxygen has not been measured and cannot be used for comparison.

The size of the gap between the frontier molecular orbitals (FMO)s can have important implications with regards to the stability of a compound. A small FMO gap can be indicative of low aromaticity ${ }^{83-85}$ with such compounds being more prone to addition rather than substitution reactions. ${ }^{81}$ IBF is susceptible to homopolymerization, ${ }^{46}$ a process which is more facile when the HOMO and LUMO are similar in energy. Since all of the substituents mentioned seem to reduce this gap we would expect these to polymerize faster than IBF itself. Since this does not appear to be the case for 1,3-diphenylisobenzofuran or TBS-IBF the steric bulk of the substituents may be preventing such a reaction from occurring.

### 3.4 Kinetic Studies of Substituted Isobenzofuran Derivatives

### 3.4.1 Reactivity of Substituted IBF Benzologues

### 3.4.1.1 Compounds of Interest

As previously mentioned, the reactivity of compounds containing an IBF moiety is of significant interest. To date there has been only one comprehensive kinetic study involving IBF and its benzologues which was published in $1988 .{ }^{8}$ The reaction of these compounds with maleic anhydride (MA) was studied in detail by Wege. ${ }^{8,13}$ Using pseudo-first order kinetics and monitoring UV/Vis absorbance he was able to collect kinetic data on eight different IBF
benzologues. When the $\log$ of the rate constants were plotted against the $\log$ of the $\mathrm{SC}_{\text {ratios }}$ a linear trend was observed (Figure 3-3). This trend suggests that there is a strong correlation between $\mathrm{SC}_{\text {ratio }}$ and reactivity. Given this, the same correlation should be seen in a similar plot using substituted IBFs so long as the substituents remained consistent. This assumption led to the kinetic evaluation of the substituted IBFs shown in Scheme 3-6.


Figure 3-3. Herndon plot created by Wege for benzannulated IBF derivatives ${ }^{8}$



41














$\rightleftharpoons$
42





Scheme 3-6

The starting materials shown in Scheme 3-6 (excluding 33) were synthesized from their respective acetal precursors using the conditions shown in Scheme 3-1. However, these were not the only synthetic targets intended for kinetic study. The phenanthro[9,10-c]furan derivative $\mathbf{5 2}$ was synthesized, but it was found that it did not appreciably react with NMM. An attempt was made to make triphenylsilyl derivatives $\mathbf{5 3}$ and $\mathbf{5 4}$ (Figure 3-4) as well, but with little success. The steric demands of the triphenylsilyl substituents seemed too great for the bay region of these compounds to accommodate. Recalling that the crystal structure of the 25c (Figure 2-3) in Section 2.2 showed significant distortions in the bay-region as a result of the TBS substituents, it not surprising that the larger triphenylsilyl substituents were not accommodated. Additionally, no examples were found in the literature of this functional group in the bay region of a molecule.


52


53


54

Figure 3-4. Compounds for which kinetic data was unattainable either because they were unreactive with NMM (52) or we were unable to synthesize them (53 and 54)

### 3.4.1.2 Obtaining Kinetic Measurements

Our method was to determine the second-order rate constants for the reactions shown in Scheme 3-6 using NMM as a dienophile. The rate constants for the reaction of $\mathbf{3 3}$ with NMM was determined for comparison to the data obtained by Rickborn. ${ }^{7}$ All IBF derivatives that we have isolated have strong fluorophores which typically disappear once a cycloadduct is formed. This property made these reactions ideal for monitoring by fluorescence spectroscopy with the exception of 41, 45 and 49 which were sufficiently slow that NMR spectroscopy was a more
appropriate way to monitor these reactions. The kinetic data for the compounds shown in
Scheme 3-6 is presented in Figure 3-5 and summarized in Table 3-3.


Figure 3-5. First order rate plots for compounds $\mathbf{2 5 c}$, 33, 43, and 47 monitored using
fluorescence (Top) Second order rate plots for compounds 41, $\mathbf{4 5}$ and $\mathbf{4 9}$ monitored using NMR spectroscopy (Bottom)

Fluorescence data was obtained by exciting the IBF fluorophore and observing the decay of its signal as the reaction proceeded. A large excess of NMM was used to both speed up the reaction and allow pseudo-first order analysis of the data. ${ }^{86}$ Special considerations had to be made for the reaction of $\mathbf{2 5 c}$ because the product, $\mathbf{4 9}$, still contains an IBF fluorophore. The fluorescence spectra of these two compounds exhibit a considerable amount of overlap and when both are present in solution this must be accounted for. This was done using Equation 3.

Equation 3. Intensity ${ }_{\text {observed }}=(\mathrm{x}) \mathrm{A}[\mathbf{2 5 c}]_{0}+(\mathrm{x}-1) \mathrm{B}[\mathbf{2 5 c}]_{0}$

Where $A$ and $B$ are equal to the product of the path length and the respective molar extinction coefficients of $\mathbf{2 5 c}$ and 49. The value x is equal to the percent of $\mathbf{2 5 c}$ left in solution. Fortunately there is a significant disparity between the fluorescence intensities of $\mathbf{2 5 c}$ and 49, otherwise this measurement would require a different method.

Table 3-2. Concentrations of IBF Derivative and NMM for Kinetic Measurements

| Compound | Concentration (M) | NMM Concentration (M) | Measurement Type |
| :---: | :---: | :---: | :---: |
| $\mathbf{2 5 c}$ | $7.62 \times 10^{-6}$ | $1.27 \times 10^{-3}$ | Fluorescence |
| $\mathbf{3 3}$ | $2.47 \times 10^{-6}$ | $3.06 \times 10^{-4}$ | Fluorescence |
| $\mathbf{4 3}$ | $5.58 \times 10^{-5}$ | $1.40 \times 10^{-3}$ | Fluorescence |
| $\mathbf{4 7}$ | $4.10 \times 10^{-6}$ | $4.50 \times 10^{-4}$ | Fluorescence |
| $\mathbf{4 1}$ | 0.0257 | 0.0234 | NMR |
| $\mathbf{4 5}$ | 0.0166 | 0.0159 | NMR |
| $\mathbf{4 9}$ | 0.0245 | 0.0245 | NMR |

The kinetics of slower reacting derivatives (41, $\mathbf{4 5}$ and 49) were measured using NMR spectroscopy. These reactions were found to exhibit significant equilibrium conditions with equilibrium constants of $\left(\mathrm{K}_{\mathrm{eq}}=48.6,108\right.$, and $24.8 \mathrm{M}^{-1}$ respectively). These equilibrium points could be reached from either direction as a solution of pure $\mathbf{5 0}$ reverted back to a mixture of itself, 49, and NMM. In addition to this it was found that heating $\left(110^{\circ} \mathrm{C}\right) \mathbf{5 0}$ under vacuum resulted in near quantitative conversion to $\mathbf{2 5 c}$ and NMM which sublimed. It would seem as if the adducts
of silyl-substituted IBFs are not particularily stable. Since use of NMR to monitor these reactions ruled out the use of excess dienophile, ${ }^{\text {vi }}$ it was necessary to use second order kinetics and observe only the initial rates. The data sets were therefore truncated when the reaction was halfway to equilibrium. The presence of this equilibrium was surprising because our experience has shown that the Diels-Alder cycloadditions of IBF derivatives typically go to completion and are not appreciably reversible. Not only does this statement hold true for the reaction of the remaining compounds in Scheme 3-6, but also for the unsubstituted parent compounds. ${ }^{8,52}$

Table 3-3. Rate constants and $\mathrm{SC}_{\text {ratios }}$ for reactions shown in Scheme 3-6

| Compound | Product | $\mathrm{SC}_{\text {ratio }}$ | $\mathrm{k}_{\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)}$ | $\mathrm{k}_{\text {rel }}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{3 3}$ | $\mathbf{5 1}$ | 3 | 21.0 | 4400 |
| $\mathbf{4 7}$ | $\mathbf{4 8}$ | 4 | 7.3 | 1500 |
| $\mathbf{4 3}$ | $\mathbf{4 4}$ | 3 | 2.4 | 500 |
| $\mathbf{2 5 c}$ | $\mathbf{4 9}$ | 3 | 0.63 | 130 |
| $\mathbf{4 5}$ | $\mathbf{4 6}$ | 3 | 0.052 | 11 |
| $\mathbf{4 1}$ | $\mathbf{4 2}$ | 2.5 | 0.050 | 10 |
| $\mathbf{4 9}$ | $\mathbf{5 0}$ | 2.5 | 0.0048 | 1 |

### 3.4.1.3 Effect of Substituent Size on Reactivity

The first trend that is obvious from the data in Table 3-3 is the effect of substituent size on the rate of reactivity. Comparison of the rates of 1,3-substituted IBF derivatives obtained in both this study and that done by Rickborn ${ }^{7}$ show a distinct trend based on size of the substituent (Table 3-4).

Table 3-4. Relative rates of 1,3 -substituted IBF derivatives

| Compound | Substituent | $\mathbf{k}_{\text {rel }}$ |
| :---: | :---: | ---: |
| $\mathbf{3 3}$ | Ph | 400 |
| 1,3-Bis(trimethylsilyl)isobenzofuran | $\mathrm{SiMe}_{3}$ | 110 |
| $\mathbf{4 3}$ | $\mathrm{Si}(\mathrm{t}-\mathrm{Bu}) \mathrm{Me}_{2}$ | 45 |
| $\mathbf{4 5}$ | $\mathrm{SiPh}_{3}$ | 1 |

[^5]As the size of the substituent increases the reaction rate is significantly slowed. In the case of 45, with triphenylsilyl as the substituent, the reaction rate is severely depressed and does not proceed to completion. In the case of 1,3-bis(trimethylsilyl)isobenzofuran the reaction proceeds two orders of magnitude faster than $\mathbf{4 5}$ and does not exhibit an appreciable equilibrium. Comparing the substituents molecular volume relative to their reactivity would be interesting and could provide a way to quantify steric effects in the Diels-Alder reaction of IBF.

### 3.4.1.4 Herndon Relationships in Substituted IBF Benzologues

The second trend which is apparent in this data can be seen when comparing the $\mathrm{SC}_{\text {ratios }}$ of these compounds to the rate constants. It was mentioned in Section 1.3 that Wege ${ }^{8}$ calculated the rate constants of a variety of benzannulated IBFs and by plotting this data against the $\mathrm{SC}_{\text {ratio }}$ of the compounds was able to make a Herndon plot (Figure 3-6). Using the data from Table 3-3 we were able to make the two additional plots shown in Figure 3-6; one of the TBS derivatives ( $\mathbf{2 5} \mathbf{c}$, 41, 43 and 49), and one of the triphenylsilyl derivatives ( 45 and 47).

- Unsubstituted (Wege)


Figure 3-6. Herndon plot of; Wege's benzannulated IBFs, TBS derivatives (25c, 41, 43 and 49), and triphenylsilyl derivatives ( 45 and 47).

An interesting feature of Figure 3-6 is the correlation between the slopes of the three series. If the correlation between reactivity and $\mathrm{SC}_{\text {ratio }}$ is based strictly on resonance energy then we would expect the slopes of these three plots to be identical. Using Wege's data ${ }^{8}$ for the unsubstituted benzologues as a reference (slope $=18$ ), we see that there is excellent correlation with the triphenylsilyl substituted compounds (slope $=17$ ). The TBS data does not show as good of correlation (slope $=24$ ), but as mentioned previously the data obtained for $\mathbf{2 5 c}$ and $\mathbf{4 9}$ may not be not be indicative of this trend due to complications at the opposite end of the naphthalenic system. If we remove these points and only plot the data for 41 and 43 the slope becomes closer to that found in the other series' $($ slope $=21)$. Obviously more data points are needed for both substituted series before any definitive predictions can be made, but this initial investigation
appears promising. The strong correlation between the slopes of these series indicates that the substituents affect each IBF benzologue equally and the full electronic nature of these species is still observed in their reactivity. This provides support for the prediction that the correlation in Herndon plots is based primarily on resonance energy. This correlation, and others like it, would be useful for predicting the relative reactivity of compounds for which the parent compound is unisolable, but a substituted derivative is.

### 3.5 Kinetics of a Bis(IBF)

Analysis of the data points in Figure 3-6 suggests that 25c, although having the same structure count ratio as $\mathbf{4 3}$, differs somewhat in reactivity. The first furan moiety in $\mathbf{2 5} \mathbf{c}$ is 3.8 times slower than 43. Considering that $\mathbf{2 5}$ chas an additional reaction site each collision is twice as likely to lead to a reaction. Therefore the intrinsic reactivity of the first furan moiety in $\mathbf{2 5 c}$ is as much as 7.6 times less reactive than $\mathbf{4 3}$. The lower reactivity of $\mathbf{2 5} \mathbf{c}$ could either be due to the increased conjugation implicit to the molecule or the additional steric bulk due to its larger size.

This same phenomenon is observed upon analysis of 41 and 49. These compounds have the same $\mathrm{SC}_{\text {ratio }}$ of 2.5 , but differ in reactivity by an order of magnitude. These compounds are comprised of the same aromatic system therefore the electronic differences are likely minimal. Since $\mathbf{4 9}$ can react to form two different isomers of $\mathbf{5 0}$ (syn and anti NMM components) it was suspected that one forms less favorably than the other thus retarding the reaction rate. However, when 49 was added to a solution of NMM it was found that both syn and anti isomers were formed in near equimolar amounts. Instead it is likely that the additional hindrance provided by the first adduct slows the reaction at both faces of 49. A crystal structure of the syn adduct was obtained (Figure 3-7), although it was not of high enough quality to analyze interatomic distances. We were unable to anisotropically refine a large portion of the atoms from this data set therefore they are shown isotropically in Figure 3-7. Since the structure of this compound was not of great interest we did not try to obtain a better data set. The same crystal used to collect the
x-ray structure was subsequently dissolved in $\mathrm{CDCl}_{3}$ and the resulting NMR spectrum used to assign the peaks associated with the syn isomer.


Figure 3-7. X-ray structure of 50. Ellipsoids drawn to $50 \%$ probability level, isotropically refined atoms shown as spheres and hydrogens are drawn with equal, fixed radii.

### 3.6 Synthesis of 1,6-diphenylnaphtho[1,2-c:5,6-c]difuran

Compound 56 was formed by the addition of phenyllithium to the dialdehyde (55) synthesized by Dibble ${ }^{54}$. Initially purification difficulties ensued and an attempt was made to cyclize the crude material to 57. This attempt failed with acids of varying strength from pyridinium $p$-toluenesulfonate (PPTS) to trichloroacetic acid (TCA). The product was eventually purified enough to carry forward by slurrying the crude product in methylene chloride and filtering. The semi-pure 56 could then be cyclized to 57 .


Scheme 3-7

Interesting stereochemical issues arise with the formation of 57 which has four chiral centers and potentially 16 different stereoisomers. Symmetry within the molecule reduces this number to 12 and if enantiomeric differences are ignored there are six chemically different diasteriomers. However, the proton NMR spectrum of 57 clearly showed only two isomers. It would seem as if the cross-naphthalene interactions were not strong enough to affect the chemical shift of the furan protons. The only stereochemistry that could be assigned by NMR was the relative positions of the protons on the same furan ring. These protons could be in either cis or trans orientations without potential for rearrangement. The cis arrangement results in two singlets at 6.25 and 6.49 ppm , and the trans arrangement results in two doublets at 6.46 and 6.69 ppm (Figure 3-8). A COSY spectrum determined that there was in fact a coupling of $\mathrm{J}<1 \mathrm{~Hz}$ between the cis protons, but this was considerably smaller than the $J=2 \mathrm{~Hz}$ value found for the trans protons. This assignment has been determined by Barfield and Sternhell ${ }^{87}$ on a similar IBF precursor using NOESY experiments, and used by other groups for assigning the stereochemistry of similar compounds ${ }^{88}$.


Figure 3-8. ${ }^{1} \mathrm{H}$ NMR spectra of all isomers of 57 (Left) and single isomer shown in Figure 3-9 (Right)

For further verification a sample exhibiting only the singlet signals by NMR was recrystallized and although the ensuing crystal structure (Figure 3-9) was low in quality ( $R_{1}=0.2864$ ), it clearly showed cis stereochemistry by both furan rings and corresponded to the lowest energy isomer as determined by AM1 modeling (Table 3-5).


Figure 3-9. X-ray crystal structure of a single isomer of 57. Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.

Table 3-5. Energies of the Six Stereoisomers of 57 Calculated by AM1 Modeling

| Isomer | End A* | End B* | Phenyl <br> Positions** | $\Delta \boldsymbol{E}$ <br> (kcal/mol) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{5 7 a}$ | trans | trans | Anti | 0 |
| $\mathbf{5 7 b}$ | trans | trans | Syn | -0.01 |
| $\mathbf{5 7 c}$ | cis | trans | Syn | -0.94 |
| $\mathbf{5 7 d}$ | cis | trans | Anti | -0.94 |
| $\mathbf{5 7 e}$ | cis | cis | Syn | -1.80 |
| $\mathbf{5 7 f}$ | cis | cis | Anti | -1.99 |

*Protons on the same side of the furan ring are cis, protons on the opposite sides are trans. End A and End B are arbitrarily chosen. **Phenyl rings on the same side of naphthalene system are in the syn conformation, those on opposite sides are in the anti conformation.

AM1 calculations (Table 3-5) show that there is an energetic preference of approximately $1 \mathrm{kcal} / \mathrm{mol}$ for the cis orientation of the furan protons. Evidence for this cis preference could be seen when different reaction conditions were utilized. When trichloroacetic acid (TCA) was used as the acid catalyst a near equimolar mixture of cis/trans isomers of 57 was recovered (Figure 3-8). When a weaker acid pyridinium $p$-toluenesulfonate (PPTS) was used a cis/trans $(85 / 15)$ mixture was recovered. Almost no energetic preference was found for the orientation of phenyl groups across the naphthalene ring.


Scheme 3-8

The stereochemical features of 57 disappear once 1,6-diphenylnaphthodifuran (25b) is generated via the base catalyzed method shown in Scheme 3-8. This compound proved to be very reactive and difficult to isolate. It quickly decomposed when placed on a silica column, but
survived purification using an alumina column. It decomposed over a few days in solution, a process which could be greatly accelerated by exposure to UV light. A derivative of this compound was isolated (25e) by utilizing the stabilizing ability of triphenylsilyl substitutents. This compound was found to be highly crystalline and could be stored at room temperature for several weeks. These compounds will be discussed in Section 4.2 with regards to their cyclophane forming capabilities.


Scheme 3-9

### 3.7 Summary

A large number of substituted IBFs have been synthesized since the generation of the parent compound. Every position of IBF has been substituted, but variations at the 1 and 3 positions are the most common. Several methods exist for substituting IBF with the method of choice varying with the substituent to be added.

Substituents can have significant electronic and steric effects on the reactivity of IBF. Electron donating groups increase its reactivity while electron withdrawing groups decrease its reactivity. The steric hindrance of these substituents has an important influence on reactivity as well and often the electronic and steric influences are conflicting. The kinetics of several substituted IBF benzologues have been measured and the reactivity of these compounds analyzed using a Herndon plot. Initial findings suggest that the steric effect of substituents is consistent
across the range of benzologues indicating that the full electronic nature of the benzologue is still observed in the kinetic data.

The synthesis of $\mathbf{2 5 b}$ required the formation of its precursor 57. Multiple isomers of this compound can be formed and these were fully analyzed using NMR spectroscopy and X-ray crystallography. The target compound, $\mathbf{2 5 b}$, was found to exhibit similar reactivity to the parent compound 25a.

### 3.7.1 Computational Details

### 3.7.1.1 Optimization and single point calculations for FMOs

Optimization and single point calculations were done using the Gaussian 03 program package. ${ }^{62}$ Geometries were optimized using B3LYP/6-31G(d) level of theory and were followed with single point calculations using B3LYP/6-311+G(2d,p) level of theory.

### 3.7.2 $\quad$-ray Data Collection Details

### 3.7.2.1 3,8-Dimethoxy-1,6-diphenyl-1,3,6,8-tetrahydronaphtho[1,2-c:5,6-c]difuran, 57.

From ethyl acetate were obtained X-ray quality crystals by slow cooling of $\mathbf{5 7}$ as colourless plates. One such crystal was coated with paraffin oil and mounted on a glass fibre. The data set was collected ${ }^{66}$ on a Bruker ApexII CCD area detector diffractometer using graphite monochromated Mo $K \alpha$ radiation. The data was corrected for absorption and Lorentz polarization using a multi-scan method. ${ }^{67}$ The structure was solved by direct methods and refined using SHELXTL. ${ }^{68}$ Aliphatic hydrogen atoms were constrained to ideal tetrahedral geometries with optimal $\mathrm{C}-\mathrm{H}$ bond lengths and refined using a riding model. Methyl groups were allowed to rotate and align with optimal electron density. Aromatic hydrogen atoms were fixed at ideal bond lengths and refined using a riding model and non-hydrogen atoms were refined anisotropically. The compound crystallized in the monoclinic $\mathrm{P} 2(1) / \mathrm{c}$ space group on a special Wyckoff site resulting in two molecules per unit cell. Agreement factors of $R=0.2864(\mathrm{I}>2 \sigma)$ and $w R=$ 0.6609 (all data) were obtained after the final least-squares cycle. To date there is no rationale for
the poor agreements factors other than poor crystal quality. Additional crystallographic details can be found in Appendix 1.

Table 3-6. Crystal data and structure refinement for 57.

Identification code 57
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=28.73^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [I>2sigma(I)]
R indices (all data)
Largest diff. peak and hole
3.7.2.2 Syn Adduct of $\mathbf{2 5 c}$ with $N$-Methyl Maleimide: $N, N$ '-Dimethyl 1,4,7,10-Diepoxy-1,2,3,4,7,8,9,10-octahydro-1,4,7,10-tetrakis(tert-butyldimethylsilyl)-2,3,8,9chrysenetetracarboxylic Acid, Diimide,50
From ethyl acetate were obtained X-ray quality crystals by slow cooling of $\mathbf{5 0}$ as colorless prisms. One such crystal was coated with paraffin oil and mounted on a glass fibre. The data set was collected ${ }^{66}$ on a Bruker ApexII CCD area detector diffractometer using graphite monochromated Mo Ka radiation. The data was corrected for absorption and Lorentz polarization using a multi-scan method. ${ }^{67}$ The structure was solved by direct methods and refined using SHELXTL. ${ }^{68}$ Aliphatic hydrogen atoms were constrained to ideal tetrahedral geometries with optimal $\mathrm{C}-\mathrm{H}$ bond lengths and refined using a riding model. Methyl groups were allowed to rotate and align with optimal electron density. Aromatic hydrogen atoms were fixed at ideal bond lengths and refined using a riding model and non-hydrogen atoms were refined anisotropically where possible. The compound crystallized in the triclinic $\mathrm{P} 2_{1} 2_{1} 2_{1}$ space group resulting in four molecules per unit cell. Agreement factors of $R=0.0406(\mathrm{I}>2 \sigma)$ and $w R=0.0953$ (all data) were obtained after the final least-squares cycle. Additional crystallographic details can be found in Appendix 1.

Table 3-7. Crystal data and structure refinement for $\mathbf{5 0}$.

| Identification code | 50 |
| :---: | :---: |
| Empirical formula | C48 H74 N2 O6 Si4 |
| Formula weight | 887.45 |
| Temperature | 296(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Orthorhombic |
| Space group | $\mathrm{P} 2_{1} 2_{1} 2_{1}$ |
| Unit cell dimensions | $a=11.799(4) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=12.598(4) \AA \quad \beta=90^{\circ}$. |
|  | $\mathrm{c}=33.550(10) \AA \quad \gamma=90^{\circ}$. |
| Volume | 4987(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.182 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.166 \mathrm{~mm}^{-1}$ |
| F(000) | 1920 |
| Crystal size | $0.21 \times 0.11 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.73 to $16.70^{\circ}$. |
| Index ranges | $-9<=\mathrm{h}<=9,-10<=\mathrm{k}<=10,-27<=1<=27$ |
| Reflections collected | 18161 |
| Independent reflections | $2749[\mathrm{R}(\mathrm{int})=0.0863]$ |
| Completeness to theta $=16.70^{\circ}$ | 99.8 \% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9844 and 0.9659 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 2749 / 0 / 563 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.062 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0406, \mathrm{wR} 2=0.0913$ |
| R indices (all data) | $\mathrm{R} 1=0.0481, \mathrm{wR} 2=0.0953$ |
| Absolute structure parameter | 0.4(2) |
| Largest diff. peak and hole | 0.182 and -0.157 e. $\AA^{-3}$ |

### 3.7.3 Experimental Details

See Chapter 2 experimental section (Section 2.3.3) for details on equipment, reagents, and characterization methods.

### 3.7.3.1 Kinetic Experiments

Procedure for measuring fast reactions: 25c, 33, 43, and 47
Chloroform solutions were made of the IBF derivative and of NMM with the NMM concentration in vast excess. These were mixed into a stirring flask and to avoid decomposition the fluorescence intensity of a new 3 mL aliquot was measured at every time interval. The decay of fluorescence signal indicated disappearance of reactant. The data was then analyzed using pseudo-first order kinetics.

Procedure for measuring slow reactions: 41, 45 and 49
In 1 mL of $\mathrm{CDCl}_{3}$ was dissolved $16.3 \mathrm{mg}(0.0245 \mathrm{mmol})$ of the IBF derivative. To this solution was added $2.73 \mathrm{mg}(0.0245 \mathrm{mmol})$ of NMM. Every time interval a proton NMR spectrum was taken with the product and reactant concentrations being determined by peak integration. The data was then analyzed by second order kinetics.

### 3.7.3.2 1,3-Bis(t-butyldimethylsilyl)isobenzofuran, 43

To 125 mL of dry THF was added 500 mg ( 3.33 mmol ) of acetal precursor (17). The solution was stirred under $\mathrm{N}_{2}$ and cooled to $-70^{\circ} \mathrm{C}$ before a catalytic amount of LDA ( 1.25 mmol ) was added followed by 14.1 mL of 1.4 M sec-butyllithium ( 19.7 mmol ). This mixture was stirred for 15 min before the addition of $1.25 \mathrm{~g}(8.30 \mathrm{mmol})$ of TBS chloride. The dark orange solution was warmed to room temperature and stirred for 1 h . The mixture was quenched with water, extracted with hexanes and dried with $\mathrm{MgSO}_{4}$. After removal of the solvent the crude product was placed on a short column of silica and eluted with hexanes. Removal of the solvent resulted in 0.396 g of product as a yellow oil (yield $=36 \%) .{ }^{1} \mathrm{H}$ NMR $\left(250 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 0.41$ $(12 \mathrm{H}, \mathrm{s}), 0.94(18 \mathrm{H}, \mathrm{s}), 6.85$ and $7.55\left(4 \mathrm{H}, \mathrm{AA}^{\prime} \mathrm{BB}^{\prime}\right) ;{ }^{13} \mathrm{C}$ NMR ( $60 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm})$
18.03, 26.68, 120.77, 123.31, 123.34, 133.97, 157.01; IR (neat) 2953, 2929, 836, 821, 807, 773 cm-1; UV/Vis (MeOH) 231 (3.5), 339 (3.3).
3.7.3.3 4,9-Bis(t-butyldimethylsilyl-4,9-epoxy-3a,4,9,9a-tetrahydro-2-methyl-2H-benzo[f]isoindole-1,3-dione, 44.
In 25 mL of chloroform was stirred $50 \mathrm{mg}(0.14 \mathrm{mmol})$ of $\mathbf{4 3}$. To this was added 16 mg $(0.14 \mathrm{mmol})$ of NMM and the solution was stirred for 2 h before removal of the solvent. The crude product was placed atop a column of silica and eluted with methylene chloride. The product was recrystallized from methanol to give 32 mg of white crystals (yield $=48 \%$ ); mp 163$167 ;{ }^{1} \mathrm{H}$ NMR ( $250 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 0.36(6 \mathrm{H}, \mathrm{s}), 0.42(6 \mathrm{H}, \mathrm{s}), 0.97(18 \mathrm{H}, \mathrm{s}), 2.17(3 \mathrm{H}, \mathrm{s}), 3.60$ $(2 \mathrm{H}, \mathrm{s}), 7.08$ and $7.16\left(4 \mathrm{H}, \mathrm{AA}^{\prime} \mathrm{BB}^{\prime}\right) ;{ }^{13} \mathrm{C}$ NMR ( $60 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) 18.5,24,28,53$, 85.7, 121.5, 121.6, 126.8, 145.4, 175; IR (KBr) 2960, 2928, 2858, 1768, 1698, 1251, 837, 824, 803, $774 \mathrm{~cm}-1$; MS (EI) m/e calc'd for $\mathrm{C}_{25} \mathrm{H}_{39} \mathrm{NO}_{3} \mathrm{Si}_{2}$ : 457.24686, found 457.24529; $457\left(\mathrm{M}^{+}, 1\right)$, 346 (39), 290 (31), 289 (100), 111 (9), 83 (12), 73 (59), 69 (23), 57 (33);

Anal. Calc. for $\mathrm{C}_{25} \mathrm{H}_{39} \mathrm{NO}_{3} \mathrm{Si}_{2}$ : C, 65.60 ; H, 8.42, N, 3.06; Found: C, 65.72, H, 8.59, N, 3.11.

### 3.7.3.4 Syn and Anti Adducts of 25c with $N$-Methyl Maleimide: N,N'-Dimethyl 1,4,7,10-Diepoxy-

 1,2,3,4,7,8,9,10-octahydro-1,4,7,10-tetrakis(tert-butyldimethylsilyl)-2,3,8,9chrysenetetracarboxylic Acid, Diimide, 50.To 25 mL of chloroform was added $0.075 \mathrm{mg}(0.11 \mathrm{mmol})$ of $\mathbf{2 5 c}$ and $0.038 \mathrm{mg}(0.34$ mmol) of NMM. The solution was stirred for 4 h and the solvent was removed. The crude extract was recrystallized from ethyl acetate to give $25 \mathrm{mg}(0.028 \mathrm{mmol})$ of white crystals as a mixture of syn and anti products (yield $=26 \%$ ); mp 111.7-114.3; 1H NMR (300 MHZ, CDC13) $\delta$ $(\mathrm{ppm})$, syn product $0.45(6 \mathrm{H}, \mathrm{s}), 0.48(6 \mathrm{H}, \mathrm{s}), 0.51(6 \mathrm{H}, \mathrm{s}), 0.64(6 \mathrm{H}, \mathrm{s}), 0.90(18 \mathrm{H}, \mathrm{s}), 1.02(18 \mathrm{H}$, s), $1.78(6 \mathrm{H}, \mathrm{s}), 3.67(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 3.68(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.40(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.82(2 \mathrm{H}, \mathrm{d}$, $\mathrm{J}=8 \mathrm{~Hz})$, anti product $0.53(6 \mathrm{H}, \mathrm{s}), 0.54(6 \mathrm{H}, \mathrm{s}), 0.56(6 \mathrm{H}, \mathrm{s}), 0.59(6 \mathrm{H}, \mathrm{s}), 0.93(18 \mathrm{H}, \mathrm{s}), 1.00$
$(18 \mathrm{H}, \mathrm{s}), 2.08(6 \mathrm{H}, \mathrm{s}), 3.70(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 3.72(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.34(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.79$ (2H, d, J = 8 Hz ); IR (crystalline) 2930, 2857, 1702, 1252, 821, 806, 771, $422 \mathrm{~cm}-1$

### 3.7.3.5 2,6-Bis(dimethoxymethyl)-1,5-naphthalene-bis(phenylmethanol), 56.

Under $\mathrm{N}_{2}$ was stirred 0.51 g of $\mathbf{5 5}$, ( 1.54 mmol ) in 100 mL of dry diethyl ether. To this was added 1.88 mL of a 1.8 M phenyllithium in cyclohexane $(3.39 \mathrm{mmol})$ at $0^{\circ} \mathrm{C}$. The solution was stirred for 1 h before being quenched with 5 mL of isopropanol. Solvent was removed except for approximately 5 mL from which the product was precipitated using methylene chloride in a solvent diffusion method. An analytical sample was recrystallized from methanol to give $0.43 \mathrm{~g}(9.68 \mathrm{mmol})$ of white crystals (yield $=63 \%) . \mathrm{mp} 197-199{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $(300 \mathrm{MHz}$, $\left.\mathrm{D}_{3} \mathrm{CCOCD}_{3}\right) \delta(\mathrm{ppm}) 3.30(12 \mathrm{H}, \mathrm{s}), 5.26(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=4 \mathrm{~Hz}), 5.77(2 \mathrm{H}, \mathrm{s}), 6.84(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=4 \mathrm{~Hz})$, $7.02(2 \mathrm{H}, \mathrm{t}, \mathrm{J}=\mathrm{X}), 7.27(4 \mathrm{H}, \mathrm{t}, \mathrm{J}=6 \mathrm{~Hz}), 7.36(4 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.48(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 8.32$ $(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{D}_{3} \mathrm{CCOCD}_{3}$ ) $\delta(\mathrm{ppm}) 52.36,53.90,68.71,68.82,123.10$, 125.63, 125.94, 127.72, 132.77, 134.26, 145.59; IR (KBr) 3406, 2938, 1690, 1493, 1449, 1351, 1234, 1176, 1108, 1045, 744, $701 \mathrm{~cm}-1$; MS (EI) m/e calc'd for $\mathrm{C}_{30} \mathrm{H}_{32} \mathrm{O}_{6}: 488.2198$, found 488.2190; 424 (46), 393 (100), 363 (3), 319 (36), 289(10), 215 (17), 181 (6), 151 (6), 105 (10), 77

Anal. Calc. for $\mathrm{C}_{30} \mathrm{H}_{32} \mathrm{O}_{6}$ : C, 73.75; H, 6.60. Found: C, 73.79; H, 6.58 .
3.7.3.6 3,8-Dimethoxy-1,6-diphenyl-1,3,6,8-tetrahydronaphtho[1,2-c:5,6-c] difuran 57. In 50 mL of methanol was stirred $56(0.50 \mathrm{~g}, 1.12 \mathrm{mmol})$. Catalytic amounts of toluenesulfonic acid was added and the solution was refluxed for a 6 h period. The solution was removed from reflux and cooled to $-10^{\circ} \mathrm{C}$ for 1 h . A white crystalline solid precipitated which proved to be a cis/trans mixture of the product 0.391 g (yield $=86 \%$ ). mp $146-148^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm})$ cis product $3.52(6 \mathrm{H}, \mathrm{s}), 6.25(2 \mathrm{H}, \mathrm{s}), 6.49(2 \mathrm{H}, \mathrm{s}), 7.35(6 \mathrm{H}, \mathrm{m}), 7.44$ $(6 \mathrm{H}, \mathrm{d}, \mathrm{J}=7 \mathrm{~Hz}), 7.55(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz})$; trans product $3.52(6 \mathrm{H}, \mathrm{s}), 6.46(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=2 \mathrm{~Hz}), 6.69$ $(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=2 \mathrm{~Hz}), 7.34(6 \mathrm{H}, \mathrm{m}), 7.44(6 \mathrm{H}, \mathrm{d}, \mathrm{J}=7 \mathrm{~Hz}), 7.54(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}),{ }^{13} \mathrm{C}$ NMR ( 75
$\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm})(\mathrm{cis} /$ trans mixture) $55.25,55.45,86.36,86.52,107.75,108.16,120.91$, 121.11, 125.74, 126.20, 128.26, 128.28, 128.47, 128.49, 128.56, 128.60, 128.64, 128.69, 128.71, 128.86, 128.93, 135.74, 136.01, 138.87, 138.96, 140.32, 140.93; IR (KBr) 2924, 2881, 1767, 1458, 1458, 1365, 1094, 965, 764, $700 \mathrm{~cm}-1$; MS (EI) m/e calc'd for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{O}_{4}: 424.1674$, found 424.1676; 424 ( $\mathrm{M}^{+}, 42$ ), 393 (100), 361(36), 319 (36), 289 (14), 215 (25), 181 (10), 151 (9), 105 (19), 77 (13);

Anal. Calc. for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{O}_{4}$ : C, 79.22; H, 5.71. Found: C, 79.06; H, 5.89.

### 3.7.3.7 1,6-Diphenylnaphtho[1,2-c:5,6-c]difuran, 25b

In 50 mL of dry diethyl ether was stirred $70 \mathrm{mg}(0.17 \mathrm{mmol})$ of $\mathbf{5 7}$. To this was added 2.0 mL of 2.5 M LDA ( 5.0 mmol ) and the reaction was stirred for 15 min . The reaction was quenched with water, extracted with diethyl ether and dried with $\mathrm{MgSO}_{4}$ before removing the solvent. The crude mixture was placed atop a short column of alumina and eluted with toluene. The solvent was removed and the resulting solid dissolved in methylene chloride and precipitated with hexanes. Filtration resulted in 27 mg of a yellow solid (yield $=44 \%$ ) which proved to be 25b. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 7.30(2 \mathrm{H}, \mathrm{t}, \mathrm{J}=8 \mathrm{~Hz}), 7.44(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 7.51(4 \mathrm{H}, \mathrm{t}$, $\mathrm{J}=8 \mathrm{~Hz}), 7.63(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 7.75(4 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 8.03(2 \mathrm{H}, \mathrm{s})$

### 3.7.3.8 1,6-Diphenyl-3,8-bis(triphenylsilyl)naphtho[1,2-c:5,6-c]difuran, 25e.

In 100 mL of dry THF was stirred $75 \mathrm{mg}(0.18 \mathrm{mmol})$ of 57 . Under $\mathrm{N}_{2}$ the solution was cooled to $-60^{\circ} \mathrm{C}$ before the addition of $2 \mathrm{~mL}(4.0 \mathrm{mmol})$ of 2.0 M LDA and $2 \mathrm{~mL}(2.8 \mathrm{mmol})$ of 1.4 M sec-butyllithium. This solution was stirred for 10 min . before the addition of $0.21 \mathrm{~g}(0.71$ mmol ) of triphenylsilyl chloride. The mixture was warmed to $20^{\circ} \mathrm{C}$ and stirred for 12 h . The reaction was quenched with 100 mL of water and the aqueous phase extracted with three 30 mL portions of chloroform. The organic phase was dried with $\mathrm{MgSO}_{4}$ and filtered. Removal of the solvent resulted in an orange oil to which was added a small amount of ethyl acetate and the solution was cooled to $-10^{\circ} \mathrm{C}$. The resulting yellow crystals were washed with methylene
chloride to give 25 mg of product (yield $=17 \%$ ). m.p. $280(\mathrm{dec}) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $(\mathrm{ppm}) 6.68(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 7.46(24 \mathrm{H}, \mathrm{m}), 7.50(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 7.66 \mathrm{~d}(12 \mathrm{H}, \mathrm{d}, \mathrm{J}=7 \mathrm{~Hz})$, 7.74, $(4 \mathrm{H}, \mathrm{d}, \mathrm{J}=7 \mathrm{~Hz}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 118.2,119.0,122.9,123.8,128.0$, $128.4,128.5,129.1,130.0,132.9,133.3,136.5,146.7,153.1 ;$ IR (crystalline) 1706, 1675, 1427, $1259,1110,766,739,695 \mathrm{~cm}-1$; UV/vis (c $1.17 \times 10^{-5}$, chloroform) $\lambda_{\max } 280,341,409,432 \mathrm{~nm}$; MS (ESI) m/e calc'd for $\mathrm{C}_{62} \mathrm{H}_{44} \mathrm{O}_{2} \mathrm{Si}_{2}$ : 876.2871, found 876.2948

## 4 Cyclophanes

### 4.1 Introduction

### 4.1.1 Cyclophanes Based on Benzene

Cyclophane chemistry has become a popular topic in organic chemistry and has been the focus of several books over the years ${ }^{89-93}$ with the most recent being by Gleiter and Hopf. ${ }^{94}$ The first cyclophane was reported by Brown and Farthing ${ }^{95}$ who dimerized $p$-xylylene (58) using vacuum pyrolysis to make [2.2]paracyclophane (59). This compound is an excellent example of a cyclophane; a macrocycle which contains one or more aromatic units embodied in a cyclic frame. ${ }^{96}$


Scheme 4-1

Cyclophanes are fundamentally interesting compounds. ${ }^{97}$ The ability to place certain groups (i.e. two aromatic systems) within close proximity of each other often results in interesting geometries ${ }^{98}$ and chemical properties. ${ }^{99,100}$ Cyclophanes also have properties that have the potential to be industrially useful. They are typically rigid structures and for this reason could find use in material science and surface chemistry. ${ }^{101}$ Similar to fullerenes, most cyclophanes have an internal cavity intrinsic to their structure and can act as a host. This property has potential to be useful for both catalysis ${ }^{102}$ and medical purposes. ${ }^{103}$

Cyclophane chemistry is a very broad topic and as such only a few examples that are particularly interesting or relevant to this thesis will be discussed in detail.

While the benzene rings of $\mathbf{5 9}$ deviate only slightly from planarity due to the strain introduced by the ethylene bridges, the benzene rings in the kinetically stabilized [1.1]paracyclophane ( $\mathbf{6 0}$ ) are very bent. ${ }^{104}$ This compound is analogous to $\mathbf{5 9}$ except the benzene rings are connected by methylene groups which adds considerably more strain to the system. An attempt to synthesize a less substituted derivative found the intended product as only a short lived intermediate before it decomposed. ${ }^{105}$ Not surprisingly this would indicate that this distorted aromatic system is quite unstable.


60


61

Figure 4-1. [1.1]paracyclophane 60 (Left) and Superphane 61 (Right)

Boekelheide ${ }^{106}$ developed the synthesis of a cyclophane similar to $\mathbf{5 9}$ except that the benzene rings are bridged by six ethylene units (61). This compound differs from 59 and $\mathbf{6 0}$ in that the benzene rings cannot distort their geometry to compensate for strain. As a result the electronic properties of "superphanes" like this compound differ from typical cyclophanes.

An example of the peculiar electronic properties that are often present in cyclophanes was demonstrated by Bickelhaupt in $1990 .{ }^{107} \mathrm{He}$ found that when a variety of chloro[5]metacyclophanes ( $\mathbf{6 2} \mathbf{a}-\mathbf{f}$ ) were treated with a nucleophile, substitution products were obtained ( $63 a-\mathrm{f}$ ). Further investigation revealed that this reaction was taking place via a $\mathrm{S}_{\mathrm{N}} \mathrm{Ar}$ mechanism which was rationalized by the lowered LUMO of 62a-f and the release of ring strain
in the intermediate. This type of nucleophilic aromatic substitution typically only proceeds when strong electron withdrawing group are present on the aromatic ring ${ }^{108}$ making this reaction somewhat novel.


## Scheme 4-2

### 4.1.2 Naphthalenophanes

Several cyclophanes have been synthesized that incorporate a naphthalene subunit.
Haenel and Staab ${ }^{109}$ made a $[2.2](2,6)$ naphthalenophane $(64)$ which was then oxidized and subjected to vacuum pyrolysis to generate $\mathbf{6 5}$.


Scheme 4-3

The primary isomer of this process was the one shown in Scheme 4-3 with the naphthalene groups staggered with respect to one another. Nishimura ${ }^{110}$ synthesized a family of naphthalenophanes connected through various positions on the naphthalene ring. One such compound that is similar to $\mathbf{6 5}$ was made through the dimerization of $\mathbf{6 6}$ using UV light. In this
case only the single isomer of $\mathbf{6 7}$ shown in Scheme 4-4 was isolated although no rationale for this selectivity was given.


66


67

## Scheme 4-4

### 4.1.3 Cyclophanes by Bodwell

Bodwell ${ }^{98,111-113}$ has synthesized a family of cyclophanes with some of the most strained aromatic systems. The aromatic systems in these compounds have even been referred to as "tortured". His method for cyclophane synthesis involves the formation of a diene such as 68 which isomerizes to a dihydropyrene like 69. Dehydrogenation of this compound generates a cyclophane such as $\mathbf{7 0}$ which is essentially a pyrene system bridged by an aliphatic tether. To date Bodwell has synthesized over ten compounds following this motif. The pyrene systems vary in strain, from the twelve atom tether which is the least strained, to 71 which is the most strained (pyrene bend angle of $93.6^{\circ}$ ). Bodwell (in collaboration with von Ragué Schleyer and Cyrański) has run NICS, HOMA, and ASE calculations (discussed in Chapter 1 and Chapter 2) on these compounds and has found that despite the fact they deviate significantly from planarity, a traditional feature of aromaticity ${ }^{35}$ they retain most of their aromatic character. ${ }^{13,114}$


Scheme 4-5


71

Figure 4-2. Cyclophane constructed by Bodwell exhibiting a pyrene bend angle of $93.6^{\circ}$

### 4.1.4 Alicyclophanes

Alicyclophanes are a variation on the cyclophane theme in that they do not possess an aromatic component, but rather a system of fused aliphatic rings. ${ }^{115}$ Despite the lack of an aromatic foundation these cyclophanes are rigid enough that their macromolecular properties can still be utilized. Butler ${ }^{115}$ developed the synthesis of 72, an alicyclophane precursor. Treatment of $\mathbf{7 2}$ with a tethered dibromide resulted in the imide moieties displacing the bromide ions to generate 73 .


72


73

Scheme 4-6

Warrener ${ }^{116}$ utilized 72 as a host molecule to generate the stabilized IBF (74). The rigid backbone ${ }^{117}$ portion of the molecule acts as a kinetic stabilizer similar to substituents discussed in Section 3.3. This IBF was stable enough that it could be stored in solution for several days and as a solid for several months with minimal decomposition. Using the same methodology Warrener also generated a "hamburger-like" molecule (75) which consists of a benzene ring "sandwiched" between two units of $\mathbf{7 2} .{ }^{118}$


74


75


Figure 4-3. Alicyclophanes synthesized by Butler and Warrener

### 4.1.5 Double Diels-Alder Approach to Cyclophanes

A third method for generating cyclophanes which is different from both the approach of Bodwell and Warrener uses a double Diels-Alder reaction. This method has been used by several groups; Stoddart ${ }^{119}$ and Klärner ${ }^{120}$ in their attempts to synthesize an aromatic belt, Müllen ${ }^{121}$ in his studies comparing conditions for cyclophane vs polymer formation, and Dibble for generating cyclophanes. ${ }^{49,50,52}$ It was alluded to in Section 1.5 .2 that cyclophanes can be made by combining
a bis(IBF) with a bis(dienophile) as in Scheme 4-7. One furan moiety will react with a dienophile moiety to generate the intermediate 76. The second furan moiety can then react with the second dienophile moiety by an intramolecular route to generate a cyclophane as the final product (77a). Once 76 is generated it can potentially react with either a molecule of reactant (furan or dienophile) or a second molecule of 76. This polymer forming process can be potentially problematic and to avoid this pathway such reactions are typically done at low concentrations.


76

## Scheme 4-7

This method has been applied in the Dibble research group to make a variety of cyclophanes including naphthophanes (77a-d), biphenylophanes (78a-i) and stilbenophanes (79ae). These compounds have a range of rigidity in their backbones and as a result different structural properties. The structural properties of 77a and 78a will be discussed in further detail in Section 4.3.1, but were not synthesized in this study.



78

79


Figure 4-4. Cyclophanes made in the Dibble research group

### 4.2 Novel Cyclophanes from Bis(IBF)s

### 4.2.1 Bis(dienophile)s

Two different types of tethered bis(dienophile)s have been synthesized in this study and used for cyclophane formation; bis(maleimide) and bis(acrylate) derivatives.

The synthesis of the tethered bis(maleimide)s proved challenging. Mixing MA and the corresponding diamine 80a-d in refluxing acetic acid (condition A, Scheme 4-8) met with some success, particularily with the shorter tether lengths. While full conversion to products was observed using 80a, use of this method for diamines 80b-d showed decreasing conversion to products as the tether length increased. Longer reaction time did not improve yields and this method was deemed unsuitable for the synthesis of 81b-d. Habibi ${ }^{122}$ utilized microwave
radiation and montmorillonite clay to synthesize a variety of bis(maleimide)s (condition B , Scheme 4-8). Mixing MA, the corresponding diamine, and KSF clay followed by irradiation with microwaves showed evidence for almost complete conversion of $\mathbf{8 0 b} \mathbf{- d}$ to $\mathbf{8 1 b} \mathbf{b}$. Although low yields ( $\sim 20 \%$ crude) ensued, likely due to extraction problems, this method was still better than the acetic acid preparation for the longer bis(maleimide)s.


Scheme 4-8

The tethered bis(acrylate)s (83a-c), which are used in polymer chemistry, ${ }^{123}$ were easily synthesized by the reaction of the corresponding diol (82a-c) with acryloyl chloride under basic conditions (Scheme 4-9). ${ }^{124}$ Although these compounds were obtained in only modest yields (40$50 \%$ ) the starting materials were inexpensive relative to the those used to make the bis(IBF)s.


Scheme 4-9

### 4.2.2 Synthesis of Imide Tethered Cyclophanes

The tethered bis(maleimide)s are attractive precursors for the synthesis of cyclophanes.
The maleimide functional group tends to react with dienes to form endo-adducts ${ }^{7,125}$ which is necessary for the cyclophane pathway to dominate over polymer formation. Due to the symmetry of the tethered bis(maleimide)s only one regioisomer can be formed when reacted with a bis(IBF)
such as 25a. Lack of symmetry became an issue, as will be discussed in Section 4.2.3, when cyclophanes were made from the tethered bis(acrylate)s.


25

$$
\begin{aligned}
& \text { a } R_{1}, R_{2}=H, H \\
& \text { b } R_{1}, R_{2}=P h, H \\
& \text { c } R_{1}, R_{2}=T B S, T B S
\end{aligned}
$$


$\mathrm{CHCl}_{3}$


77

## Scheme 4-10

Compound 77a has previously been synthesized by reacting $\mathbf{2 5 a}$ with $\mathbf{8 1} \mathbf{a}^{50,52}$ It was found during the synthesis that the polymerization pathways, described in Scheme 4-7, were significant as seen in the crude ${ }^{1} \mathrm{H}$ NMR spectrum (Figure 4-5). In the synthesis of 77e, which was formed at a similar rate to 77 a, multiple side products were also detected in the crude mixture. However, the silylated derivative (25c) reacted with 81a quite cleanly. In fact the crude ${ }^{1}$ H NMR spectrum of $\mathbf{7 7 f}$ showed minimal side products with the main impurity being excess starting material due to imperfect stoichiometry (Figure 4-5). It was established that $\mathbf{2 5 c}$ was much less reactive than $\mathbf{2 5 a}$ (Section 3.4) and the second furan moiety in $\mathbf{2 5}$ c exhibited an equilibrium, a quality not condusive to cyclophane formation. Since it was unclear if $\mathbf{7 7 f}$ could be formed in significant quantity at all, its clean formation was unexpected. It is likely the reduced reactivity of $\mathbf{2 5 c}$ that makes it more selective towards cyclophane formation and less selective towards polymerization. Once the first furan moiety reacts with the tethered bis(dienophile) the steric hindrance is likely too great for a second molecule of 81a to react. As a result the second furan moiety of $\mathbf{2 5 c}$ preferentially reacts with the second maleimide moiety of 81a. Furthermore it was observed that in the presence of NMM it took several hours for the
equilibrium between adducts $\mathbf{4 9}$ and $\mathbf{5 0}$ to establish, by contrast complete conversion to $\mathbf{7 7 f}$ took only minutes. Obviously the bulky substituents hamper the intermolecular reaction more than they hamper the intramolecular reaction.


Figure 4-5. Crude ${ }^{1} \mathrm{H}$ NMR sections of 77a, 77e (aromatic region obscured by phenyl protons therefore not shown) and 77f

Other than the differences implicit in the formation of 77a, 77e, and 77f, and the peaks associated with their substituents, there is little variation in the ${ }^{1} \mathrm{H}$ NMR spectra of these compounds. Signals for equivalent protons typically appear within 0.1 ppm of their expected values and coupling patterns appear to be the same. Based on this data it is unlikely that these compounds differ significantly in structure.

Cyclophane $\mathbf{7 7 f}$ is not particularily stable as it has a low decomposition point $\left(\sim 165^{\circ} \mathrm{C}\right)$ relative to other cyclophanes. Other evidence for the low stability of this compound came from a mass spectrum using electron spray ionization (ESI). ESI is a soft ionization technique and does
not usually cause fragmentation of a molecule. When pure 77f was subjected to ESI the mass spectrum clearly showed three fragments; $\mathbf{7 7 f}$, as well as peaks corresponding to $\mathbf{2 5 c}$ and $\mathbf{8 1 a}$. The presence of these peaks in the mass spectrum can be rationalized by two retro Diels-Alder reactions which generates the starting materials.

### 4.2.3 Synthesis of Acrylate Tethered Cyclophanes

### 4.2.3.1 Regioselectivity Issues

Difficulty with the synthesis of the tethered bis(maleimide)s and challenging purification of the cyclophanes derived from these tethers led us to explore the use of bis(acrylate) tethers. The tethered bis(acrylate)s were easily synthesized and there were initial successes at purifying the ensuing cyclophanes as these compounds appeared to have higher crystallinity. However, because the acrylate functional groups are not symmetrical, regioselectivity of the Diels-Alder reactions became an issue. It is possible to form three different regioisomers of these cyclophanes as shown in Scheme 4-11. In the a isomers the carbonyl functional groups are adjacent to the bay regions for both ends of the cyclophane resulting in molecules with $\mathrm{C}_{2}$ symmetry. By contrast the $\mathbf{b}$ isomers have one carbonyl adjacent to the bay region, but at the other end of the cyclophane the carbonyl is on the side opposite the bay region. These isomers do not have $\mathrm{C}_{2}$ symmetry and would be expected to have a much different NMR spectrum than the a isomers. For the $\mathbf{c}$ isomers neither carbonyl is adjacent to the bay region and these molecules do exhibit $C_{2}$ symmetry.




a in-in

b in-out


C out-out

$$
\begin{aligned}
\mathrm{X}= & 84\left(\mathrm{CH}_{2}\right)_{3} \\
& 85\left(\mathrm{CH}_{2}\right)_{4} \\
& 86 \mathrm{H}_{3} \mathrm{CC} \equiv \mathrm{CCH}_{3}
\end{aligned}
$$

## Scheme 4-11

All three of these isomers could theoretically be formed, but when the three carbon tethered bis(acrylate) (83a) was used only $\mathbf{8 4 a}$ was isolated in significant yield. The reason for this is likely due to the length of the tethered bis(acrylate). The distance between carbonyls is the shortest in the in-in isomers, therefore it was suspected that 83a was not long enough to generate $\mathbf{8 4 b}$ or $\mathbf{8 4}$. This means that if the first Diels-Alder cycloaddition results in the carbonyl being adjacent to the bay region as in intermediate $\mathbf{8 7 a}$ the second cycloaddition occurs best if the second carbonyl is adjacent to the other bay region. However, if the first cycloaddition results in intermediate $\mathbf{8 7 b}$ then the second cycloaddition will not be favorable in either case and an unproductive polymerization path may ensue.


87a


87b

Figure 4-6. Intermediates 87a and 87b

This hypothesis was investigated by calculating the energies of the different isomers for compounds $\mathbf{8 4}, \mathbf{8 5}$, and $\mathbf{8 6}$. Based on the values in Table $4-1$ the in-in isomer is favored for $\mathbf{8 4}$. However, the in-in isomers are not as strongly favored for cyclophanes $\mathbf{8 5}$ and $\mathbf{8 6}$ compared to 84. Based on these values the four carbon (83b) and alkyne bis(acrylate)s (83c) should be long enough that the in-out isomers and perhaps even the out-out isomers of $\mathbf{8 5}$ and $\mathbf{8 6}$ will be formed. Confirmation of this was obtained with the isolation of significant amounts of both $\mathbf{8 5 b}$ and $\mathbf{8 6 b}$. In principle 85 c and 86 c could be obtained as well, however the formation of these isomers is still the least energetically favorable. Considering that statistically only a small amount of these compounds would be obtained anyway ( $25 \%$ ), it is not surprising that there was not a significant amount of the out-out isomers generated.

Table 4-1. Total and Relative Energies for Isomers of Cyclophanes 84, 85, and 86 as Calculated by AM1 modeling

|  |  |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| Cyclophane | $\mathbf{8 4}(\mathbf{k c a l} / \mathbf{m o l})$ |  | $\mathbf{8 5}(\mathbf{k c a l} / \mathbf{m o l})$ |  | $\mathbf{8 6}(\mathbf{k c a l} / \mathbf{m o l})$ |  |
| Isomer | $\mathbf{E}$ | $\mathbf{E}_{\text {rel }}$ | $\mathbf{E}$ | $\mathbf{E}_{\text {rel }}$ | $\mathbf{E}$ | $\mathbf{E}_{\text {rel }}$ |
| $\mathbf{a}$ (in-in) | -5467.7 | 0.0 | -5750.7 | 0.0 | -5471.4 | 0.0 |
| $\mathbf{b}$ (in-out) | -5465.2 | +2.6 | -5749.1 | +1.6 | -5471.0 | +0.4 |
| $\mathbf{c}$ (out-out) | -5462.7 | +5.0 | -5748.2 | +2.5 | -5470.4 | +1.0 |

Regioisomers, while interesting, are irksome if one wants to synthesize a significant amount of a single product. For this reason we investigated the directing effects of phenyl substituents on cyclophane formation. By reacting 25b with 83a-c (Scheme 4-12) we found that
phenyl groups were effective at directing Diels-Alder cycloadditions to the formation of orthoproducts. When the longer tether, $\mathbf{8 3 b}$, was reacted with $\mathbf{2 5 b}$ a mixture of regioisomers was not obtained. Instead the crude ${ }^{1} \mathrm{H}$ NMR spectrum, shown in Figure 4-7, revealed that a single symmetrical isomer predominated which proved to be the product analogous to $\mathbf{8 5 a} \mathbf{( 8 8 b}$ ). Similar results were obtained upon synthesis of $\mathbf{8 8 a}$ and $\mathbf{8 8 c}$ with only a single regioisomer being isolated.


Scheme 4-12


Figure 4-7. Section of crude ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{8 5 b}$ and $\mathbf{8 8 b}$. Multiple isomers are present in the crude ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{8 5 b}$.

It was established that reducing the reactivity of $\mathbf{2 5 a}$ by adding silyl substituents (generating 25c) resulted in cyclophane formation dominating over side products. It was therefore hoped that the same effect would be seen when $\mathbf{2 5 e}$ was reacted with a tethered bis(maleimide) (81a). While the formation of ensuing cyclophane (77g, Scheme 4-13) was not as clean as the formation of 77f, the conversion was still cleaner than in the case of either 77a or 77e. It was also hoped that when this compound was reacted with a tethered bis(acrylate) that the regiospecific effects seen for $\mathbf{2 5 b}$ would be retained and only one isomer would be isolated. Initial investigations indicate that $\mathbf{2 5 e}$ reacts when mixed with a tethered bis(acrylate), however the expected adduct peaks do not appear, so it is unclear as to what reaction is occurring.


Scheme 4-13

### 4.3 Structural Analysis of Cyclophanes

### 4.3.1 Structural Analysis of 77a and 78a

### 4.3.1.1 Analysis of 77a

An interesting structural properties inherent to many cyclophanes is the close proximity of functional groups. In the cases of 77a and 78a the methylene groups from the tether portion of
the molecule are in close proximity to their respective $\pi$-systems. Although these molecules have been analyzed prior to this study, ${ }^{49,50,126}$ further investigation of this interaction was thought to be necessary to fully understand the geometries of these molecules.

A crystal structure was obtained of $\mathbf{7 7 a}$ (Figure 4-8) which shows the central methylene protons angled towards the $\pi$-system. ${ }^{126}$ Since these protons point towards the center of the naphthalene system they experience a strong shielding effect from the ring current. This effect is seen in the proton NMR spectrum with these protons appearing upfield of TMS at -1.41 ppm . There is also evidence that $\mathbf{7 7 a}$ is somewhat strained. There is a slight warp associated with the aromatic system and the geometry around the central methylene has a large C23-C24-C25 bond angle of $115.17(13)^{\circ}$. This large angle was not expected because based on the geometry of the unreacted tether $\mathbf{8 1 a}(\mathrm{N}-\mathrm{N}$ distance $=4.98 \AA(\mathrm{AM} 1))$ it should easily span the distance beneath the fused rings $(\mathrm{N}-\mathrm{N}$ distance $=4.85 \AA$ ). To compensate for the large central angle the $\mathrm{N} 1-\mathrm{C} 25-$ C24 and the N2-C23-C24 angles are $108.51(13)^{\circ}$ and $108.10(13)^{\circ}$ respectively. Furthermore the C23-C24 and the C24-C25 bond lengths are slightly compressed to $1.523(2) \AA$ and $1.518(2) \AA$ respectively. This odd geometry would seem to suggest that the tether is not being stretched by the fused ring system, but there is a strong repulsion between the $\pi$-system of the naphthalene ring and the tether. This repulsion forces the tether to adopt peculiar angles.

Tsuzuki ${ }^{127}$ has performed calculations on the interaction between the naphthalene $\pi$ system and a molecule of methane. It was found that methane with two hydrogens facing the aromatic system has a C $-\pi$ equilibrium distance between $3.4 \AA$ and $3.5 \AA$ depending on where the methane interacts with the aromatic system. If this distance is significantly reduced the interaction quickly becomes destabilizing. In 77a the orientation of the central methylene is analogous to one of the methane orientations in Tsuzuki's study, but the distance from C24 to the aromatic plane is only $3.34 \AA$. This suggests that it is energetically unfavorable for C24 to be as close to the aromatic system as it is. Thus the C23-C24-C25 bond angle must be especially large
because C24 cannot be any closer to the aromatic system and is being pushed away from the aromatic system.


Figure 4-8. X-ray crystal structure of cyclophane 77a showing a C- $\pi$ distance of $3.34 \AA$ for C24.
Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.
The shape of an MO can be determined based on the atomic orbitals (AO) that contribute to it. For an unperturbed $\pi$-system we would expect no $S$ character in the MO (no contribution from S atomic orbitals). In a Diels-Alder adduct such as $\mathbf{4 4}$ (Section 3.4) there is some S character to the $\pi$-system. There are non-zero values for the 5 S orbitals ${ }^{\text {vii }}$ (Table 4-2) on all the carbon atoms that make up the benzene moiety meaning the $\mathrm{p}_{\mathrm{x}}$ atomic orbitals are being polarized. However, this polarization is relatively insignificant as most of the 5 S atomic eigenvalues are small. This would indicate that the $\pi$-system is relatively unperturbed by either the ring junction or the $N$-methyl group. The same effect is seen in the orbitals of a non-silylated derivative of $\mathbf{5 0}$, small polarizations which are relatively insignificant.

[^6]

Figure 4-9. Depiction of the HOMO of $\mathbf{4 4}$ as calculated by B3LYP/6-311+G(2d,p)//B3LYP/631(d). Red and green depict opposite orbital phase.

Table 4-2. Atomic Eigenvalues and Orbital Polarizations for HOMO and HOMO-1 of 44

|  | Atomic Eigenvalues |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Orbital | C 1 | C 2 | C 3 | C 4 | C 5 | C 6 |
| HOMO | C |  |  |  |  |  |
| 2PX | 0.098 | 0.098 | node | -0.107 | -0.107 | node |
| 3PX | 0.150 | 0.150 |  | -0.163 | -0.163 |  |
| 4PX | 0.140 | 0.140 |  | -0.143 | -0.143 |  |
| 5PX | 0.190 | 0.201 |  | -0.025 | -0.030 |  |
| 5S | 0.074 | 0.027 |  | -0.063 | -0.039 |  |
| Polarization | $<0.1$ | $<0.1$ |  | $<0.1$ | $<0.1$ |  |
| w.r.t. tether | towards | towards |  | towards | towards |  |
| HOMO-1 | C 1 | C 2 | C 3 | C 4 | C 5 | C 6 |
| 2PX | 0.064 | -0.065 | -0.127 | -0.062 | 0.063 | 0.127 |
| 3PX | 0.099 | -0.100 | -0.192 | -0.095 | 0.096 | 0.192 |
| 4PX | 0.064 | -0.065 | -0.173 | -0.077 | 0.077 | 0.173 |
| 5PX | -0.075 | 0.084 | -0.145 | -0.041 | 0.040 | 0.145 |
| 5S | -0.233 | 0.212 | 0.021 | 0.038 | -0.038 | -0.027 |
| Polarization | $>0.1$ | $>0.1$ | $<0.1$ | $<0.1$ | $<0.1$ | $<0.1$ |
| w.r.t. tether | towards | towards | away | away | away | away |

In a cyclophane such as 77a interaction between the tether and the $\pi$-system might cause a strong polarization of the MOs. This compound was modeled using B3LYP/6-31G(d) theory and the model showed good correlation with the X-ray crystal structure (Figure 4-8). Calculated
bond lengths and angles were typically within $1 \%$ of the experimental values with an overall RMSD of $0.09957 \AA$. The MOs were calculated and the atomic eigenvalues for the HOMO and HOMO-1 are shown in (Table 4-3). Closer inspection shows that the $p_{y}$ orbitals are generally ${ }^{\text {viii }}$ being polarized away from the tether side of the $\pi$-system. This suggests that there is a strong $\pi$ tether interaction which is compensated for through orbital polarization.


Figure 4-10. Depiction of the HOMO of 77a as calculated by B3LYP/6-311+G(2d,p)//B3LYP/631(d). Red and green depict opposite orbital phase.

[^7]Table 4-3. Atomic Eigenvalues and Orbital Polarizations for HOMO and HOMO-1 of 77a

| Atomic <br> Orbital | Atomic Eigenvalues |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| HOMO | C7 | C8 | C9 | C14 | C15 | C16 |  |
| 2PY | 0.087 | 0.111 | node | node | -0.111 | -0.052 |  |
| 3PY | 0.133 | 0.168 | - | - | -0.167 | -0.079 |  |
| 4PY | 0.127 | 0.156 | - | - | -0.154 | -0.079 |  |
| 5PY | 0.042 | 0.169 | - | - | -0.026 | -0.035 |  |
| 5S | -0.388 | -0.073 | - | - | 0.412 | 0.460 |  |
| Polarization | $>0.1$ | $<0.1$ |  |  | $>0.1$ | $>0.1$ |  |
| w.r.t. tether | away | away | - | - | away | away |  |
| HOMO-1 | C7 | C8 | C9 | C14 | C15 | C16 |  |
| 2PY | -0.085 | node | 0.110 | 0.110 | node | -0.116 |  |
| 3PY | -0.130 | - | 0.167 | 0.167 | - | -0.174 |  |
| 4PY | -0.100 | - | 0.136 | 0.136 | - | -0.159 |  |
| 5PY | 0.039 | - | 0.074 | -0.088 | - | -0.070 |  |
| 5S | -0.069 | - | -0.219 | -0.127 | - | 0.195 |  |
| Polarization | $<0.1$ |  | $>0.1$ | $>0.1$ |  | $>0.1$ |  |
| w.r.t. tether | towards | - | away | away | - | away |  |

### 4.3.1.2 Analysis of 78a

The crystal structure of cyclophane 78a exhibits many of the same peculiar structural features seen in 77a; The bond angles about the methylene atoms near the $\pi$-system (C14 and C16) are especially large ( $115.25(15)$ and $115.89(15) \AA$ ). By contrast the angle about the methylene between them (C15) is only $108.73(14) \AA$. The $\mathrm{N}-\mathrm{N}$ distance in the unreacted tether (81c) is $7.48 \AA$ by AM1 modeling, but the $\mathrm{N}-\mathrm{N}$ distance is only $7.31 \AA$ in 78a. These features suggest that the tether is not being stretched by the aromatic system. Instead there is evidence for a strong repulsive $\pi$-tether interaction (as in 77a) which is further discussed.

While the interaction in 77a is analogous to methane stacked on naphthalene, the same interaction in 78a is analogous to methane stacked on benzene. In this cyclophane there are two such interactions with $\mathrm{C}-\pi$ distances of 3.54 and $3.52 \AA$ (Figure $4-11$ ). In an earlier publication Tsuzuki ${ }^{128}$ performed calculations on a molecule of methane stacked on a benzene ring. In this
study Tsuzuki determined the $\mathrm{C}-\pi$ equilibrium distance to be $3.6 \AA$, greater than the $\mathrm{C}-\pi$ distances found for 78a. The large angles about C14 and C16 might also be rationalized by the $\pi$ system pushing on the nearby methylene groups.


Figure 4-11. X-ray crystal structure of 78a showing C- $\pi$ distances of 3.52 and $3.54 \AA$ for C14 and C 16 respectively. Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.

Prior to analysis of 78a's orbitals it was necessary to construct a computational model. A model of 78a was calculated, but the geometry showed only reasonable correlation with the crystal structure (RMSD of $0.294 \AA$ ). The primary source of deviation between the two models is the difference in the rotation of the biphenyl groups. In the calculated model the phenyl groups are rotated $20.0^{\circ}$ relative to each other while in the crystal structure this torsion angle is only $3.8^{\circ}$. The other obvious difference is the exaggerated tether angles in the calculated model relative to the crystal structure. For example the angles about C14 and C16 are larger in the calculated model than in the crystal structure ( $116.97^{\circ}$ vs $115.25(15)$ and $\left.115.89(15)^{\circ}\right)$ and the angle about C15 is smaller ( $107.94^{\circ}$ vs $\left.108.74(14)^{\circ}\right)$.

The planar biphenyl moiety can be explained by crystal packing forces. For example biphenyl itself is found to be planar in solid state, but not in the gas phase. ${ }^{129}$ Likewise, investigation of the crystal packing of 78a (Figure 4-12) reveals that its tether is interacting with the $\pi$-system of an adjacent molecule with an intermolecule $\mathrm{C}-\pi$ distance of $3.59 \AA$. This would
counter the intramolecular $\mathrm{C}-\pi$ interaction and average the angles in the tether relative to the calculated model.


Figure 4-12. Crystal packing model of 78a showing intermolecular C15- $\pi$ distance of $3.59 \AA$. Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.

This rationale gave us confidence in the geometry of the calculated model and we chose to use it for our orbital analysis. Orbital polarizations shown in Table 4-4 are not as definitive in 78a as they were in 77a. Inspection of the HOMO shows that the 5 S orbitals tend to be polarizing the $p_{y}$ orbitals away from the tether although this is not the case for every atom. The HOMO -1 does not show the expected polarization for any of the atoms, instead the orbitals seem to be polarized towards the tether. Given that most of the polarizations are small it could be the interaction between the $\pi$-system and the tether is not as strong in this molecule as it was in 77a and therefore the polarizations are not clearly in one direction or the other.


Figure 4-13. Depiction of the HOMO of 78a as calculated by B3LYP/6-311+G(2d,p)//B3LYP/631(d). Red and green depict opposite orbital phase.

Table 4-4. Atomic Eigenvalues and Orbital Polarizations for HOMO and HOMO-1 of 78a

|  | Atomic Eigenvalues |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Orbital | C 30 | C 31 | C 32 | C 33 | C 34 |  |
| HOMO | C 29 | C 2.058 |  |  |  |  |
| 2PY | -0.053 | -0.105 | node | 0.085 | 0.097 | 0.058 |
| 3PY | -0.080 | -0.161 |  | 0.128 | 0.148 | 0.086 |
| 4PY | -0.080 | -0.141 |  | 0.121 | 0.120 | 0.086 |
| 5PY | -0.113 | -0.017 |  | 0.043 | 0.062 | 0.045 |
| 5S | -0.156 | 0.140 |  | -0.096 | 0.071 | -0.121 |
| Polarization | $>0.1$ | $>0.1$ |  | $<0.1$ | $<0.1$ | $>0.1$ |
| w.r.t. tether | toward | away |  | away | towards | away |
| HOMO-1 | C 29 | C 30 | C 31 | C 32 | C 33 | C 34 |
| 2PY | 0.102 | node | -0.067 | -0.090 | node | 0.085 |
| 3PY | 0.155 |  | -0.101 | -0.135 |  | 0.128 |
| 4PY | 0.126 |  | -0.090 | -0.122 |  | 0.117 |
| 5PY | 0.060 |  | -0.032 | -0.021 |  | 0.012 |
| 5S | 0.213 |  | -0.112 | -0.057 |  | 0.029 |
| Polarization | $>0.1$ |  | $>0.1$ | $<0.1$ |  | $<0.1$ |
| w.r.t. tether | toward |  | toward | toward |  | toward |

There is definite interaction between the tethers of 77a and 78a and their respective $\pi$ systems. In 77a there is evidence of a strong $\pi$-tether interaction with peculiar angles in the tether, strong orbital polarizations, a destabilizing $\mathrm{C}-\pi$ distance for C 24 , and a tether that is too long to easily fit between the oxa-bicycle rings. The angles in the tether of 78a are even more exaggerated. However, other evidence for interaction between the tether and the $\pi$-system is weaker. The orbitals are not strongly polarized in one direction or another and the $\mathrm{C}-\pi$ distance is larger than in 77a. It is possible that the longer tether is more easily pushed away from the $\pi$ system therefore the evidence for the interaction between the two is diminished.

### 4.3.2 Structural Analysis of Acrylate Cyclophanes

### 4.3.2.1 Analysis of 84a

The ester tether of $\mathbf{8 4} \mathbf{a}$ is more flexible than the imide tether of $\mathbf{7 7} \mathbf{a}$. The most obvious evidence of this is seen in the crystal structure where the tether is found to be disordered, a feature not found in 77a. There were two tether conformations that were modeled which will be referred to as the primary chain (the most well refined chain) and the secondary chain (the least well refined chain) which are shown in Figure 4-14. A conformational search was performed to determine the best geometry for the tether. The lowest energy conformation found by the conformational search was minimized further using B3LYP/6-31G(d), which was found adept at predicting the geometry of $\mathbf{7 7 a}$ and $\mathbf{2 5} \mathbf{c}^{\mathrm{ix}}$. This global minimum corresponded well with the primary tether geometry shown in Figure 4-14.

[^8]

Figure 4-14. Left) X-ray structure of $\mathbf{8 4}$ a showing the primary tether chain. Right) X-ray structure of $\mathbf{8 4 a}$ showing the secondary tether chain with isotropic atoms C20' and C21'. Ellipsoids drawn to $50 \%$ probability level and hydrogens are drawn with equal, fixed radii.

The primary chain shown in Figure 4-14 is well behaved and refined nicely with reasonable bond lengths and angles throughout the tether. The secondary chain is not as well behaved and we believe this is because the molecule exhibits $\mathrm{C}_{2}$ symmetry, but the lattice site does not. The second rotamer does not fit the packing forces as well therefore the tether adopts a slightly higher energy conformation which is the origin of this "elbow" disorder. We were unable to obtain reasonable anisotropic representations of $\mathrm{C} 20^{\prime}$ and $\mathrm{C} 21^{\prime}$ because of the additional disorder associated with these two atoms. Analysis of the torsion angles shown in Table 4-5 shows that there are differences of up to $20^{\circ}$ between angles that should be the same. However, there is very good correlation in the angle that does not involve either C20' or C21'. Additionally, each chain adopts the same conformation when optimized which was also found to be the global minimum. If it were not for the additional disorder associated with these atoms it is suspected that the primary and secondary chains would in fact be rotamers.

Table 4-5. Tether Torsion Angles for Primary and Disordered Chains in the X-ray Crystal Structure of 84a (best correlation between angles is highlighted)

| Primary Chain | Angle $\left({ }^{\circ}\right)$ | Secondary (Disordered) Chain | Angle $\left({ }^{\circ}\right)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(14)-\mathrm{C}(19)-\mathrm{O}(4)-\mathrm{C}(20)$ | $168.1(3)$ | $\mathrm{C}\left(22^{\prime}\right)-\mathrm{O}\left(6^{\prime}\right)-\mathrm{C}(23)-\mathrm{C}(18)$ | $168.2(6)$ |
| $\mathrm{C}(19)-\mathrm{O}(4)-\mathrm{C}(20)-\mathrm{C}(21)$ | $-178.1(4)$ | $\mathrm{C}\left(21^{\prime}\right)-\mathrm{C}\left(22^{\prime}\right)-\mathrm{O}\left(6^{\prime}\right)-\mathrm{C}(23)$ | $172.2(10)$ |
| $\mathrm{O}(4)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $165.3(3)$ | $\mathrm{C}\left(20^{\prime}\right)-\mathrm{C}\left(21^{\prime}\right)-\mathrm{C}\left(22^{\prime}\right)-\mathrm{O}\left(6^{\prime}\right)$ | $145.5(18)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{O}(6)$ | $-65.1(4)$ | $\mathrm{O}\left(4^{\prime}\right)-\mathrm{C}\left(20^{\prime}\right)-\mathrm{C}\left(21^{\prime}\right)-\mathrm{C}\left(22^{\prime}\right)$ | $-55(3)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{O}(6)-\mathrm{C}(23)$ | $-83.0(4)$ | $\mathrm{C}(19)-\mathrm{O}\left(4^{\prime}\right)-\mathrm{C}\left(20^{\prime}\right)-\mathrm{C}\left(21^{\prime}\right)$ | $-96.3(19)$ |
| $\mathrm{C}(22)-\mathrm{O}(6)-\mathrm{C}(23)-\mathrm{C}(18)$ | $-174.9(3)$ | $\mathrm{C}(14)-\mathrm{C}(19)-\mathrm{O}\left(4^{\prime}\right)-\mathrm{C}\left(20^{\prime}\right)$ | $-167.4(12)$ |

The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{8 4 a}$ is relatively interesting and provides evidence as to how the tether behaves in solution. The increased flexibility associated with this molecule means that the central methylene protons (Figure 4-15) can rotate away from the $\pi$-system and do not experience the same shielding effect as those in $\mathbf{7 7 a}$. From the ${ }^{1} \mathrm{H}$ NMR data summarized in Table 4-6 we can see that these protons appear at 1.18 ppm which is only 0.8 ppm upfield of their positions in the unreacted bis(acrylate). This is a much smaller upfield shift than that seen in 77a for which the same protons are shifted over 3 ppm from their position in the unreacted bis(maleimide). The protons that experience the greatest shift relative to their positions in the unreacted bis(acrylate) are those adjacent to the ester functional group (H20B/H22B). These protons are shifted about 1.5 ppm upfield due to the shielding effect of the naphthalene. By contrast these protons' geminal counterparts, H20A and H22A, appear close to where they are expected at 3.54 ppm . The large disparity in chemical shift between geminal protons suggests that the tether does not rotate freely on the NMR time scale and the solid state structure is representative of how the molecule exists in solution. However, for H 21 A and H 21 B to be shift equivalent there must be some rotation in the tether allowing them to exchange positions. A molecular dynamics (MD) simulation was run of this compound at 500 K . As expected the tether primarily adopted the conformation shown in Figure $4-15$ with H21B angling towards the naphthalene ring. However, during the simulation it would periodically shift through an energy barrier with both H21A and H21B facing the ring (a tether conformation analogous to that found
for 77a) to reach an orientation equivalent to that shown in Figure 4-15 except with H21A angling towards the naphthalene ring (secondary tether orientation shown in Figure 4-14). It is this conformational change which allows for H 21 A and H 21 B to be shift equivalent.

Table 4-6. ${ }^{1}$ H NMR Chemical Shifts for $\mathbf{8 4 a}$

| Atoms | Chemical Shift (ppm) | Atoms | Chemical Shift (ppm) |
| :---: | :---: | :---: | :---: |
| H1/H10 | 7.75 | H13A/H15B | 2.23 |
| H2/H9 | 7.55 | H13B/H15A | 1.63 |
| H12/H16 | 6.18 | H20A/H22A | 3.54 |
| H11/H17 | 5.69 | H21A/H21B | 1.18 |
| H14/H18 | 3.54 | H20B/H22B | 2.44 |



Figure 4-15. Calculated geometry of $\mathbf{8 4 a}$ with labeled protons

Unlike 77a, in which the $\mathrm{C}-\mathrm{H}$ bonds are parallel to the naphthalene ring, the $\mathrm{C}-\mathrm{H}$ bonds are mainly perpendicular to the naphthalene ring in 84a. This type of tether orientation is what was found in the cyclophanes made by Warrener ${ }^{116}$ and Bodwell ${ }^{98}$ who have both used flexible hydrocarbon tethers. The bond angles O6-C22-C21, C22-C21-C20 and C21-C20-O4 are $112.22^{\circ}, 113.60^{\circ}$ and $106.28^{\circ}$ respectively. This large range of angles suggests that the tether does not smoothly span the distance between the oxa-bicyclo rings, but must adopt these awkward angles to accommodate the distance.

An experiment was done in which a model of $\mathbf{7 7 a}$ was taken and by simply deleting and changing atoms it was converted into a model of 84a except with the same tether orientation as 77a. This model was then subjected to an AM1 optimization. During the optimization it was observed that the tether slowly changed from the orientation of 77a to its "native" conformation that had previously been found to be the global minimum. This model was then converted back to 77a by reinserting the missing atoms and subjecting it to an AM1 optimization. The tether began shifting towards the initial conformation (that found for 77a), but reached a small energy barrier before it reached the original conformation. Regardless, we can safely say that the tether orientation seen in $\mathbf{7 7 a}$ is not a local minimum for $\mathbf{8 4 a}$ and vice versa.

### 4.3.2.2 Analysis of $\mathbf{8 5 a}$ and $\mathbf{8 5 b}$

No crystal structures were obtained for $\mathbf{8 5 a}$ or $\mathbf{8 5 b}$, therefore computational models and NMR data were used for structural analysis. Conformational searches were done to determine the ideal tether conformations and the resulting geometries minimized using B3LYP/6-31G(d) theory. The four carbon tether is more than long enough to span the distance between the oxabicycle rings and must adopt some slightly peculiar angles ranging from 109.39 to $113.95^{\circ}$ to adequately fit. The angles in the asymmetric isomer ( $\mathbf{8 5 b}$ ) cover a much smaller range ( 111.40 to $113.81^{\circ}$ ) possibly due to few steric requirements. Neither $\mathbf{8 5 a}$ nor $\mathbf{8 5}$ b has a significant warp in its naphthalene ring which suggests there is enough flexibility in the four carbon tether that it accommodates for any strain rather than it being taken up by the $\pi$-system.

The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{8 5}$ a clearly shows that the molecule is symmetric with naphthalene protons ( H 1 and H 2 ), the bridgehead protons ( H 3 and H 4 ), and the ring junction protons (H5, H6 and H7) appearing at chemical shifts very close to those found in 84a. However, the shifts for the tether protons vary significantly between the two molecules. An important difference between them is the evidence that the tether rotates much more freely in $\mathbf{8 5 a}$, while it does not in $\mathbf{8 4 a}$. The chemical shifts of H 10 and H 11 are equivalent and there is only a 0.9 ppm
disparity between the geminal protons adjacent to the ester group (H8 and H9, Table 4-7), as opposed to over approximately 1.1 ppm in $\mathbf{8 4 a}$. An MD simulation at 500 K showed that the tether undergoes much more rotation than that found for $\mathbf{8 4 a}$ with all methylene atoms rotating through $360^{\circ}$ during the simulation.


Figure 4-16. Calculated geometry (B3LYP/6-31G(d)) with labeled protons of $\mathbf{8 5 a}$ (Left, symmetry equivalent protons are not labeled) and $\mathbf{8 5 b}$ (Right)

The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{8 5 b}$ is significantly more complicated than the spectrum of $\mathbf{8 5 a}$ (Figure 4-17). The lack of symmetry in the molecule means that all 22 protons are nonequivalent and exhibit their own NMR signal. This is most notable in the region downfield of 5 ppm where there are more signals associated with the aromatic and bridgehead protons.


Figure 4-17. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{8 5 a}$ (Top, slight evidence of $\mathbf{8 5 b}$ in baseline) and $\mathbf{8 5 b}$
(Bottom)

Table 4-7. Proton Chemical Shifts of $\mathbf{8 5 a}$ and $\mathbf{8 5 b}$

| Proton | Shift (ppm) |  | Proton | Shift (ppm) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 85a |  |  |  | 85a | 85b |
|  | A | 7.86 | 7.81 | H7 | A | 3.59 | 3.55 |
|  | B |  | 7.72 |  | B |  | 3.55 |
| H2 | A | 7.57 | 7.58 | H8 | A | 4.18 | 3.55 |
|  | B |  | 7.46 |  | B |  | 3.55 |
| H3 | A | 6.13 | 5.99 | H9 | A | 3.31 | 3.84 |
|  | B |  | 6.12 |  | B |  | 3.29 |
| H4 | A | 5.64 | 5.8 | H10 | A | 0.27 | 1.14 |
|  | B |  | 5.66 |  | B |  | 0.008 |
| H5 | A | 2.48 | 2.43 | H11 | A | 0.27 | 1.04 |
|  | B |  | 2.43 |  | B |  | 0.008 |
| H6 | A | 1.86 | 1.83 |  |  |  |  |
|  | B |  | 1.83 |  |  |  |  |

### 4.3.2.3 Analysis of $\mathbf{8 6 a}$ and $\mathbf{8 6 b}$

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{8 6 a}$ and $\mathbf{8 6 b}$ are quite similar (Table 4-8) and fewer protons in the tether simplify the alkyl region significantly. The most notable feature of the NMR spectrum of $\mathbf{8 6 b}$ is the presence of two couplings in the H 8 and H 9 protons. The large coupling ( $\mathrm{J}=15 \mathrm{~Hz}$ )
can be attributed to the geminal coupling between the H 8 and H 9 protons. Also present is a very fine coupling $(\mathrm{J}=\sim 2.5 \mathrm{~Hz})$ which make the overall signal a doublet of triplets. This coupling can only be explained by a 5 bond coupling through the alkyne between $8 / 9 \mathrm{~A}$ and $8 / 9 \mathrm{~B}$. This feature is not present in 86a as the symmetry in the molecule makes the A and B protons homotopic.


Figure 4-18. Calculated geometry with labeled protons of 86a (Left) and 86b (Right)

Table 4-8. Proton Chemical Shifts of 86a and 86b

| Proton | Shift <br> 86pm) |  | Proton | Shift (ppm) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 86b |  |  | $\mathbf{8 6 a}$ | $\mathbf{8 6 b}$ |  |
| H1 | A | 7.81 | 7.84 | H6 | A | 1.93 | 1.92 |
|  | B |  | 7.77 |  | B |  | 1.82 |
| H2 | A | 7.51 | 7.54 | H7 | A | 3.52 | 3.55 |
|  | B |  | 7.49 |  | B |  | 3.55 |
| H3 | A | 6.01 | 6.11 | H8 | A | 4.41 | 4.66 |
|  | B |  | 5.97 |  | B |  | 4.73 |
| H4 | A | 5.52 | 5.61 | H9 | A | 3.95 | 3.98 |
|  | B |  | 5.78 |  | B |  | 4.39 |
| H5 | A | 2.39 | 2.47 |  |  |  |  |
|  | B |  | 2.47 |  |  |  |  |

It has been seen in previous cyclophanes that different tethers exert different distortions upon the aromatic system. For naphthalene systems this can be quantified by measuring the angle between the planes made by the individual benzene rings. More distorted systems will have a larger angle between these planes and less distorted systems will have planes near $0^{\circ}$. In the case of 77a there is a significant concave warp with respect to the tether (Table 4-9). There are only
slight warps $\left(<2^{\circ}\right)$ for $\mathbf{8 4 a}$ and $\mathbf{8 5 a}$ a suggesting that the tether is easily accommodated beneath the fused ring system. Interestingly in the case of $\mathbf{8 6 a}$ the naphthalene system exhibits a convex warp with respect to the tether. In this molecule the alkyne tether is both long enough and rigid enough that it pushes out on the oxa-bicyclo rings, which in turn warps the naphthalene ring. This effect is not seen in $\mathbf{8 6 b}$ as the different structure allows any strain to be taken up by the angle about the oxygen atoms ( 115.50 and $116.12^{\circ}$ ).

Table 4-9. Angle between the Aromatic Planes for Naphthalenic Cyclophanes

| Compound | Angle Between Planes ( ${ }^{\circ}$ ) |
| :---: | :---: |
| $\mathbf{7 7 a}$ | 7.61 |
| $\mathbf{8 4 a}$ | 1.68 |
| $\mathbf{8 5 a}$ | -1.82 |
| $\mathbf{8 6 a}$ | -6.39 |

### 4.4 Future Directions: Macromolecular Stuctures from Anthra[1,2-c:5,6-c]difuran

The concept of an aromatic belt (a cyclic structure made up of entirely aromatic units) is an intriguing one. The synthesis of such a molecule has been actively pursued by several groups that have been mentioned previously. ${ }^{113,119,120}$ Cyclophanes made from the right combination of bis(IBF) and bis(dienophile) can serve as precursors to generating an aromatic belt. It is beyond the scope of this writing to discuss in detail progress that has been made towards the synthesis of an aromatic belt. However, the use of anthracene derivatives towards the synthesis of such a molecule will be discussed.

Anthra[1,2-c:5,6-c]difuran (93) could be synthesized using similar conditions as used to make 30 (Section 5.2). This molecule has the $\mathrm{C}_{2}$ axis of symmetry perpendicular to the aromatic plane that is common to many of the bis(IBF)s made in the Dibble research group (26-29).



## Scheme 4-14

Compound 92 can also be converted to 94 , which can in turn be used to make 95
(Scheme 4-14). This bis(quinone) can be reacted with $\mathbf{9 3}$ to form a cyclophane adduct (96). Aromatization of this adduct results in a more traditional aromatic belt (97). Although this belt is "kinked" its diameter is approximately the same as a [10]cyclacene. These aromatic belts are of particular interest as they resemble a section of a single walled carbon nanotube. Nanotubes have become molecules of interest due to their interesting and potentially useful properties. ${ }^{94}$



97

Scheme 4-15

### 4.5 Summary

Cyclophanes are structurally interesting compounds. They can be synthesized by a variety of methods including dimerization, dehydrogenation, double substitution, and double Diels-Alder cycloaddition approaches.

Using the double Diels-Alder cycloaddition approach we have synthesized two types of tethered bis(dienophile)s, bis(maleimide) and bis(acrylate) varieties. Synthesis of tethered bis(maleimide)s proved to have certain pitfalls although a new microwave technique shows significant promise. By contrast tethered bis(acrylate)s are synthesized much more easily. We have shown that the regiochemical issues present in their reaction with a bis(IBF) can be controlled through the addition of phenyl substituents.

The structural features of these cyclophanes are also of significant interest. Two such cyclophanes, synthesized from tethered bis(maleimide)s, show evidence of strong interaction between the $\pi$-system and the tether which introduces distortions into tether's geometry. The cyclophanes synthesized from tethered bis(acrylate)s have more flexible tethers and as a result have interesting NMR spectra.

Under similar reaction conditions an isomer of $\mathbf{3 0}$ could be synthesized, anthra[1,2-c:5,6c]difuran (93). Coupling of this compound with a bis(dienophile) (95) would result in an adduct that could be aromatized to form an aromatic belt resembling a section of a single walled carbon nanotube.

Further structural studies could be done on some of the cyclophanes including more crystallography and variable temperature NMR.

### 4.5.1 Computational Details

### 4.5.1.1 Conformational search for compounds 84a, 84b, 84c, 85a, 85b, and 85c

Random torsion variation method available in HyperChem $7.5^{61}$ was used to identify low energy conformations. Tether torsion angles were varied and the resulting conformation minimized using the MM+ force field. This procedure was repeated for 1000 iterations. Potential minima were further optimized using AM1 theory and from these the lowest energy conformation was taken to be the global minimum.

### 4.5.1.2 Optimization and single point calculations for 77a, 78a, 84a, 85a, 85b, 86a, and 86b

Optimization and single point calculations were done using the Gaussian 03 program package. ${ }^{62}$ Geometries were optimized using B3LYP/6-31G(d) level of theory and were followed with single point calculations using B3LYP/6-311+G(2d,p) level of theory. Orbitals were calculated and viewed using the Gaussview 4.1 program package. ${ }^{65}$

### 4.5.1.3 RMSD Calculations for 25c, 77a, and 78b

Using the RMSD fit and overlay feature of HyperChem $7.5^{61}$ the X-ray crystal structure and calculated structure were overlaid and the RMS error calculated.

### 4.5.1.4 Molecular Dynamics Simulations of 84a and 85a

Simulations were run using HyperChem $7.5^{61}$ and the MM+ force field. Geometries optimized at B3LYP/6-31G(d) level of theory were heated in vacuo to 500 K over 10 ps . Using 0.001 ps time step sizes the simulation was allowed to proceed for 1000 ps with data being collected every 10 time steps. The temperature was chosen as such in order to see a significant amount of movement using a shorter simulation time. Additionally a lack of movement at a higher temperature suggests that at a lower temperature there would not be any movement either.

### 4.5.2 $\quad X$-ray Data Collection Details

4.5.2.1 $1^{1}, 1^{4}, 1^{7}, 1^{10}$-diepoxy- $1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro- $1(2,9)$ chrysena- 3,7 -dioxa-2,8-
diona cyclooctaphane, 84

From 1:1 chloroform/ethyl acetate were obtained X-ray quality crystals by slow cooling of 84 as colourless prisms. One such crystal was coated with paraffin oil and mounted on a glass fibre. The data set was collected ${ }^{66}$ on a Bruker ApexII CCD area detector diffractometer using graphite monochromated Mo K $\alpha$ radiation. The data was corrected for absorption and Lorentz polarization using a multi-scan method. ${ }^{67}$ The structure was solved by direct methods and refined using SHELXTL. ${ }^{68}$ Aliphatic hydrogen atoms were constrained to ideal tetrahedral geometries with optimal $\mathrm{C}-\mathrm{H}$ bond lengths and refined using a riding model. Methyl groups were allowed to
rotate and align with optimal electron density. Aromatic hydrogen atoms were fixed at ideal bond lengths and refined using a riding model and non-hydrogen atoms were refined anisotropically. The compound crystallized in the monoclinic $\mathrm{P} 2_{1} / \mathrm{c}$ space group resulting in four molecule per unit cell. The tether part of the molecule was disordered and the secondary chain was modeled as a separate part. Chemically equivalent bonds were restrained to be equal lengths and thermal parameters were restrained. Agreement factors of $R=0.0579$ ( $\mathrm{I}>2 \sigma$ ) and $w R=0.1744$ (all data) were obtained after the final least-squares cycle. Additional crystallographic details can be found in Appendix 1.

Table 4-10. Crystal data and structure refinement for 84a

| Identification code | 84a |
| :---: | :---: |
| Empirical formula | C23 H20 O6 |
| Formula weight | 392.39 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{c}$ |
| Unit cell dimensions | $a=14.2500(13) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=7.8987(7) \AA \quad \beta=95.7520(10)^{\circ}$. |
|  | $\mathrm{c}=16.1812(15) \AA \quad \gamma=90^{\circ}$. |
| Volume | 1812.1(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.438 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.104 \mathrm{~mm}^{-1}$ |
| F(000) | 824 |
| Crystal size | $0.33 \times 0.19 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.53 to $27.42^{\circ}$. |
| Index ranges | $-18<=\mathrm{h}<=18,-10<=\mathrm{k}<=10,-20<=1<=20$ |
| Reflections collected | 19966 |
| Independent reflections | $4116[\mathrm{R}(\mathrm{int})=0.0484]$ |
| Completeness to theta $=25.25^{\circ}$ | 99.9 \% |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4116 / 0 / 283 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.037 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0579, \mathrm{wR} 2=0.1490$ |
| R indices (all data) | $\mathrm{R} 1=0.0981, \mathrm{wR} 2=0.1744$ |
| Largest diff. peak and hole | 0.603 and -0.218 e. $\AA^{-3}$ |

### 4.5.3 Experimental Details

See Chapter 2 experimental section (Section 2.3.3) for details on equipment, reagents, and characterization methods.

### 4.5.3.1 Propane-1,3-diacrylate, 83a.

In 125 mL of methylene chloride was stirred 4.0 g ( 52.5 mmol ) of propane-1,3-diol (82a).
To the mixture was added a catalytic amount of DMAP and $25 \mathrm{~mL}(165 \mathrm{mmol})$ triethylamine. The mixture was cooled to $0^{\circ} \mathrm{C}$ and $8.93 \mathrm{~mL}(110 \mathrm{mmol})$ of acryloyl chloride was added dropwise. The reaction mixture was then refluxed for a 14 h period before being washed with 1.0 M HCl . The organic phase was dried over $\mathrm{MgSO}_{4}$, filtered and evaporated. The resulting liquid was placed atop a silica column and was eluted with a 9:1 mixture of petroleum ether/ethyl acetate. Evaporation of eluant resulted in of a yellow liquid which was stored at $-10^{\circ} \mathrm{C}$. bp 107$109{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) 1.89(2 \mathrm{H}, \mathrm{m}), 4.09,(4 \mathrm{H}, \mathrm{m}), 5.66,(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=10$ $\mathrm{Hz}), 5.95(2 \mathrm{H}, \mathrm{dd}, \mathrm{J}=10,17 \mathrm{~Hz}), 6.23(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=17 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm})$ 27.65, 60.77, 128.08, 130.35, 165.31; IR (neat) 2967, 1725, 1636, 1620, 1409, 1297, 1273, 1185, 1062, $985,810 \mathrm{~cm}-1$; MS (ESI) m/e calc'd for $\mathrm{C}_{9} \mathrm{H}_{12} \mathrm{O}_{4}: 184.0735$, found 184.0729;

Anal. Calc. for $\mathrm{C}_{9} \mathrm{H}_{12} \mathrm{O}_{4}$ : C, $58.68 ; \mathrm{H}, 6.58$. Found: C, 58.83; H, 6.46.

### 4.5.3.2 Butane-1,4-diacrylate, 83b.

In 125 mL of methylene chloride was stirred $3.67 \mathrm{~mL}(58.8 \mathrm{mmol})$ of butane-1,4-diol (82b). To the mixture was added a catalytic amount of DMAP and 25 mL ( 165 mmol ) of triethylamine. The mixture was cooled to $0^{\circ} \mathrm{C}$ and 9.7 mL ( 120 mmol )of acryloyl chloride was added dropwise. The reaction mixture was then refluxed for a 14 h period before being washed with 1.0 M HCl . The organic phase was dried over $\mathrm{MgSO}_{4}$, filtered and evaporated. The resulting liquid was placed atop a silica column and was eluted with a 9:1 mixture of petroleum ether/ethyl acetate. Evaporation of eluant resulted in 5.36 g (46\%) of a yellow liquid which was stored at $-10^{\circ} \mathrm{C}$. bp $113-115^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right), \delta(\mathrm{ppm}) 1.68(4 \mathrm{H}, \mathrm{m}), 4.10(4 \mathrm{H}, \mathrm{m})$,
$5.74(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=10 \mathrm{~Hz}), 6.02(2 \mathrm{H}, \mathrm{dd}, \mathrm{J}=10,17 \mathrm{~Hz}), 6.30(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=17 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( 75 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) 25.20,63.86,128.34,130.60,165.97$; IR (neat) 2961, 1725, 1637, 1620, 1410, 1297, 1272, 1189, 1061, 985, 811, $734 \mathrm{~cm}-1 ; \mathrm{MS}(\mathrm{ESI} / \mathrm{EI}) \mathrm{m} / \mathrm{e}$ calc'd for $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{4}$ : 198.0892, found 198.0386; 126 (30), 85 (14), 71 (42), 55 (100);

Anal. Calc. for $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{4}$ : C, 60.58; H, 7.13. Found: C, 60.76; H, 6.91 .

### 4.5.3.3 2-Butyne-1,4-diacrylate, 83c.

In 125 mL of methylene chloride was stirred $5.0 \mathrm{~g}(58.1 \mathrm{mmol})$ of butyne-1,4-diol ( $\mathbf{8 2 c}$ ).
To the mixture was added a catalytic amount of DMAP and $28 \mathrm{~mL}(175 \mathrm{mmol})$ triethylamine. The mixture was cooled to $0^{\circ} \mathrm{C}$ and $9.9 \mathrm{~mL}(122 \mathrm{mmol})$ of acryloyl chloride was added dropwise. The reaction mixture was then refluxed for a 14 h period before being washed with 1.0 M HCl . The organic phase was dried over $\mathrm{MgSO}_{4}$, filtered and evaporated. The resulting liquid was placed atop a silica column and was eluted with a 9:1 mixture of petroleum ether/ethyl acetate. Evaporation of eluant resulted in an orange liquid which was stored at $-10^{\circ} \mathrm{C}$. bp $118-119{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) 4.73(4 \mathrm{H}, \mathrm{s}), 5.81(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=10 \mathrm{~Hz}), 6.06(2 \mathrm{H}, \mathrm{dd}, \mathrm{J}=10,17$ $\mathrm{Hz}), 6.38(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=17 \mathrm{~Hz}),{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) 51.84,80.63,127.44,131.54$, 164.78; IR (neat) 2920, 1733, 1635, 1408, 1296, 1258, 1173, 1050, 982, $809 \mathrm{~cm}-1$; MS (ESI/EI) $\mathrm{m} / \mathrm{e}$ calc'd for $\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{O}_{4}: 194.0579$, found 194.0572;

Anal. Calc. for $\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{O}_{4}$ : C, 61.85; H, 5.19. Found: C, 62.07; H, 4.95 .
4.5.3.4 4,14:7,11-Diepoxy-4,7,11,14-tetrakis(t-butyldimethylsilyl)-2,9-propanonaphtho[1,2-f:5,6-f']diisoindole-1,3,8,10-tetrone, 3a,4,7,7a,10a,11,14,14a-octahydro(2R,3aR,4S,7R,7aS,9R,10aR,11S,14R,14aS)-rel- (9CI), 77c.

To 50 mL of chloroform was added $103 \mathrm{mg}(0.155 \mathrm{mmol})$ of difuran $\mathbf{2 5 c}$ and 37 mg $(0.158 \mathrm{mmol})$ of maleimide tether. This mixture was stirred for 30 minutes before the solvent was removed. The crude product was placed atop a column of silica and was eluted with $80 \%$ ethyl acetate in chloroform. The collected product was recrystallized from a $3: 1$ mixture of ethyl acetate and chloroform to give 98 mg of white crystals (yield $=70 \%$ ) $\mathrm{mp} 164.5-166.3^{\circ} \mathrm{C} ; 1 \mathrm{H}$

NMR (300 MHZ, CDCl3) $\delta(\mathrm{ppm})-1.49(2 \mathrm{H}, \mathrm{p}, \mathrm{J}=4.2 \mathrm{~Hz}), 0.432,(6 \mathrm{H}, \mathrm{s}), 0.464(6 \mathrm{H}, \mathrm{s}), 0.489$ $(6 \mathrm{H}, \mathrm{s}), 0.654(6 \mathrm{H}, \mathrm{s}), 0.810(18 \mathrm{H}, \mathrm{s}), 1.029(18 \mathrm{H}, \mathrm{s}), 2.52(2 \mathrm{H}, \mathrm{m}), 2.72(2 \mathrm{H}, \mathrm{m}), 3.63(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=$ $7.5 \mathrm{~Hz}), 3.74(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=7.5 \mathrm{~Hz}), 7.38(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8.4 \mathrm{~Hz}), 7.74(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8.4 \mathrm{~Hz}) ; 13 \mathrm{C}$ NMR (75 MHz, CDCl3), $\delta(\mathrm{ppm})-6.4,-6.2,-5.5,-4.4,18.1,18.4,25.7,25.9,27.5,34.4,50.7,53.4$, 86.0, 87.9, 119.7, 126.1, 128.5, 143.1, 144.5, 173.5, 173.6; IR (crystalline) 2857, 1700, 1390, 1250, 1219, 1124, 985, 822, 771, 672, 653, 583, 548, $416 \mathrm{~cm}-1$; MS (ESI) m/e calc'd for $\mathrm{C}_{49} \mathrm{H}_{74} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Si}_{4}: 898.4619$, found 898.4627; 899.5 (M+, 19), 665.4 (42), 257.1 (100);

Anal. Calc. for $\mathrm{C}_{49} \mathrm{H}_{74} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Si}_{4}$ : C, 65.44; H, 8.29; N, 3.11. Found: 65.65; H, 8.45; N, 2.95 .
4.5.3.5 $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy- $1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,9)chrysena- 3,7-dioxa-2,8diona cyclooctaphane, 84.
Acetal precursor ( $100 \mathrm{mg}, 4.2 \mathrm{mmol}$ ) was dissolved in 30 mL of dry diethyl ether and cooled to $0^{\circ} \mathrm{C}$ under nitrogen. Excess LDA ( $2.0 \mathrm{~mL}, 2.0 \mathrm{M}$ ) was added via syringe and the mixture was stirred for 30 min . The reaction was quenched with water and extracted several times with ether. The combined extracts were washed once with brine, dried with $\mathrm{MgSO}_{4}$, and filtered. Meanwhile, 91 mg ( 0.49 mmol ) of 83a was dissolved in 50 mL of chloroform. The two solutions, ether and chloroform, were added dropwise over 3 h to a flask containing 500 mL of refluxing chloroform. This mixture was refluxed overnight before removing the solvent by evaporation. The resulting crude product was placed on top of a column of silica and eluted with a 1:9 ethyl acetate/hexanes mixture. The product was recrystallized from a mixture of chloroform and ethyl acetate to give 14 mg of white crystals (yield $=8.5 \%) \mathrm{mp} 400{ }^{\circ} \mathrm{C}(\mathrm{dec}) ;{ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 1.18(2 \mathrm{H}, \mathrm{m}), 1.63(2 \mathrm{H}, \mathrm{dd}, \mathrm{J}=3.9,12 \mathrm{~Hz}), 2.32(2 \mathrm{H}, \mathrm{m}), 2.44(2 \mathrm{H}, \mathrm{m})$, $3.54(4 \mathrm{H}, \mathrm{m}), 5.69(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 6.18(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 7.55(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.75(2 \mathrm{H}, \mathrm{d}, \mathrm{J}$ $=8 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) 28.4,31.3,45.7,51.9,80.2,81.0,119.5,125.1$, 127.1, 139.9, 143.8, 171.8; IR (crystalline) 2960, 1714, 1252, 1043, 802, 775, $540 \mathrm{~cm}-1$; MS (EI)
$\mathrm{m} / \mathrm{e}$ calc'd for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{O}_{6}: 392.1256$, found 392.1260; $393\left(\mathrm{M}^{+1}, 13\right)$, $392\left(\mathrm{M}^{+}, 45\right)$, $209(46), 208$ (100), 152 (9), 55 (25);

Anal. Calc. for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{O}_{6}$ : C, 70.40; H, 5.14. Found: C, 70.16, H, 5.23.

### 4.5.3.6 $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy- $1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,9)chrysena- 3,8-dioxa-2,9diona cyclononaphane, 85.

Acetal precursor ( $100 \mathrm{mg}, 0.42 \mathrm{mmol}$ ) was dissolved in 30 mL of dry diethyl ether and cooled to $0^{\circ} \mathrm{C}$ under nitrogen. Excess LDA ( 2.0 mL of a 2.0 M solution) was added via syringe and the mixture was stirred for 30 min . The reaction was quenched with water and extracted several times with ether. The combined extracts were washed once with brine, dried with $\mathrm{MgSO}_{4}$, and filtered. Meanwhile, $91 \mathrm{mg}(0.46 \mathrm{mmol})$ of $\mathbf{8 3 b}$ was dissolved in 50 mL of chloroform. The two solutions, ether and chloroform, were added dropwise over 3 h to a flask containing 500 mL of refluxing chloroform. This mixture was refluxed overnight before removing the solvent by evaporation. The resulting crude product was placed on top of a column of silica and eluted with a 2:1 chloroform/ethyl acetate mixture. The product was slurried in ethyl acetate and filtered to give 41 mg of white powder as a mixture of of isomers (yield $=25 \%$ ) mp $160{ }^{\circ} \mathrm{C}(\mathrm{dec}) ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) \mathbf{8 5 a} 0.27(4 \mathrm{H}, \mathrm{m}), 1.86(2 \mathrm{H}, \mathrm{dd}, \mathrm{J}=5,12 \mathrm{~Hz})$, $2.48(2 \mathrm{H}, \mathrm{ddd}, \mathrm{J}=5,5,12 \mathrm{~Hz}), 3.31(2 \mathrm{H}, \mathrm{m}), 3.59(2 \mathrm{H}, \mathrm{m}), 4.18(2 \mathrm{H}, \mathrm{m}), 5.64,(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz})$, $6.13(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 7.57(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.86(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}) ; \mathbf{8 5 b} 0.08(2 \mathrm{H}, \mathrm{m}), 1.04(2 \mathrm{H}$, m), $1.14(2 \mathrm{H}, \mathrm{m}), 1.83(2 \mathrm{H}, \mathrm{m}), 2.43(2 \mathrm{H}, \mathrm{m}), 3.29(1 \mathrm{H}, \mathrm{m}), 3.55(4 \mathrm{H}, \mathrm{m}), 3.84(1 \mathrm{H}, \mathrm{m}), 5.66$ $(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 5.80(1 \mathrm{H}, \mathrm{J}=5 \mathrm{~Hz}), 5.99(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 6.12(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 7.46(1 \mathrm{H}, \mathrm{d}$, $\mathrm{J}=8 \mathrm{~Hz}), 7.58(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.72(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.81(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR $(75$ $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) \mathbf{8 5 b} 23.2,23.5,29.7,30.9,45.0,46.3,63.6,64.3,79.1,79.8,80.9,81.5$, 118.4, 119.9, 123.38, 123.41, 139.1, 139.5, 143.4, 143.6, 170.6, 170.8; IR (crystalline) 1707, 1263, 1205, 1165, 1051, 1032, 1014, 876, 855, 808, 798, $777 \mathrm{~cm}-1$; MS (ESI) m/e calc'd for $\mathrm{C}_{24} \mathrm{H}_{22} \mathrm{O}_{6}: 406.1410$, found 406.1410
$1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy- $1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,9)chrysena- 3,8 -dioxa- 2,9 diona cyclonona-5-yn-phane, 86.

Acetal precursor ( $100 \mathrm{mg}, 0.42 \mathrm{mmol}$ ) was dissolved in 50 mL of dry diethyl ether and cooled to $0^{\circ} \mathrm{C}$ under nitrogen. Excess LDA ( $1.8 \mathrm{~mL}, 2.0 \mathrm{M}$ ) was added via syringe and the mixture was stirred for 30 min . The reaction was quenched with water and extracted several times with ether. The combined extracts were washed once with brine, dried with $\mathrm{MgSO}_{4}$, and filtered. Meanwhile, $81 \mathrm{mg}(0.42 \mathrm{mmol})$ of $\mathbf{8 3 c}$ was dissolved in 50 mL of chloroform. The two solutions, ether and chloroform, were added drop wise over 3 h to a flask containing 500 mL of refluxing chloroform. This mixture was refluxed overnight before removing the solvent by evaporation. The resulting crude product was placed on top of a column of silica and eluted with a 2:1 chloroform/ethyl acetate mixture. The product was slurried in ethyl acetate mixture to give 35 mg of white powder (yield $=21 \%) \mathrm{mp} 250{ }^{\circ} \mathrm{C}(\mathrm{dec}) ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 86 \mathbf{a}$ $1.93(2 \mathrm{H}, \mathrm{dd}, \mathrm{J}=3,11 \mathrm{~Hz}), 2.39(2 \mathrm{H}, \mathrm{m}), 3.52(2 \mathrm{H}, \mathrm{m}), 3.95(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=15 \mathrm{~Hz}), 4.41,(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=$ $15 \mathrm{~Hz}), 5.52(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 6.01(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 7.51(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8 \mathrm{~Hz}), 7.81(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=8$ Hz); 86b $1.82(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=3.6,12 \mathrm{~Hz}), 1.92(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=4.2,12 \mathrm{~Hz}), 2.47(2 \mathrm{H}, \mathrm{m}), 3.55(2 \mathrm{H}, \mathrm{m})$, $3.98(1 \mathrm{H}, \mathrm{dt}, \mathrm{J}=2.5$ and 15 Hz$), 4.39(1 \mathrm{H}, \mathrm{dt}, \mathrm{J}=2.5$ and 15 Hz$), 4.66(1 \mathrm{H}, \mathrm{dt}, \mathrm{J}=2.5$ and 15 $\mathrm{Hz}), 4.73(1 \mathrm{H}, \mathrm{dt}, \mathrm{J}=2.5$ and 15 Hz$), 5.61(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=4.8 \mathrm{~Hz}), 5.78(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5.1 \mathrm{~Hz}), 5.97(1 \mathrm{H}$, $\mathrm{d}, \mathrm{J}=5.1 \mathrm{~Hz}), 6.11(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5.1), 7.49(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8.4 \mathrm{~Hz}), 7.54(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8.1 \mathrm{~Hz}), 7.77(1 \mathrm{H}$, d, $\mathrm{J}=8.1 \mathrm{~Hz}), 7.84(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8.1 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta(\mathrm{ppm}) \mathbf{8 6 b} 30.2,30.5$, $44.7,46.3,51.3,52.4,78.5,78.8,78.8,79.1,80.6,81.2,118.3,120.2,123.6,124.0,125.0,126.7$, 139.1, 139.3, 142.3, 143.7, 169.9, 170.2; IR (crystalline) 1721, 1428, 1375, 1263, 1236, 1150, 1024, 976, 899, 868, 844, 810, 730, 595, 547, 489, $436 \mathrm{~cm}-1$; MS (EI) m/e calc'd for $\mathrm{C}_{24} \mathrm{H}_{18} \mathrm{O}_{6}$ : 402.38, found 402.1101; $402.1103\left(\mathrm{M}^{+}, 15\right), 209(26), 208$ (100), 152 (12), 55 (37)

## 5 Progress Towards the Synthesis of Anthra[1,2-c:7,8-c]difuran

### 5.1 Cyclophanes with Anthracene Subunits

Miller ${ }^{130}$ synthesized a bis(dienophile) (98) with an anthracene subunit during his investigations into polyacenes (Figure 5-1). Subsequently Mathewson ${ }^{131}$ used a similar compound coupled with a bis(diene) in attempt to generate an aromatic belt precursor. Unfortunately he was unable to form the intended adduct although the particular diene/dienophile combination that was used may not have been optimal for cyclophane formation. Other cyclophanes containing anthracene subunits have been synthesized by Masci ${ }^{132}$, but are structurally unrelated therefore will not be discussed here.


Figure 5-1. Bis(dienophile) synthesized by Miller

### 5.2 Synthesis of Anthra[1,2-c:7,8-c]difuran

At present most of the bis(IBF)s that have been synthesized in the Dibble research group (26-29) have possessed a $C_{2}$ axis of symmetry perpendicular to the aromatic plane. As a result this property will be inherent to any cyclophane that is made from these molecules. For this reason we chose to explore the synthesis of a bis(IBF) based on anthracene which does not have this type of symmetry. Anthra[1,2-c:7,8-c]difuran (30) fits this description as it has a $\mathrm{C}_{2}$ axis parallel to the aromatic plane, but not perpendicular to it. It has two furan moieties and can therefore undergo two Diels-Alder cycloadditions. The reaction of the first furan moiety has a
$\mathrm{SC}_{\text {ratio }}$ of 2.5 while we would expect the second furan moiety to experience a slight decrease in reactivity with a $\mathrm{SC}_{\text {ratio }}$ of 2.33 . This drop in $\mathrm{SC}_{\text {ratio }}$ is seen in other bis(IBF)s connected through an aromatic system ( $\mathbf{2 5}$ and $\mathbf{2 9}$ ) and does not seem to significantly hamper cyclophane formation.

65\%
99



30


102


Scheme 5-1

The synthesis towards $\mathbf{3 0}$ first required the synthesis of 1,8-dibromoanthracene (101). Commercially available 1,8 -dichloroanthraquinone was brominated under the relatively harsh conditions described by Virgili ${ }^{133}$ (Scheme 5-1, steps 1-3). A significant amount of side product was isolated during this reaction as a thick dark paste bound to the surface of the flask. This side product was insoluble in most solvents and only by soaking in concentrated sulfuric acid could the flask be recovered. The reduction of $\mathbf{9 9}$ proved to be difficult as the procedure described by Virgili involved a two step reduction with poor yields. Attempts to reduce both ketone moieties at once using aqueous ammonia as described for the reduction of 1,8 -dichloroantraquinone by House ${ }^{134}$ (Scheme 5-2) resulted in loss of the bromine atoms and the isolation of anthracene.


Scheme 5-2

The reduction was instead done using two steps as in Scheme 5-1, but the yields described by Virgili were increased by using longer reaction times and warmer conditions. Once 101 was synthesized it could be converted into the diepoxide (102) by generating the corresponding aryne (103) as a hypothetical intermediate and reacting it with furan.


Scheme 5-3

A poor yield (17\%) was obtained of $\mathbf{1 0 2}$ and it was found difficult to purify. Avoiding this purification step, crude $\mathbf{1 0 2}$ was reacted with dipytet which resulted in the formation of $\mathbf{3 0}$ as seen by ${ }^{1} \mathrm{H}$ NMR spectroscopy. Addition of NMM to the crude mixture resulted in the immediate formation of adduct peaks associated with $\mathbf{1 0 4}$ suggesting that the furan moieties are quite reactive.


## Scheme 5-4

An advantage of using a synthetic scheme that proceeds through a diepoxide such as $\mathbf{1 0 2}$ is the unique opportunity to create a bis(dienophile). Treatment of crude $\mathbf{1 0 2}$ with acid aromatized the terminal rings to generate the dihydroxybenzo[m]tetraphene (105). This is as far as this synthesis has been performed to date. However, $\mathbf{1 0 5}$ can in principle be converted to the bis(quinone) (106), which could then react with a bis(IBF). The full potential of this synthetic route will be discussed in more detail in Section 5.3.


Scheme 5-5

### 5.3 Future Directions: Macromolecular Structures from Anthra[1,2-c:7,8-c]difuran

As alluded to in the previous section there is more work to be done regarding the anthra[1,2-c:7,8-c]difuran project. Aside from the synthesis, purification, and characterization of $\mathbf{3 0}, \mathbf{1 0 2}, 105$, and 106, potential exists for the synthesis of a peculiar aromatic belt. Reaction of $\mathbf{3 0}$ and $\mathbf{1 0 6}$ will result in the formation of the adduct 107. The oxa-bicyclo and quinone rings could potentially be aromatized to form a non-traditional aromatic belt (108). While upon initial inspection one might expect this compound to be planar this is not the case. In fact it is
sufficiently strained that the compound adopts a bowl type conformation as predicted by AM1 modeling (Scheme 5-6).


30
$+$


106



108

## Scheme 5-6

If $\mathbf{1 0 8}$ can be formed there is potential for even further investigation of this system.
Rather than reducing 100 to 101 a protected alcohol derivative could be formed instead (109). This functionalized dibromoanthracene could be carried through the synthetic steps as in Scheme 5-1, Scheme 5-5, and Scheme 5-6 until a functionalized belt (110) is formed. What is exciting about having functionalized belts is they could potentially be connected through the alcohols to form a molecular capsule (111) as shown in Scheme 5-7. This molecule has a large cavity which could be used to host a variety of molecules.


Scheme 5-7

### 5.4 Summary

Preliminary results towards the synthesis anthra[1,2-c:7,8-c]difuran (30) have been discussed. There are five synthetic steps from commercially available starting material to obtain 30, however some of these steps are hampered by low yields. A similar synthesis can be used to make the bis(dienophile) 106. Coupling of this compound with $\mathbf{3 0}$ would generate a cyclophane adduct which could be aromatized to a aromatic belt. If this compound can be synthesized successfully a functionalized derivative of $\mathbf{3 0}$ might be made as well (109). The aromatic belt made from this compound (110) will have substituents which could be used to connect two belt units together and generate a molecular capsule (111).

### 5.4.1 Experimental Details

Experimental procedure for $\mathbf{9 9}$ and characterization data for $\mathbf{1 0 0}$ and $\mathbf{1 0 1}$ has previously been published ${ }^{133}$ and will not be presented here.

### 5.4.1.1 1,8-Dibromoanthrone, 100

In 125 mL of methanol was stirred $12 \mathrm{~g}(32.8 \mathrm{mmol})$ of 1,8 -dibromoanthraquinone (99).
To this was added $9.0 \mathrm{~g}(240 \mathrm{mmol})$ of $\mathrm{NaBH}_{4}$ over 30 min . This mixture was stirred for 24 h before the addition of 30 mL of concentrated HCl . This solution was refluxed for 16 h before cooling. The yellow precipitate was filtered off which proved to be $9: 1$ mixture of starting material and $\mathbf{1 0 0}$ which was not purified further. After drying, $8.2 \mathrm{~g}(23 \mathrm{mmol})$ of yellow solid was collected (crude yield $=65 \%$ ).

### 5.4.1.2 1,8-Dibromoanthracene, 101

In 200 mL of dimethoxyethane was stirred $15 \mathrm{~g}(42.6 \mathrm{mmol})$ of a $9: 1$ mixture of $1,8-$ dibromoanthrone (99) and 1,8-dibromoanthraquinone (100). This solution was flushed with $\mathrm{N}_{2}$ for 15 min before the addition of $5 \mathrm{~g}(132 \mathrm{mmol})$ of $\mathrm{NaBH}_{4}$. The solution was stirred for 3 h during which it turned a bright orange color. An additional $2 \mathrm{~g}(52.9 \mathrm{mmol})$ of $\mathrm{NaBH}_{4}$ and 75 mL of methanol were added to the solution which was stirred for 24 h . The reaction was then quenched with 10 mL of glacial acetic acid followed by 10 mL of concentrated HCl . The resulting yellow solution was stirred for 3 h before removal of the solvent and the yellow precipitate filtered off. After drying $10.6 \mathrm{~g}(31.5 \mathrm{mmol})$ of $\mathbf{1 0 1}$ was obtained (yield $=74 \%$ ).

### 5.4.1.3 1,4,10,13-Diepoxy-1,4,10,13-tetrahydrobenzo[m]tetraphene, 102

In 100 mL of dry THF was stirred $5 \mathrm{~g}(128 \mathrm{mmol})$ of $\mathrm{NaNH}_{2}$ under $\mathrm{N}_{2}$. To this was slowly added 5 mL of dry tert-butanol over 30 min and this suspension was stirred an additional 1 h. Meanwhile a solution of $1.8 \mathrm{~g}(5.4 \mathrm{mmol})$ of 1,8 -dibromoanthracene $(\mathbf{1 0 1}), 5 \mathrm{~mL}$ of furan and a minimal amount of dry THF, (enough to dissolve the dibromide) was made. This solution was slowly added to first solution and the resulting mixture stirred for 1 h during which it turned
black. The reaction was quenched with 100 mL of water and extracted with chloroform. The crude material was placed atop a column of silica and eluted with a 4:1 mixture of ethyl acetate in hexanes. A dark solid was obtained which was found to be $0.29 \mathrm{~g}(0.94 \mathrm{mmol})$ of $\mathbf{1 0 2}$ as a mixture of syn and anti products (yield $=17 \%) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(250 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 6.01(1 \mathrm{H}$, s), $6.47(1 \mathrm{H}, \mathrm{s}), 7.31(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 7.36(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=5 \mathrm{~Hz}), 7.59(2 \mathrm{H}, \mathrm{d}, \mathrm{J}=9 \mathrm{~Hz}), 7.79(2 \mathrm{H}, \mathrm{d}$, $\mathrm{J}=9 \mathrm{~Hz}), 8.30(1 \mathrm{H}, \mathrm{s}), 8.54(1 \mathrm{H}, \mathrm{s})$

### 5.4.1.4 Anthra[1,2-c:7,8-c]difuran, 30

In 50 mL of chloroform was stirred $200 \mathrm{mg}(0.65 \mathrm{mmol})$ of $\mathbf{1 0 2}$. To this was added 310 $\mathrm{mg}(1.30 \mathrm{mmol})$ of dipytet and the mixture was stirred 2 h . The solvent was evaporated and the crude material placed atop a column of silica. Elution with methylene chloride resulted in collection of a yellow solid with evidence of the difuran in its ${ }^{1} \mathrm{H}$ NMR spectrum. Addition of NMM to the reaction mixture showed adduct formation and several peaks were identified as being associate with $\mathbf{3 0}$.

### 5.4.1.5 Dihydroxybenzo[m]tetraphene, 105

In 50 mL of methanol was stirred $100 \mathrm{mg}(0.32 \mathrm{mmol})$ of $\mathbf{1 0 2}$. To this was added 20 mL of concentrated HCl and the mixture was stirred for 6 h . The organic solvent was evaporated and the black solid filtered off which had a ${ }^{1} \mathrm{H}$ NMR spectrum suggesting that $\mathbf{1 0 5}$ had been formed.

## References

(1) Rickborn, B. In Advances in Theoretically Interesting Molecules; Thummel, R. P., Ed.; J.A.I. Press: Greenwich, CT, 1989; Vol. 1, p 1-134.
(2) Friedrichsen, W. In In Houben-Weyl, Methoden der Organtschen Chemie; Kreher, R., Ed.; Thieme Verlag: Stuttgart, Germany, 1994; Vol. E6b, p 163-216.
(3) Wege, D. In Advances in Theoretically Interesting Molecules; Thummel, R. P., Ed.; J. A. I. Press: Greenwich, CT, 1998; Vol. 4, p 1-52.
(4) Friedrichsen, W. In Adv. in Heterocycl. Chem.; Katritzky, A. R., Ed.; Academic Press: London, UK, 1999; Vol. 73, p 1-96.
(5) Friedrichsen, W. In Adv. Heterocycl. Chem.; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: London, UK, 1980; Vol. 26, p 135.
(6) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. J. Am. Chem. Soc. 1996, 118, 6317-6318.
(7) Tobia, D.; Rickborn, B. J. Org. Chem. 1987, 52, 2611-2615.
(8) Moursounidis, J.; Wege, D. Aust. J. Chem. 1988, 41, 235-49.
(9) Watson, K. A.; Bass, R. G. High Perform. Polym. 2000, 12, 299-314.
(10) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T. J. Am. Chem. Soc. 1993, 115, 1594-1595.
(11) Chuang, S.; Sander, M.; Jarrosson, T.; James, S.; Rozumov, E.; Khan, S. I.; Rubin, Y. J. Org. Chem. 2007, 72, 2716-2723.
(12) Sander, M.; Jarrosson, T.; Chuang, S. C.; Khan, S. I.; Rubin, Y. J. Org. Chem. 2007, 72, 2724-2731.
(13) Thibault, M. E.; Pacarynuk, L. A.; Closson, T. L. L.; Dibble, P. W. Tetrahedron Lett. 2001, 42, 789-791.
(14) Kekulé, A. Bull. Soc. Chim. Fr. 1865, 3, 98.
(15) De Proft, F.; Geerlings, P. Chem. Rev. 2001, 101, 1451-1464.
(16) Gomes, J. A. N. F.; Mallion, R. B. Chem. Rev. 2001, 101, 1349-1384.
(17) Streitwieser, A. Molecular Orbital Theory for Organic Chemists; Wiley: New York, 1961.
(18) Palmer, M. H.; Kennedy, S. M. F. J. Chem. Soc., Perkin Trans. 2 1974, 15, 19721999.
(19) Palmer, M. H.; Kennedy, S. M. F. J. Chem. Soc., Perkin Trans. 2 1976, 81-89.
(20) Dewar, M. J. S.; De Llano, C. J. Am. Chem. Soc. 1969, 91, 789-795.
(21) Dewar, M. J. S.; Gleicher, G. J. J. Am. Chem. Soc. 1965, 87, 685-692.
(22) Dewar, J. S.; Harget, A. J.; Trinajstic, N.; Worley, S. D. Tetrahedron 1970, 26, 4505-4516.
(23) Hess, B. A.; Schaad, L. J. J. Am. Chem. Soc. 1971, 93, 305-310.
(24) Hess, B. A.; Schaad, L. J.; Holyoke, C. W. Tetrahedron 1972, 28, 3657-3667.
(25) Gutman, I.; Milun, M.; Trinajstić, N. J. Am. Chem. Soc. 1977, 99, 1692-1704.
(26) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Golduss, B. Angew. Chem. Int. Ed. Eng. 1995, 34, 337-340.
(27) Jursic, B. S. J. Heterocyclic Chem. 1996, 33, 1079-1081.
(28) Chacko, E.; Bornstein, J.; Sardella, D. J. J. Am. Chem. Soc. 1977, 99, 8248-8251.
(29) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. Angew. Chem. Int. Ed. Eng. 1996, 35, 2638-2641.
(30) Martínez, A.; Vázquez, M.-V.; Carreón-Macedo, J. L.; Sansores, L. E.; Salcedo, R. Tetrahedron 2003, 59, 6415-6422.
(31) Wege, D. Tetrahedron Lett. 1971, 25, 2337-2338.
(32) McCulloch, R.; Rye, A. R.; Wege, D. Tetrahedron Lett. 1969, 60, 5231-5234.
(33) Schleyer, P. v. R.; Pühlhofer, F. Org. Lett. 2002, 4, 2873-2876.
(34) Cyrañski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. J. Org. Chem. 2002, 67, 1333-1338.

Krygowski, T. M.; Cyrañski, M. K. Chem. Rev. 2001, 101, 1385-1420.
Kruszewski, J.; Krygowski, T. M. Tetrahedron Lett. 1972, 36, 3839-3842

Krygowski, T. M. J. Chem. Inf. Comput. Sci. 1993, 33, 70-78.
Herndon, W. C. J. Chem. Educ. 1974, 58, 10-15.
Herndon, W. C. J. Org. Chem. 1975, 40, 3583-3586.
(40) Fieser, L. F.; Haddadin, M. J. J. Am. Chem. Soc. 1964, 86, 2081-2082.
(41) Wittig, G.; Harle, H. Ann. 1959, 623, 17-34.
(42) Warrener, R. N. J. Am. Chem. Soc. 1971, 93, 2346-2348.
(43) Wiersum, U. E.; Mijs, W. J. J. Chem. Soc., Chem. Commun. 1972, 347-348.
(44) Smith, J. G.; Dibble, P. W. J. Org. Chem. 1983, 48, 5361-5362.
(45) McCormick, J. P.; Shinmyozu, T. J. Org. Chem. 1982, 47, 4011-4012.
(46) Naito, K.; Rickborn, B. J. Org. Chem. 1980, 45, 4061-4062.
(47) Mikami, K.; Ohmura, H. Organic Letters 2002, 4, 3355-3357.
(48) Stringer, M. B.; Wege, D. Tetrahedron Lett. 1980, 21, 3831-3834.
(49) Fischer, K. E., University of Lethbridge, 2005.
(50) Thibault, M. E., University of Lethbridge, 2004.
(51) Smith, J. G.; Dibble, P. W.; Sandborn, R. E. J. Org. Chem. 1986, 51, 3762-3768.
(52) Thibault, M. E.; Closson, T. L. L.; Manning, S. C.; Dibble, P. W. J. Org. Chem. 2003, 68, 8373-8378.
(53) Boeré, R. T.; Robbins, S. J. Acta Cryst. 2008, E64, o363.
(54) Yu, D. W.; Preuss, K. E.; Cassis, P. R.; Dontem Dejikhangsar, T.; Dibble, P. W. Tetrahedron Lett. 1996, 37, 8845-8848.
(55) Rodrigo, R.; Knabe, S. M.; Taylor, N. J.; Rajapaksa, D.; Chernishenko, M. J. J. Org. Chem. 1986, 51, 3973-3978.
(56) Lu, J.; Ho, D. M.; Vogelaar, N. J.; Kraml, C. M.; Bernhard, S.; Byrne, N.; Kim, L. R.; Pascal, R. A. J. Am. Chem. Soc. 2006, 128, 17043-17050.
(57) Boeré, R. T.; Dibble, P. W.; Fischer, K. E. Acta Cryst. 2008, E64, o686.
(58) Lynch, V. M.; Fairhurst, R. A.; Magnus, P.; Davis, B. E. Acta Cryst. 1995, C51, 780-782.
(59) Egorochkin, A. N.; Vyazankin, N. S.; Skobeleva, S. E.; Khorshchev, S. Y.; Chernyshev, E. A.; Savushkina, V. I.; Kuz'min, O. V. Chem. of Heterocyclic Compounds 1972, 8, 956-958.
(60) Lukevits, E.; Demicheva, L. E.; Popelis, Y. Y. Chem. of Heterocyclic Compounds 2005, 32, 387-395.
(61) HyperChem (2005), HyperChem Release 7.52, Hypercube, Inc.
(62) Gaussian 03 Revision D.01, F., M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
(63) Sousa, S. F.; Fernandes, P. A.; Ramos, M. J. J. Phys. Chem. A 2007, 111, 1043910452.
(64) Merrick, J. P.; Moran, D.; Radom, L. J. Phys. Chem. A 2007, 111, 11683-11700.
(65) GaussView Version 4.1.2, D. I., Roy; Keith, Todd; and Millam, John; Semichem, Inc., Shawnee Mission, KS, 2007.
(66) Bruker (2006). APEX2 and SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
(67) Sheldrick, G. M. (2004). SADABS. University of Göttingen, Germany.
(68) Sheldrick, G. M. (2003). SHELXTL, Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
(70) Broom, N. J. P.; Sammes, P. G. J. Chem. Soc., Chem. Commun. 1978, 4, 162164.
(71) Contreras, L.; Slemon, C. E.; MacLean, D. B. Tetrahedron Lett. 1978, 44, 42374240.
(72) Makhlouf, M.; Rickborn, B. J. Org. Chem. 1981, 46, 5460-5460.
(73) Chen, C. W.; Beak, P. J. Org. Chem. 1986, 51, 3325-3334.
(74) Padwa, A.; Eidell, C. ARKIVOC 2003, 14, 62-76.
(75) Russell, R. A.; Marsden, D. E.; Sterns, M.; Warrener, R. N. Aust. J. Chem. 1981, 34, 1223-1234.
(76) Smith, J. G.; Welankiwar, S. S.; Shantz, B. S.; Lai, E. H.; Chu, N. G. J. Org. Chem. 1980, 45, 1817-1824.
(77) Heaney, H.; Ley, S. V.; Price, A. P.; Sharma, R. P. Tetrahedron Lett. 1972, 30, 3067.
(78) Sustmann, R.; Schubert, R. Angew. Chem. Int. Ed. Eng. 1972, 11, 840.
(79) Ess, D. H.; Jones, G. O.; Houk, K. N. Adv. Synth. Catal. 2006, 348, 2337-2361.
(80) Domingo, L. R.; Chamorro, E.; Pérez, P. J. Phys.Chem. A 2008, 112, 4046-4053.
(81) Margetic, D.; Warrener, R. N.; Dibble, P. W. J. Mol. Model 2004, 10, 87-93.
(82) Young, R. H.; Feriozi, D. T. J. Chem. Soc., Chem. Commun. 1972, 841-842.
(83) Bean, G. P. J. Org. Chem. 1998, 63, 2497-2506.
(84) Zhou, Z.; Parr, R. G. J. Am. Chem. Soc. 1989, 111, 7371-7379.
(85) Pearson, R. G. J. Org. Chem. 1989, 54, 1423-1430.
(86) Laidler, K. J.; Meiser, J. H.; Sanctuary, B. C. Physical Chemistry; Houghton Mifflin Company: Boston, 2003.
(87) Barfield, M.; Spear, R. J.; Sternhell, S. J. Am. Chem. Soc. 1975, 97, 5160-5167.
(88) Martin, C.; Mailliet, P.; Maddaluno, J. J. Org. Chem. 2001, 66, 3797-3805.
(89) Smith, B. H. Bridged Aromatic Compounds; Academic Press: New York, 1964.
(90) Vögtle, F. Cyclophane Chemistry; John Wiley and Sons: Chichester, 1993.
(91) Tsuji, T. In Advances in Strained and Interesting Organic Molecules Halton, B., Ed., Eds.; JAI Press: Stamford, CT, 1999; Vol. 7, p 103-152.
(92) Keehn, P. M.; Rosenfeld, S. M. Cyclophanes; Academic Press: New York, 1983; Vol. 1.
(93) Keehn, P. M.; Rosenfeld, S. M. Cyclophanes; Academic Press: New York, 1983; Vol. 2.
(94) Gleiter, R.; Hopf, H.; Eds. Modern Cyclophane Chemistry; Wiley-VCH: Weinheim, 2004. Brown, C. J.; Farthing, A. C. Nature 1949, 164, 915-916. Smith, B. H.; Eds.; Academic Press: New York and London, 1964. Cram, D. J.; Cram, J. M. Acc. Chem. Res. 1971, 4, 204-213.
(98) Bodwell, G. J.; Bridson, J. N.; Cyrañski, M. K.; Kennedy, J. W. J.; Krygowski, T. M.; Mannion, M. R.; Miller, D. O. J. Org. Chem. 2003, 68, 2089-2098.
(99) Cram, D. J. Rec. of Chem. Prog. 1959, 20, 1959.
(100) Staab, H. A.; Krieger, C.; Wahl, P.; Kay, K., -Y Chem. Ber. 1987, 120, 551-558.
(101) Greiner, A. Trends Polym. Sci. 1997, 5, 12-16.
(102) Diederich, F.; Schürmann, G.; Chao, I. J. Org. Chem. 1988, 53, 2744-2757.
(103) Peterson, B. R.; Diederich, F. Angew. Chem. Int. Ed. Eng. 1994, 33, 1625-1628.
(104) Kawai, H.; Suzuki, T.; Ohkita, M.; Tsuji, T. Angew. Chem. Int. Ed. Eng. 1998, 37, 817-819.
(105) Tsuji, T.; Ohkita, M.; Nishida, S. J. Am. Chem. Soc. 1993, 115, 5284-5285.
(106) Sekine, Y.; Brown, M.; Boekelheide, V. J. Am. Chem. Soc. 1979, 101, 31263127.
(107) Kraakman, P. A.; Valk, J. M.; Niederlander, H. A. G.; Brouwer, D. B. E.; Bickelhaupt, F. M.; De Wolf, W. H.; Bickelhaupt, F.; Stam, C. H. J. Am. Chem. Soc. 1990, 112, 6638-6646.
(108) Crampton, M. R. Organic Reaction Mechanisms 2003, 275, 275.
(109) Haenel, M.; Staab, H. A. Tetrahedron Lett. 1970, 11, 3585-3588.
(110) Takeuchi, M.; Tuihiji, T.; Nishimura, J. J. Org. Chem. 1993, 58, 7388-7392.
(111) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J.; Mannion, M. R. Chem. Eur. J. 1999, 5, 1823-1827.
(112) Bodwell, G. J.; Miller, D. O.; Vermeij, R. J. Organic Letters 2001, 3, 2093-2096.
(113) Zhang, B.; Manning, G. P.; Dobrowolski, M. A.; Cyrañski, M. K.; Bodwell, G. J. Organic Letters 2008, 10, 273-276.
(114) Dobrowolski, M. A.; Cyrañski, M. K.; Merner, B. L.; Bodwell, G. J.; Wu, J. I.; Schleyer, P. v. R. J. Org. Chem. 2008, 73, 8001-8009.
(115) Butler, D. N.; Shang, M.; Warrener, R. N. Tetrahedron Lett. 2000, 41, 59855989.
(116) Warrener, R. N.; Shang, M.; Butler, D. N. Chem. Commun. 2001, 1550-1551.
(117) Warrener, R. N.; Schultz, A. C.; Houghton, M. A.; Butler, D. N. Tetrahedron 1997, 53, 3991-4012.
(118) Butler, D. N.; Shang, M.; Warrener, R. N. Chem. Commun. 2001, 159-160.
(119) Ashton, P. T.; Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathais, J. P.; Raymo, F. M.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. J. Am. Chem. Soc. 1993, 115, 5422-5429.
(120) Klarner, R. G.; Benkhoff, J.; Boese, R.; Wigger, A. E. Tetrahedron Lett. 1994, 35, 73-76.
(121) Pollmann, M.; Müllen, K. J. Am. Chem. Soc. 1994, 116, 2318-2323.
(122) Habibi, D.; Marvi, O. ARKIVOC 2006, 13, 8-15.
(123) Loan, D. T. B.; Panayotov, I. M. Eur. Polym. J. 1996, 32, 977-962.
(124) Francois, H.; Henri, J. Comptes Rendus des Ceances de l'Academie des Sciences, Serie C Sciences Chimiques 1972, 274, 639-641.
(125) Tobia, D.; Harrison, R.; Phillips, B.; White, T. L.; DiMare, M.; Rickborn, B. J. Org. Chem. 1993, 58, 6701-6706.
(126) Thibault, M. E.; Parvez, M.; Dibble, P. W. Acta Cryst. 2008, E64, o1837.
(127) Tsuzuki, S.; Honda, K.; Fujii, A.; Uchimaru, T.; Mikami, M. Phys. Chem. Chem. Phys. 2008, 10, 2860-2865.
(128) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. J. Am. Chem. Soc. 2000, 122, 3746-3753.
(129) G.-P.Charbonneau, Y. D. Acta Cryst. 1977, 33.
(130) Thomas, A. D.; Miller, L. L. J. Org. Chem. 1986, 51, 4160-4169.
(131) Mathewson, D., University of Western Ontario, 2004.
(132) Masci, B.; Pasquale, S.; Thuéry, P. Organic Letters 2008, 10, 4835-4838.
(133) Pérez-Trujillo, M.; Maestre, I.; Jaime, C.; Alvarez-Larena, A.; Piniella, J. F.; Virgili, A. Tetrahedron: Asymmetry 2005, 16, 3084-3093.
(134) House, H. O.; Hrabie, J. A.; VanDerveer, D. J. Org. Chem. 1986, 51, 921-929.

## Appendix 1: Additional Crystallographic Details

Table A1- 1. Crystal data and structure refinement for 25c.

| Identification code | 25c |
| :---: | :---: |
| Empirical formula | C38 H64 O2 Si4 |
| Formula weight | 665.25 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=6.8355(5) \AA \quad \alpha=72.0720(10)^{\circ}$. |
|  | $b=11.3386(8) \AA \quad \beta=88.2660(10)^{\circ}$. |
|  | $\mathrm{c}=14.1413(10) \AA \quad \gamma=79.7590(10)^{\circ}$. |
| Volume | 1025.84(13) $\AA^{3}$ |
| Z | 1 |
| Density (calculated) | $1.077 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.174 \mathrm{~mm}^{-1}$ |
| F(000) | 364 |
| Crystal size | $0.22 \times 0.09 \times 0.04 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.92 to $25.03^{\circ}$. |
| Index ranges | $-8<=\mathrm{h}<=8,-13<=\mathrm{k}<=13,-16<=1<=16$ |
| Reflections collected | 9931 |
| Independent reflections | $3604[\mathrm{R}(\mathrm{int})=0.0300]$ |
| Completeness to theta $=25.03^{\circ}$ | 99.7 \% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9933 and 0.9626 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3604 / 0 / 209 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.024 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I}$ ] $]$ | $\mathrm{R} 1=0.0391, \mathrm{wR} 2=0.0893$ |
| R indices (all data) | $\mathrm{R} 1=0.0526, \mathrm{wR} 2=0.0960$ |
| Largest diff. peak and hole | 0.333 and -0.188 e. $A^{-3}$ |

Table A1- 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{2 5} \mathbf{c}$. $U(e q)$ is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

| Atom | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{Si}(1)$ | $3092(1)$ | $2178(1)$ | $2648(1)$ | $21(1)$ |
| $\mathrm{Si}(2)$ | $-446(1)$ | $6720(1)$ | $2919(1)$ | $21(1)$ |
| $\mathrm{C}(2)$ | $4236(3)$ | $3714(2)$ | $3890(1)$ | $20(1)$ |
| $\mathrm{O}(1)$ | $1512(2)$ | $4437(1)$ | $2936(1)$ | $23(1)$ |
| $\mathrm{C}(4)$ | $1594(3)$ | $5319(2)$ | $3423(1)$ | $21(1)$ |
| $\mathrm{C}(3)$ | $3285(3)$ | $4885(2)$ | $4035(1)$ | $19(1)$ |
| $\mathrm{C}(1)$ | $3105(3)$ | $3466(2)$ | $3217(1)$ | $21(1)$ |
| $\mathrm{C}(7)$ | $3957(3)$ | $6957(2)$ | $5582(1)$ | $24(1)$ |
| $\mathrm{C}(6)$ | $3196(3)$ | $6495(2)$ | $4933(1)$ | $24(1)$ |
| C(5) | $4124(3)$ | $5349(2)$ | $4746(1)$ | $19(1)$ |
| C(13) | $650(3)$ | $7956(2)$ | $1935(1)$ | $26(1)$ |
| C(14) | $2315(3)$ | $8374(2)$ | $2382(2)$ | $36(1)$ |
| C(11) | $-1645(3)$ | $7409(2)$ | $3878(2)$ | $31(1)$ |
| C(15) | $-972(3)$ | $9102(2)$ | $1485(2)$ | $38(1)$ |
| C(12) | $-2347(3)$ | $6126(2)$ | $2356(2)$ | $33(1)$ |
| C(16) | $1526(4)$ | $7423(2)$ | $1107(2)$ | $40(1)$ |
| C(21) | $5013(3)$ | $801(2)$ | $3295(2)$ | $33(1)$ |
| C(23) | $3600(3)$ | $2784(2)$ | $1279(1)$ | $27(1)$ |
| C(26) | $3728(4)$ | $1729(2)$ | $800(2)$ | $39(1)$ |
| C(24) | $1924(4)$ | $3854(2)$ | $754(2)$ | $42(1)$ |
| C(22) | $576(3)$ | $1748(2)$ | $2849(2)$ | $38(1)$ |
| C(25) | $5565(4)$ | $3273(2)$ | $1138(2)$ | $45(1)$ |

Table A1- 3. Bond lengths $[\AA \AA]$ and angles $\left[{ }^{\circ}\right]$ for 25 c.

| $\mathrm{Si}(1)-\mathrm{C}(22)$ | $1.859(2)$ | $\mathrm{C}(7)-\mathrm{H}(7)$ | 0.9500 |
| :--- | :--- | :--- | :--- |
| $\mathrm{Si}(1)-\mathrm{C}(21)$ | $1.861(2)$ | $\mathrm{C}(6)-\mathrm{C}(5)$ | $1.439(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(1)$ | $1.8722(19)$ | $\mathrm{C}(6)-\mathrm{H}(6)$ | 0.9500 |
| $\mathrm{Si}(1)-\mathrm{C}(23)$ | $1.889(2)$ | $\mathrm{C}(5)-\mathrm{C}(5)$ | $1.393(4)$ |
| $\mathrm{Si}(2)-\mathrm{C}(12)$ | $1.865(2)$ | $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.529(3)$ |
| $\mathrm{Si}(2)-\mathrm{C}(11)$ | $1.865(2)$ | $\mathrm{C}(13)-\mathrm{C}(15)$ | $1.531(3)$ |
| $\mathrm{Si}(2)-\mathrm{C}(4)$ | $1.8846(19)$ | $\mathrm{C}(13)-\mathrm{C}(16)$ | $1.535(3)$ |
| $\mathrm{Si}(2)-\mathrm{C}(13)$ | $1.890(2)$ | $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(2)-\mathrm{C}(1)$ | $1.368(3)$ | $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(2)-\mathrm{C}(7)$ | $1.426(3)$ | $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | $1.442(2)$ | $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9800 |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | $1.374(2)$ | $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~B})$ | 0.9800 |
| $\mathrm{O}(1)-\mathrm{C}(4)$ | $1.387(2)$ | $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(4)-\mathrm{C}(3)$ | $1.387(3)$ | $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(3)-\mathrm{C}(5)$ | $1.443(2)$ | $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{C}(6)$ | $1.345(3)$ | $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{C}(2)$ | $1.426(3)$ | $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9800 |


| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9800 | $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7)$ | 120.6 |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 0.9800 | $\mathrm{C}(2)-\mathrm{C}(7)-\mathrm{H}(7)$ | 120.6 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9800 | $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(5)$ | 122.92(17) |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9800 | $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{H}(6)$ | 118.5 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 0.9800 | $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{H}(6)$ | 118.5 |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 0.9800 | $\mathrm{C}(5)-\mathrm{C}(5)-\mathrm{C}(6)$ | 120.3(2) |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 0.9800 | $\mathrm{C}(5)-\mathrm{C}(5)-\mathrm{C}(3)$ | 118.0(2) |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 0.9800 | $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(3)$ | 121.63(16) |
| $\mathrm{C}(23)-\mathrm{C}(25)$ | $1.527(3)$ | $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(15)$ | 109.00(17) |
| $\mathrm{C}(23)-\mathrm{C}(24)$ | $1.529(3)$ | $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(16)$ | 108.18(18) |
| $\mathrm{C}(23)-\mathrm{C}(26)$ | $1.535(3)$ | $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(16)$ | 109.14(17) |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 0.9800 | $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{Si}(2)$ | 110.65(14) |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 0.9800 | $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{Si}(2)$ | 109.65(14) |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 0.9800 | $\mathrm{C}(16)-\mathrm{C}(13)-\mathrm{Si}(2)$ | 110.19(14) |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 0.9800 | $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~B})$ | 0.9800 | $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 0.9800 | $\mathrm{H}(14 \mathrm{~A})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 0.9800 | $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 0.9800 | $\mathrm{H}(14 \mathrm{~A})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 0.9800 | $\mathrm{H}(14 \mathrm{~B})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | 0.9800 | $\mathrm{Si}(2)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~B})$ | 0.9800 | $\mathrm{Si}(2)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 0.9800 | $\mathrm{H}(11 \mathrm{~A})-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~B})$ | 109.5 |
|  |  | $\mathrm{Si}(2)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(22)-\mathrm{Si}(1)-\mathrm{C}(21)$ | 110.01(10) | $\mathrm{H}(11 \mathrm{~A})-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(22)-\mathrm{Si}(1)-\mathrm{C}(1)$ | 106.36(9) | $\mathrm{H}(11 \mathrm{~B})-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(21)-\mathrm{Si}(1)-\mathrm{C}(1)$ | 109.08(9) | $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(22)-\mathrm{Si}(1)-\mathrm{C}(23)$ | 111.15(10) | $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(21)-\mathrm{Si}(1)-\mathrm{C}(23)$ | 111.12(10) | $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(23)$ | 108.98(9) | $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(12)-\mathrm{Si}(2)-\mathrm{C}(11)$ | 108.96(10) | $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(12)-\mathrm{Si}(2)-\mathrm{C}(4)$ | 105.32(9) | $\mathrm{H}(15 \mathrm{~B})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(11)-\mathrm{Si}(2)-\mathrm{C}(4)$ | 114.26(9) | $\mathrm{Si}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(12)-\mathrm{Si}(2)-\mathrm{C}(13)$ | 110.60(9) | $\mathrm{Si}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(11)-\mathrm{Si}(2)-\mathrm{C}(13)$ | 109.75(9) | $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(4)-\mathrm{Si}(2)-\mathrm{C}(13)$ | 107.85(9) | $\mathrm{Si}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(7)$ | 131.91(17) | $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 108.05(16) | $\mathrm{H}(12 \mathrm{~B})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)$ | 120.05(16) | $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{O}(1)-\mathrm{C}(4)$ | 110.69(14) | $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(1)-\mathrm{C}(4)-\mathrm{C}(3)$ | 106.83(15) | $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(1)-\mathrm{C}(4)-\mathrm{Si}(2)$ | 109.55(12) | $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{Si}(2)$ | 143.18(14) | $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | 106.96(16) | $\mathrm{H}(16 \mathrm{~B})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(5)$ | 133.20(17) | $\mathrm{Si}(1)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(5)$ | 119.80(16) | $\mathrm{Si}(1)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{O}(1)$ | 107.46(15) | $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{Si}(1)$ | 137.95(14) | $\mathrm{Si}(1)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{Si}(1)$ | 114.51(13) | $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(2)$ | 118.82(17) | $\mathrm{H}(21 \mathrm{~B})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 109.5 |


| $\mathrm{C}(25)-\mathrm{C}(23)-\mathrm{C}(24)$ | $109.17(18)$ | $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 109.5 |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(25)-\mathrm{C}(23)-\mathrm{C}(26)$ | $108.91(18)$ | $\mathrm{H}(24 \mathrm{~A})-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(26)$ | $108.50(17)$ | $\mathrm{H}(24 \mathrm{~B})-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(25)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $109.80(14)$ | $\mathrm{Si}(1)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $109.97(14)$ | $\mathrm{Si}(1)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(26)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $110.45(14)$ | $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(23)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 109.5 | $\mathrm{Si}(1)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(23)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 109.5 | $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(26 \mathrm{~A})-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 109.5 | $\mathrm{H}(22 \mathrm{~B})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(23)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 109.5 | $\mathrm{C}(23)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | 109.5 |
| $\mathrm{H}(26 \mathrm{~A})-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 109.5 | $\mathrm{C}(23)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(26 \mathrm{~B})-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 109.5 | $\mathrm{H}(25 \mathrm{~A})-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 109.5 | $\mathrm{C}(23)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~B})$ | 109.5 | $\mathrm{H}(25 \mathrm{~A})-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(24 \mathrm{~A})-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~B})$ | 109.5 | $\mathrm{H}(25 \mathrm{~B})-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 109.5 |

Symmetry transformations used to generate equivalent atoms:
\#1 -x+1,-y+1,-z+1

Table A1- 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 25c.

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :---: |
|  |  |  |  |  |  |  |
| $\mathrm{Si}(1)$ | $23(1)$ | $19(1)$ | $24(1)$ | $-9(1)$ | $-2(1)$ | $-2(1)$ |
| $\mathrm{Si}(2)$ | $20(1)$ | $20(1)$ | $22(1)$ | $-6(1)$ | $-2(1)$ | $0(1)$ |
| $\mathrm{C}(2)$ | $22(1)$ | $18(1)$ | $19(1)$ | $-7(1)$ | $0(1)$ | $-3(1)$ |
| $\mathrm{O}(1)$ | $23(1)$ | $21(1)$ | $24(1)$ | $-9(1)$ | $-6(1)$ | $1(1)$ |
| $\mathrm{C}(4)$ | $26(1)$ | $19(1)$ | $20(1)$ | $-9(1)$ | $1(1)$ | $-3(1)$ |
| $\mathrm{C}(3)$ | $21(1)$ | $17(1)$ | $17(1)$ | $-4(1)$ | $1(1)$ | $-2(1)$ |
| $\mathrm{C}(1)$ | $23(1)$ | $19(1)$ | $21(1)$ | $-6(1)$ | $0(1)$ | $1(1)$ |
| $\mathrm{C}(7)$ | $25(1)$ | $20(1)$ | $26(1)$ | $-11(1)$ | $-2(1)$ | $2(1)$ |
| $\mathrm{C}(6)$ | $22(1)$ | $23(1)$ | $24(1)$ | $-7(1)$ | $-6(1)$ | $3(1)$ |
| $\mathrm{C}(5)$ | $23(1)$ | $18(1)$ | $17(1)$ | $-6(1)$ | $2(1)$ | $-3(1)$ |
| $\mathrm{C}(13)$ | $29(1)$ | $22(1)$ | $24(1)$ | $-6(1)$ | $1(1)$ | $-2(1)$ |
| $\mathrm{C}(14)$ | $37(1)$ | $28(1)$ | $42(1)$ | $-6(1)$ | $5(1)$ | $-13(1)$ |
| $\mathrm{C}(11)$ | $28(1)$ | $32(1)$ | $32(1)$ | $-11(1)$ | $4(1)$ | $1(1)$ |
| $\mathrm{C}(15)$ | $47(1)$ | $27(1)$ | $33(1)$ | $-2(1)$ | $-4(1)$ | $2(1)$ |
| $\mathrm{C}(12)$ | $24(1)$ | $34(1)$ | $38(1)$ | $-11(1)$ | $-5(1)$ | $-2(1)$ |
| $\mathrm{C}(16)$ | $53(2)$ | $37(1)$ | $30(1)$ | $-10(1)$ | $11(1)$ | $-7(1)$ |
| $\mathrm{C}(21)$ | $40(1)$ | $22(1)$ | $35(1)$ | $-11(1)$ | $-7(1)$ | $3(1)$ |
| $\mathrm{C}(23)$ | $31(1)$ | $27(1)$ | $25(1)$ | $-11(1)$ | $-4(1)$ | $-4(1)$ |
| $\mathrm{C}(26)$ | $54(2)$ | $34(1)$ | $31(1)$ | $-17(1)$ | $-2(1)$ | $-4(1)$ |
| $\mathrm{C}(24)$ | $59(2)$ | $33(1)$ | $28(1)$ | $-8(1)$ | $-11(1)$ | $6(1)$ |
| $\mathrm{C}(22)$ | $32(1)$ | $38(1)$ | $51(2)$ | $-21(1)$ | $6(1)$ | $-11(1)$ |
| $\mathrm{C}(25)$ | $50(2)$ | $56(2)$ | $35(1)$ | $-15(1)$ | $9(1)$ | $-23(1)$ |

Table A1- 5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for $\mathbf{2 5 c}$.

| Atom | x | $y$ | $z$ | U(eq) |
| :--- | ---: | ---: | ---: | :--- |
|  |  |  |  |  |
|  | 3302 | 7717 | 5687 | 28 |
| H(7) | 1992 | 6945 | 4583 | 29 |
| H(6) | 2926 | 8970 | 1853 | 43 |
| H(14A) | 3324 | 7637 | 2704 | 43 |
| H(14B) | 1764 | 8781 | 2874 | 43 |
| H(14C) | -3061 | 7722 | 3706 | 37 |
| H(11A) | -1005 | 8107 | 3903 | 37 |
| H(11B) | -1500 | 6761 | 4529 | 37 |
| H(11C) | -1524 | 9453 | 2009 | 46 |
| H(15A) | -2031 | 8846 | 1184 | 46 |
| H(15B) | -399 | 9741 | 975 | 46 |
| H(15C) | -2929 | 5507 | 2879 | 39 |
| H(12A) | -1715 | 5728 | 1872 | 39 |
| H(12B) | -3394 | 6831 | 2020 | 39 |
| H(12C) | 473 | 7169 | 799 | 48 |
| H(16A) | 2568 | 6690 | 1391 | 48 |
| H(16B) | 2096 | 8070 | 604 | 48 |
| H(16C) | 4806 | 567 | 4013 | 39 |
| H(21A) | 6337 | 1021 | 3155 | 39 |
| H(21B) | 4906 | 89 | 3056 | 39 |
| H(21C) | 3969 | 2061 | 88 | 46 |
| H(26A) | 2474 | 1406 | 890 | 46 |
| H(26B) | 4821 | 1046 | 1116 | 46 |
| H(26C) | 1839 | 4542 | 1044 | 50 |
| H(24A) | 661 | 3543 | 837 | 50 |
| H(24B) | 2198 | 4163 | 44 | 50 |
| H(24C) | 391 | 1215 | 2441 | 45 |
| H(22A) | -435 | 2515 | 2659 | 45 |
| H(22B) | 448 | 1288 | 3552 | 45 |
| H(22C) | 5810 | 3601 | 427 | 54 |
| H(25A) | 6650 | 2585 | 1457 | 54 |
| H(25B) | 5497 | 3948 | 1442 | 54 |
| H(25C) |  |  |  |  |

Table A2-1. Crystal data and structure refinement for 25d.

| Identification code | 25d |
| :---: | :---: |
| Empirical formula | C46 H80 O2 Si4 |
| Formula weight | 777.46 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{c}$ |
| Unit cell dimensions | $a=15.8079(18) \AA \quad \alpha=90^{\circ}$. |
|  | $b=11.5759(13) \AA \quad \beta=111.856(2)^{\circ}$. |
|  | $\mathrm{c}=14.0484(16) \AA \quad \gamma=90^{\circ}$. |
| Volume | 2385.9(5) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.082 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.158 \mathrm{~mm}^{-1}$ |
| F(000) | 856 |
| Crystal size | $0.28 \times 0.28 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.24 to $19.04^{\circ}$. |
| Index ranges | $-14<=\mathrm{h}<=14,-10<=\mathrm{k}<=10,-12<=1<=12$ |
| Reflections collected | 15324 |
| Independent reflections | $1936[\mathrm{R}(\mathrm{int})=0.0549]$ |
| Completeness to theta $=19.04^{\circ}$ | 99.9 \% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9838 and 0.9567 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 1936 / 12 / 163 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 2.624 |
| Final R indices [ $1>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.2122, \mathrm{wR} 2=0.5330$ |
| R indices (all data) | $\mathrm{R} 1=0.2589, \mathrm{wR} 2=0.5741$ |
| Largest diff. peak and hole | 1.568 and -0.487e. $\AA^{-3}$ |

Table A2-2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters ( $\AA^{2} \mathrm{x}$ $10^{3}$ ) for $\mathbf{2 5 d}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{i j}$ tensor.

| Atom | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | :---: | ---: | :---: | :---: |
| $\mathrm{C}(1)$ | $6134(12)$ | $9883(14)$ | $2395(12)$ | $72(5)$ |
| $\mathrm{C}(2)$ | $5823(11)$ | $10148(13)$ | $1368(11)$ | $56(4)$ |
| $\mathrm{C}(3)$ | $6381(11)$ | $11050(15)$ | $1251(11)$ | $66(5)$ |
| $\mathrm{C}(4)$ | $7027(12)$ | $11272(13)$ | $2188(13)$ | $75(5)$ |
| $\mathrm{C}(5)$ | $5064(11)$ | $9741(14)$ | $456(10)$ | $61(4)$ |
| $\mathrm{C}(6)$ | $4516(13)$ | $8845(15)$ | $551(12)$ | $75(5)$ |
| $\mathrm{C}(7)$ | $3764(12)$ | $8456(16)$ | $-301(13)$ | $82(5)$ |
| $\mathrm{C}(11)$ | $7822(13)$ | $13579(15)$ | $1880(13)$ | $100(6)$ |
| $\mathrm{C}(12)$ | $7922(18)$ | $12740(20)$ | $3984(13)$ | $155(11)$ |
| $\mathrm{C}(13)$ | $9156(18)$ | $11410(20)$ | $2820(20)$ | $151(9)$ |
| $\mathrm{C}(14)$ | $8899(17)$ | $10900(20)$ | $1644(19)$ | $142(8)$ |
| $\mathrm{C}(15)$ | $9210(30)$ | $10320(40)$ | $3540(40)$ | $280(20)$ |
| $\mathrm{C}(21)$ | $6430(40)$ | $9700(30)$ | $4550(17)$ | $370(40)$ |
| $\mathrm{C}(22)$ | $4777(13)$ | $8421(17)$ | $3103(13)$ | $106(7)$ |
| $\mathrm{C}(23)$ | $6745(19)$ | $7430(20)$ | $3390(20)$ | $140(9)$ |
| $\mathrm{C}(24)$ | $6180(20)$ | $6750(30)$ | $2410(30)$ | $194(12)$ |
| $\mathrm{C}(25)$ | $6620(30)$ | $6750(40)$ | $4390(30)$ | $254(17)$ |
| $\mathrm{C}(26)$ | $7540(40)$ | $7560(40)$ | $3470(40)$ | $251(17)$ |
| $\mathrm{C}(27)$ | $7730(50)$ | $7790(60)$ | $2430(60)$ | $380(30)$ |
| $\mathrm{C}(28)$ | $7650(40)$ | $6140(50)$ | $3950(40)$ | $330(30)$ |
| $\mathrm{O}(1)$ | $6877(8)$ | $10569(10)$ | $2880(7)$ | $77(4)$ |
| $\mathrm{Si}(1)$ | $5974(5)$ | $8882(5)$ | $3383(3)$ | $113(3)$ |
| $\mathrm{Si}(2)$ | $8027(4)$ | $12298(5)$ | $2754(3)$ | $95(3)$ |

Table A2- 3. Bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ] for 25d.

| $\mathrm{C}(1)-\mathrm{O}(1)$ | $1.370(16)$ | $\mathrm{C}(12)-\mathrm{Si}(2)$ | $1.87(2)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.374(19)$ | $\mathrm{C}(13)-\mathrm{C}(15)$ | $1.60(5)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)$ | $1.896(16)$ | $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.66(3)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | $1.42(2)$ | $\mathrm{C}(13)-\mathrm{Si}(2)$ | $2.03(3)$ |
| $\mathrm{C}(2)-\mathrm{C}(5)$ | $1.47(2)$ | $\mathrm{C}(21)-\mathrm{Si}(1)$ | $1.79(2)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | $1.36(2)$ | $\mathrm{C}(22)-\mathrm{Si}(1)$ | $1.861(19)$ |
| $\mathrm{C}(3)-\mathrm{C}(7)$ | $1.39(2)$ | $\mathrm{C}(23)-\mathrm{C}(26)$ | $1.22(5)$ |
| $\mathrm{C}(4)-\mathrm{O}(1)$ | $1.356(17)$ | $\mathrm{C}(23)-\mathrm{C}(24)$ | $1.55(4)$ |
| $\mathrm{C}(4)-\mathrm{Si}(2)$ | $1.899(18)$ | $\mathrm{C}(23)-\mathrm{C}(25)$ | $1.69(5)$ |
| $\mathrm{C}(5)-\mathrm{C}(5)$ | $1.36(3)$ | $\mathrm{C}(23)-\mathrm{C}(28)$ | $2.02(7)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | $1.39(2)$ | $\mathrm{C}(23)-\mathrm{Si}(1)$ | $2.08(3)$ |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | $1.41(2)$ | $\mathrm{C}(26)-\mathrm{C}(27)$ | $1.62(7)$ |
| $\mathrm{C}(6)-\mathrm{H}(6)$ | 0.9500 | $\mathrm{C}(26)-\mathrm{C}(28)$ | $1.77(6)$ |
| $\mathrm{C}(7)-\mathrm{C}(3)$ | $1.39(2)$ |  |  |
| $\mathrm{C}(7)-\mathrm{H}(7)$ | 0.9500 | $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $107.4(13)$ |
| $\mathrm{C}(11)-\mathrm{Si}(2)$ | $1.874(18)$ | $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{Si}(1)$ | $108.3(11)$ |


| C(2)-C(1)-Si(1) | $144.2(14)$ | $\mathrm{C}(26)-\mathrm{C}(23)-\mathrm{C}(28)$ | $60(3)$ |
| :--- | :--- | :--- | :---: |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | $107.0(14)$ | $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(28)$ | $93(2)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(5)$ | $134.5(15)$ | $\mathrm{C}(25)-\mathrm{C}(23)-\mathrm{C}(28)$ | $67(2)$ |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(5)$ | $118.5(14)$ | $\mathrm{C}(26)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $118(3)$ |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(7)$ | $130.4(18)$ | $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $105.7(19)$ |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | $107.7(14)$ | $\mathrm{C}(25)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $97(2)$ |
| $\mathrm{C}(7)-\mathrm{C}(3)-\mathrm{C}(2)$ | $121.9(15)$ | $\mathrm{C}(28)-\mathrm{C}(23)-\mathrm{Si}(1)$ | $159(2)$ |
| $\mathrm{O}(1)-\mathrm{C}(4)-\mathrm{C}(3)$ | $108.2(15)$ | $\mathrm{C}(23)-\mathrm{C}(26)-\mathrm{C}(27)$ | $117(5)$ |
| $\mathrm{O}(1)-\mathrm{C}(4)-\mathrm{Si}(2)$ | $114.6(12)$ | $\mathrm{C}(23)-\mathrm{C}(26)-\mathrm{C}(28)$ | $83(4)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{Si}(2)$ | $137.2(14)$ | $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{C}(28)$ | $118(5)$ |
| $\mathrm{C}(5)-\mathrm{C}(5)-\mathrm{C}(6)$ | $122.7(19)$ | $\mathrm{C}(26)-\mathrm{C}(28)-\mathrm{C}(23)$ | $37(2)$ |
| $\mathrm{C}(5)-\mathrm{C}(5)-\mathrm{C}(2)$ | $117.8(19)$ | $\mathrm{C}(4)-\mathrm{O}(1)-\mathrm{C}(1)$ | $109.7(11)$ |
| $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(2)$ | $119.5(13)$ | $\mathrm{C}(21)-\mathrm{Si}(1)-\mathrm{C}(22)$ | $112.1(18)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | $121.0(14)$ | $\mathrm{C}(21)-\mathrm{Si}(1)-\mathrm{C}(1)$ | $103.3(9)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{H}(6)$ | 119.5 | $\mathrm{C}(22)-\mathrm{Si}(1)-\mathrm{C}(1)$ | $115.0(8)$ |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{H}(6)$ | 119.5 | $\mathrm{C}(21)-\mathrm{Si}(1)-\mathrm{C}(23)$ | $113(2)$ |
| $\mathrm{C}(3)-\mathrm{C}(7)-\mathrm{C}(6)$ | $118.0(16)$ | $\mathrm{C}(22)-\mathrm{Si}(1)-\mathrm{C}(23)$ | $108.5(10)$ |
| $\mathrm{C}(3)-\mathrm{C}(7)-\mathrm{H}(7)$ | 121.0 | $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(23)$ | $104.9(10)$ |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7)$ | 121.0 | $\mathrm{C}(12)-\mathrm{Si}(2)-\mathrm{C}(11)$ | $109.7(11)$ |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(14)$ | $107(2)$ | $\mathrm{C}(12)-\mathrm{Si}(2)-\mathrm{C}(4)$ | $102.2(8)$ |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{Si}(2)$ | $106(2)$ | $\mathrm{C}(11)-\mathrm{Si}(2)-\mathrm{C}(4)$ | $107.8(8)$ |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{Si}(2)$ | $104.5(16)$ | $\mathrm{C}(12)-\mathrm{Si}(2)-\mathrm{C}(13)$ | $118.4(13)$ |
| $\mathrm{C}(26)-\mathrm{C}(23)-\mathrm{C}(24)$ | $112(4)$ | $\mathrm{C}(11)-\mathrm{Si}(2)-\mathrm{C}(13)$ | $111.5(10)$ |
| $\mathrm{C}(26)-\mathrm{C}(23)-\mathrm{C}(25)$ | $114(4)$ | $\mathrm{C}(4)-\mathrm{Si}(2)-\mathrm{C}(13)$ | $106.4(9)$ |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(25)$ | $107(3)$ |  |  |

Symmetry transformations used to generate equivalent atoms:
\#1-x+1,-y+2,-z

Table A2- 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 25d.

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}(1)$ | $92(13)$ | $76(11)$ | $51(13)$ | $-14(9)$ | $29(10)$ | $-29(10)$ |
| $\mathrm{C}(2)$ | $77(11)$ | $66(10)$ | $28(11)$ | $11(8)$ | $25(9)$ | $4(9)$ |
| $\mathrm{C}(3)$ | $75(11)$ | $105(14)$ | $13(11)$ | $-5(9)$ | $9(9)$ | $10(11)$ |
| $\mathrm{C}(4)$ | $114(14)$ | $78(11)$ | $46(12)$ | $16(10)$ | $46(11)$ | $13(10)$ |
| $\mathrm{C}(5)$ | $88(12)$ | $67(12)$ | $40(12)$ | $0(8)$ | $39(12)$ | $-5(10)$ |
| $\mathrm{C}(6)$ | $120(15)$ | $83(13)$ | $31(11)$ | $6(8)$ | $38(11)$ | $4(12)$ |
| $\mathrm{C}(7)$ | $85(12)$ | $116(14)$ | $44(12)$ | $3(11)$ | $22(10)$ | $-19(11)$ |
| $\mathrm{C}(11)$ | $148(17)$ | $101(14)$ | $69(12)$ | $10(10)$ | $61(11)$ | $-14(12)$ |
| $\mathrm{C}(12)$ | $210(20)$ | $220(20)$ | $53(12)$ | $-44(14)$ | $67(14)$ | $-120(20)$ |
| $\mathrm{C}(21)$ | $770(90)$ | $310(40)$ | $57(16)$ | $-120(20)$ | $180(30)$ | $-400(60)$ |
| $\mathrm{C}(22)$ | $129(16)$ | $123(15)$ | $77(13)$ | $27(11)$ | $54(11)$ | $-33(13)$ |
| $\mathrm{O}(1)$ | $107(9)$ | $88(8)$ | $31(6)$ | $14(6)$ | $20(6)$ | $-3(7)$ |
| $\mathrm{Si}(1)$ | $172(6)$ | $114(5)$ | $33(3)$ | $12(3)$ | $14(3)$ | $-52(4)$ |
| $\mathrm{Si}(2)$ | $101(4)$ | $146(5)$ | $36(3)$ | $-2(3)$ | $22(3)$ | $-32(3)$ |

Table A3- 1. Crystal data and structure refinement for 57.

| Identification code | 57 |
| :---: | :---: |
| Empirical formula | C28 H24 O4 |
| Formula weight | 424.47 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2 $/$ /c |
| Unit cell dimensions | $a=5.353(2) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=8.306(4) \AA \quad \beta=90.104(6)^{\circ}$. |
|  | $\mathrm{c}=23.008(10) \AA \quad \gamma=90^{\circ}$. |
| Volume | 1022.9(8) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.378 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.091 \mathrm{~mm}^{-1}$ |
| F(000) | 448 |
| Crystal size | $0.20 \times 0.13 \times 0.07 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.77 to $28.73^{\circ}$. |
| Index ranges | $-6<=\mathrm{h}<=7,-11<=\mathrm{k}<=11,-31<=1<=30$ |
| Reflections collected | 11170 |
| Independent reflections | $2493[\mathrm{R}(\mathrm{int})=0.0442]$ |
| Completeness to theta $=28.73{ }^{\circ}$ | 94.0\% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9936 and 0.9820 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 2493 / 0 / 146 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 5.692 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.2864, \mathrm{wR} 2=0.6593$ |
| R indices (all data) | $\mathrm{R} 1=0.2991, \mathrm{wR} 2=0.6609$ |
| Largest diff. peak and hole | 1.485 and -1.024 e. $\AA^{-3}$ |

Table A3- 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 57 . U(eq) is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

| Atom | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{O}(2)$ | $5775(16)$ | $4583(8)$ | $856(3)$ | $31(2)$ |
| $\mathrm{O}(1)$ | $4268(15)$ | $1997(8)$ | $1002(3)$ | $29(2)$ |
| $\mathrm{C}(7)$ | $10780(20)$ | $309(11)$ | $-223(4)$ | $22(2)$ |
| $\mathrm{C}(5)$ | $8780(20)$ | $2928(12)$ | $-174(4)$ | $31(3)$ |
| $\mathrm{C}(10)$ | $8390(30)$ | $343(13)$ | $1741(5)$ | $37(3)$ |
| $\mathrm{C}(4)$ | $7230(20)$ | $2285(13)$ | $265(4)$ | $29(2)$ |
| $\mathrm{C}(6)$ | $10610(20)$ | $1943(12)$ | $-410(4)$ | $27(2)$ |
| $\mathrm{C}(9)$ | $6240(20)$ | $-221(12)$ | $1495(4)$ | $26(2)$ |
| $\mathrm{C}(11)$ | $9140(30)$ | $-219(14)$ | $2295(5)$ | $37(3)$ |
| $\mathrm{C}(1)$ | $5070(30)$ | $3129(12)$ | $580(5)$ | $34(3)$ |
| $\mathrm{C}(3)$ | $7420(20)$ | $734(12)$ | $453(4)$ | $24(2)$ |
| $\mathrm{C}(2)$ | $5446(19)$ | $453(12)$ | $909(4)$ | $23(2)$ |
| $\mathrm{C}(14)$ | $4850(20)$ | $-1370(15)$ | $1756(5)$ | $36(3)$ |
| $\mathrm{C}(12)$ | $7520(30)$ | $-1397(15)$ | $2567(5)$ | $39(3)$ |
| $\mathrm{C}(13)$ | $5510(30)$ | $-1959(15)$ | $2306(5)$ | $42(3)$ |
| $\mathrm{C}(8)$ | $7650(30)$ | $4473(14)$ | $1266(5)$ | $38(3)$ |

Table A3- 3. Bond lengths $[\AA]$ and angles [ $\left.{ }^{\circ}\right]$ for 57.

| $\mathrm{O}(2)-\mathrm{C}(8)$ | $1.380(15)$ | $\mathrm{C}(11)-\mathrm{C}(12)$ | $1.451(18)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{O}(2)-\mathrm{C}(1)$ | $1.416(13)$ | $\mathrm{C}(11)-\mathrm{H}(11)$ | 0.9500 |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | $1.418(13)$ | $\mathrm{C}(1)-\mathrm{H}(1)$ | 1.0000 |
| $\mathrm{O}(1)-\mathrm{C}(2)$ | $1.444(12)$ | $\mathrm{C}(3)-\mathrm{C}(7)$ | $1.399(15)$ |
| $\mathrm{C}(7)-\mathrm{C}(3)$ | $1.399(15)$ | $\mathrm{C}(3)-\mathrm{C}(2)$ | $1.509(14)$ |
| $\mathrm{C}(7)-\mathrm{C}(7)$ | $1.422(18)$ | $\mathrm{C}(2)-\mathrm{H}(2)$ | 1.0000 |
| $\mathrm{C}(7)-\mathrm{C}(6)$ | $1.427(13)$ | $\mathrm{C}(14)-\mathrm{C}(13)$ | $1.402(16)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | $1.391(16)$ | $\mathrm{C}(14)-\mathrm{H}(14)$ | 0.9500 |
| $\mathrm{C}(5)-\mathrm{C}(4)$ | $1.412(15)$ | $\mathrm{C}(12)-\mathrm{C}(13)$ | $1.315(19)$ |
| $\mathrm{C}(5)-\mathrm{H}(5)$ | 0.9500 | $\mathrm{C}(12)-\mathrm{H}(12)$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(9)$ | $1.364(17)$ | $\mathrm{C}(13)-\mathrm{H}(13)$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | $1.415(15)$ | $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(10)-\mathrm{H}(10)$ | 0.9500 | $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(4)-\mathrm{C}(3)$ | $1.363(14)$ | $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(4)-\mathrm{C}(1)$ | $1.536(16)$ |  |  |
| $\mathrm{C}(6)-\mathrm{H}(6)$ | 0.9500 | $\mathrm{C}(8)-\mathrm{O}(2)-\mathrm{C}(1)$ | $116.4(8)$ |
| $\mathrm{C}(9)-\mathrm{C}(14)$ | $1.352(16)$ | $\mathrm{C}(1)-\mathrm{O}(1)-\mathrm{C}(2)$ | $110.8(8)$ |
| $\mathrm{C}(9)-\mathrm{C}(2)$ | $1.520(13)$ | $\mathrm{C}(3)-\mathrm{C}(7)-\mathrm{C}(7)$ | $117.1(11)$ |
|  |  |  |  |


| $\mathrm{C}(3)-\mathrm{C}(7)-\mathrm{C}(6)$ | 121.2(9) | $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{H}(13)$ | 120.2 |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(7)-\mathrm{C}(7)-\mathrm{C}(6)$ | 121.6(12) | $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(4)$ | 118.3(10) | $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{H}(5)$ | 120.9 | $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{H}(5)$ | 120.9 | $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 119.9(11) | $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10)$ | 120.0 | $\mathrm{H}(8 \mathrm{~B})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109. |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10)$ | 120.0 |  |  |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | 122.7(11) |  |  |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(1)$ | 109.7(9) |  |  |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(1)$ | 127.5(10) |  |  |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | 119.1(10) |  |  |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{H}(6)$ | 120.5 |  |  |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{H}(6)$ | 120.5 |  |  |
| $\mathrm{C}(14)-\mathrm{C}(9)-\mathrm{C}(10)$ | 121.5(10) |  |  |
| $\mathrm{C}(14)-\mathrm{C}(9)-\mathrm{C}(2)$ | 120.0(10) |  |  |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(2)$ | 118.4(9) |  |  |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)$ | 116.2(11) |  |  |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11)$ | 121.9 |  |  |
| $\mathrm{C}(12)-\mathrm{C}(11)-\mathrm{H}(11)$ | 121.9 |  |  |
| $\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{O}(1)$ | 109.9(8) |  |  |
| $\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{C}(4)$ | 113.5(10) |  |  |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(4)$ | 104.4(8) |  |  |
| $\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{H}(1)$ | 109.6 |  |  |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{H}(1)$ | 109.6 |  |  |
| $\mathrm{C}(4)-\mathrm{C}(1)-\mathrm{H}(1)$ | 109.6 |  |  |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(7)$ | 121.1(10) |  |  |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | 108.3(9) |  |  |
| $\mathrm{C}(7) \# 1-\mathrm{C}(3)-\mathrm{C}(2)$ | 130.5(9) |  |  |
| $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 105.8(8) |  |  |
| $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{C}(9)$ | 108.5(7) |  |  |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(9)$ | 118.6(9) |  |  |
| $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{H}(2)$ | 107.8 |  |  |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2)$ | 107.8 |  |  |
| $\mathrm{C}(9)-\mathrm{C}(2)-\mathrm{H}(2)$ | 107.8 |  |  |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{C}(13)$ | 120.6(12) |  |  |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{H}(14)$ | 119.7 |  |  |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14)$ | 119.7 |  |  |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{C}(11)$ | 122.1(11) |  |  |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12)$ | 119.0 |  |  |
| $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{H}(12)$ | 119.0 |  |  |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | 119.6(12) |  |  |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{H}(13)$ | 120.2 |  |  |

Table A3- 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 57.

| Atom | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{O}(2)$ | $42(5)$ | $20(4)$ | $30(4)$ | $2(3)$ | $8(3)$ | $11(3)$ |
| $\mathrm{O}(1)$ | $36(4)$ | $22(4)$ | $30(4)$ | $2(3)$ | $8(3)$ | $2(3)$ |
| $\mathrm{C}(7)$ | $31(6)$ | $14(4)$ | $20(4)$ | $-1(3)$ | $2(4)$ | $-13(4)$ |
| $\mathrm{C}(5)$ | $45(7)$ | $21(5)$ | $26(5)$ | $-3(4)$ | $3(5)$ | $-8(5)$ |
| $\mathrm{C}(10)$ | $52(8)$ | $27(6)$ | $31(5)$ | $8(4)$ | $-5(5)$ | $-10(5)$ |
| $\mathrm{C}(4)$ | $33(6)$ | $28(5)$ | $27(5)$ | $-5(4)$ | $-3(4)$ | $1(4)$ |
| $\mathrm{C}(6)$ | $43(7)$ | $19(5)$ | $18(4)$ | $9(4)$ | $-5(4)$ | $1(4)$ |
| $\mathrm{C}(9)$ | $35(6)$ | $21(5)$ | $21(4)$ | $1(4)$ | $1(4)$ | $3(4)$ |
| $\mathrm{C}(11)$ | $44(7)$ | $39(6)$ | $27(5)$ | $-5(5)$ | $-3(5)$ | $-2(5)$ |
| $\mathrm{C}(1)$ | $53(8)$ | $22(5)$ | $27(5)$ | $1(4)$ | $-3(5)$ | $10(5)$ |
| $\mathrm{C}(3)$ | $32(6)$ | $21(5)$ | $19(4)$ | $2(3)$ | $-2(4)$ | $2(4)$ |
| $\mathrm{C}(2)$ | $22(5)$ | $26(5)$ | $20(4)$ | $-1(4)$ | $-1(4)$ | $1(4)$ |
| $\mathrm{C}(14)$ | $37(7)$ | $43(7)$ | $28(5)$ | $-3(5)$ | $10(5)$ | $-5(5)$ |
| $\mathrm{C}(12)$ | $55(8)$ | $38(6)$ | $25(5)$ | $7(4)$ | $1(5)$ | $3(6)$ |
| $\mathrm{C}(13)$ | $59(9)$ | $36(6)$ | $32(6)$ | $15(5)$ | $0(6)$ | $2(6)$ |
| $\mathrm{C}(8)$ | $63(9)$ | $25(5)$ | $25(5)$ | $-5(4)$ | $-1(5)$ | $1(5)$ |

Table A3- 5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 57.

| Atom | $x$ | $y$ | $z$ | $U(e q)$ |
| :--- | ---: | ---: | ---: | :--- |
|  |  |  |  |  |
| $H(5)$ | 8570 | 4006 | -303 | 37 |
| $H(10)$ | 9379 | 1113 | 1540 | 44 |
| $H(6)$ | 11741 | 2353 | -692 | 32 |
| $H(11)$ | 10627 | 153 | 2478 | 44 |
| $H(1)$ | 3677 | 3343 | 299 | 41 |
| $H(2)$ | 4166 | -290 | 741 | 27 |
| $H(14)$ | 3409 | -1781 | 1565 | 43 |
| $H(12)$ | 7920 | -1773 | 2946 | 47 |
| $H(13)$ | 4521 | -2759 | 2489 | 51 |
| $H(8 A)$ | 7160 | 3707 | 1569 | 57 |
| $H(8 B)$ | 7938 | 5533 | 1441 | 57 |
| $H(8 C)$ | 9191 | 4099 | 1079 | 57 |

Table A4- 1. Crystal data and structure refinement for $\mathbf{5 0}$.

| Identification code | 50 |
| :---: | :---: |
| Empirical formula | C48 H74 N2 O6 Si4 |
| Formula weight | 887.45 |
| Temperature | 296(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Orthorhombic |
| Space group | $\mathrm{P} 2_{1} 2_{1} 2_{1}$ |
| Unit cell dimensions | $a=11.799(4) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=12.598(4) \AA \quad \beta=90^{\circ}$. |
|  | $\mathrm{c}=33.550(10) \AA \quad \gamma=90^{\circ}$. |
| Volume | 4987(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.182 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.166 \mathrm{~mm}^{-1}$ |
| F(000) | 1920 |
| Crystal size | $0.21 \times 0.11 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.73 to $16.70^{\circ}$. |
| Index ranges | $-9<=\mathrm{h}<=9,-10<=\mathrm{k}<=10,-27<=1<=27$ |
| Reflections collected | 18161 |
| Independent reflections | $2749[\mathrm{R}(\mathrm{int})=0.0863]$ |
| Completeness to theta $=16.70^{\circ}$ | 99.8\% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.9844 and 0.9659 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 2749 / 0 / 563 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.062 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0406, \mathrm{wR} 2=0.0913$ |
| R indices (all data) | $\mathrm{R} 1=0.0481, \mathrm{wR} 2=0.0953$ |
| Absolute structure parameter | 0.4(2) |
| Largest diff. peak and hole | 0.182 and -0.157 e. $\AA^{-3}$ |

Table A4- 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{5 0}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| Atom | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| Si(1) | 345(2) | 11457(2) | 1246(1) | 36(1) |
| Si(2) | 3186(2) | 6117(2) | 2176(1) | 34(1) |
| Si(3) | 4223(2) | 11075(2) | 399(1) | 29(1) |
| Si(4) | 7150(2) | 5643(2) | 1364(1) | 32(1) |
| O(6) | 2312(5) | 11157(4) | 827(2) | 19(1) |
| $\mathrm{O}(5)$ | 5120(5) | 5892(4) | 1746(2) | 23(1) |
| C(13) | 3697(10) | 5075(7) | 1387(3) | 36(3) |
| C(11) | 3921(7) | 6077(7) | 1666(2) | 18(2) |
| C(10) | 4020(12) | 7001(8) | 1378(3) | 18(3) |
| C (12) | 5570(7) | 5889(8) | 1340(3) | 25(2) |
| C(14) | 4834(8) | 4949(7) | 1165(4) | 34(3) |
| C(9) | 5013(10) | 6859(8) | 1165(4) | 22(3) |
| C(30) | 1328(8) | 10565(8) | 947(2) | 25(2) |
| C (7) | 4509(13) | 8332(9) | 759(3) | 26(3) |
| C(6) | 3540(11) | 8555(12) | 979(3) | 20(3) |
| C(5) | 2864(14) | 9445(10) | 907(3) | 17(2) |
| C(3) | 1468(9) | 8769(12) | 1351(3) | 31(2) |
| C(2) | 2125(14) | 7929(9) | 1440(2) | 20(2) |
| C(4) | 1861(12) | 9555(8) | 1098(3) | 17(2) |
| C(8) | 5250(8) | 7515(11) | 840(3) | 22(3) |
| C(33) | 895(8) | 10291(7) | 509(3) | 26(2) |
| C(29) | 5105(8) | 5780(8) | 2672(2) | 56(3) |
| C (25) | 3143(7) | 7509(7) | 2365(3) | 52(3) |
| C(24) | 3981(8) | 5275(7) | 2548(2) | 35(3) |
| C(26) | 1746(7) | 5559(7) | 2111(2) | 47(3) |
| C(27) | 3222(8) | 5193(8) | 2920(3) | 64(3) |
| C(32) | 2021(8) | 10053(9) | 284(3) | 31(3) |
| C(28) | 4191(8) | 4154(7) | 2393(3) | 61(3) |
| C(31) | 2945(7) | 10353(8) | 601(3) | 22(2) |
| $\mathrm{C}(20)$ | 7297(7) | 4461(6) | 1693(2) | 50(3) |
| C(19) | 7722(7) | 5316(8) | 862(2) | 54(3) |
| C(38) | 4887(7) | 10310(6) | -17(2) | 44(3) |
| C(37) | 5298(8) | 11426(7) | 794(3) | 30(2) |
| C(42) | 6163(8) | 12173(7) | 603(3) | 53(3) |
| C(41) | 5964(8) | 10478(7) | 956(3) | 54(3) |
| C(39) | 3591(7) | 12311(6) | 188(2) | 38(3) |
| C(48) | 182(9) | 12554(8) | 1966(3) | 76(4) |
| $\mathrm{C}(44)$ | -1012(8) | 10818(9) | 1311(3) | 101(4) |
| C(45) | 161(11) | 12672(7) | 941(3) | 99(5) |
| C(16) | 4520(14) | 5015(6) | 734(3) | 32(3) |
| C(17) | 2852(8) | 5411(7) | 315(3) | 53(3) |
| $\mathrm{O}(3)$ | 5179(6) | 4943(4) | 451(2) | 36(2) |
| $\mathrm{N}(1)$ | 3384(10) | 5220(6) | 705(3) | 33(2) |
| C(46) | 2051(10) | 12380(18) | 1698(4) | 232(13) |


| $\mathrm{C}(43)$ | $973(9)$ | $11842(8)$ | $1732(3)$ | $42(3)$ |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{C}(47)$ | $1059(17)$ | $10859(11)$ | $1994(3)$ | $193(10)$ |
| $\mathrm{C}(21)$ | $7471(9)$ | $7118(8)$ | $1979(3)$ | $72(3)$ |
| $\mathrm{C}(18)$ | $7934(8)$ | $6802(7)$ | $1578(3)$ | $38(3)$ |
| $\mathrm{C}(22)$ | $7899(8)$ | $7765(8)$ | $1312(3)$ | $79(4)$ |
| $\mathrm{C}(23)$ | $9169(8)$ | $6507(7)$ | $1639(3)$ | $69(3)$ |
| $\mathrm{C}(40)$ | $4763(8)$ | $11984(7)$ | $1140(3)$ | $61(3)$ |
| $\mathrm{C}(15)$ | $2820(13)$ | $5267(7)$ | $1063(4)$ | $34(3)$ |
| $\mathrm{O}(1)$ | $1831(7)$ | $5399(5)$ | $1097(2)$ | $49(2)$ |
| $\mathrm{O}(2)$ | $-760(6)$ | $9123(5)$ | $582(2)$ | $45(2)$ |
| $\mathrm{C}(1)$ | $3211(12)$ | $7794(10)$ | $1273(3)$ | $24(3)$ |
| $\mathrm{N}(2)$ | $888(10)$ | $8544(7)$ | $309(2)$ | $32(2)$ |
| $\mathrm{O}(8)$ | $2652(6)$ | $8353(5)$ | $20(2)$ | $42(2)$ |
| $\mathrm{C}(34)$ | $180(11)$ | $9307(10)$ | $478(3)$ | $34(3)$ |
| $\mathrm{C}(36)$ | $537(7)$ | $7444(8)$ | $265(2)$ | $46(3)$ |
| $\mathrm{C}(35)$ | $1938(11)$ | $8897(9)$ | $177(3)$ | $27(3)$ |

Table A4- 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for 50.

| $\mathrm{Si}(1)-\mathrm{C}(44)$ | $1.805(9)$ | $\mathrm{C}(14)-\mathrm{C}(16)$ | $1.495(12)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Si}(1)-\mathrm{C}(45)$ | $1.853(9)$ | $\mathrm{C}(14)-\mathrm{H}(14)$ | 0.9800 |
| $\mathrm{Si}(1)-\mathrm{C}(43)$ | $1.856(9)$ | $\mathrm{C}(9)-\mathrm{C}(8)$ | $1.396(11)$ |
| $\mathrm{Si}(1)-\mathrm{C}(30)$ | $1.903(9)$ | $\mathrm{C}(30)-\mathrm{C}(4)$ | $1.507(12)$ |
| $\mathrm{Si}(2)-\mathrm{C}(26)$ | $1.852(8)$ | $\mathrm{C}(30)-\mathrm{C}(33)$ | $1.593(11)$ |
| $\mathrm{Si}(2)-\mathrm{C}(25)$ | $1.866(9)$ | $\mathrm{C}(7)-\mathrm{C}(8)$ | $1.378(10)$ |
| $\mathrm{Si}(2)-\mathrm{C}(24)$ | $1.887(9)$ | $\mathrm{C}(7)-\mathrm{C}(6)$ | $1.389(12)$ |
| $\mathrm{Si}(2)-\mathrm{C}(11)$ | $1.918(8)$ | $\mathrm{C}(7)-\mathrm{H}(7)$ | 0.9300 |
| $\mathrm{Si}(3)-\mathrm{C}(39)$ | $1.867(8)$ | $\mathrm{C}(6)-\mathrm{C}(5)$ | $1.396(12)$ |
| $\mathrm{Si}(3)-\mathrm{C}(38)$ | $1.868(8)$ | $\mathrm{C}(6)-\mathrm{C}(1)$ | $1.432(11)$ |
| $\mathrm{Si}(3)-\mathrm{C}(31)$ | $1.886(9)$ | $\mathrm{C}(5)-\mathrm{C}(4)$ | $1.354(11)$ |
| $\mathrm{Si}(3)-\mathrm{C}(37)$ | $1.888(9)$ | $\mathrm{C}(5)-\mathrm{C}(31)$ | $1.540(12)$ |
| $\mathrm{Si}(4)-\mathrm{C}(19)$ | $1.859(8)$ | $\mathrm{C}(3)-\mathrm{C}(2)$ | $1.346(10)$ |
| $\mathrm{Si}(4)-\mathrm{C}(20)$ | $1.862(8)$ | $\mathrm{C}(3)-\mathrm{C}(4)$ | $1.383(11)$ |
| $\mathrm{Si}(4)-\mathrm{C}(18)$ | $1.871(10)$ | $\mathrm{C}(3)-\mathrm{H}(3)$ | 1.9300 |
| $\mathrm{Si}(4)-\mathrm{C}(12)$ | $1.892(9)$ | $\mathrm{C}(2)-\mathrm{C}(1)$ | 0.9300 |
| $\mathrm{O}(6)-\mathrm{C}(30)$ | $1.437(9)$ | 0.9300 |  |
| $\mathrm{O}(6)-\mathrm{C}(31)$ | $1.470(8)$ | $\mathrm{C}(8)-\mathrm{H}(8)$ | $1.502(13)$ |
| $\mathrm{O}(5)-\mathrm{C}(11)$ | $\mathrm{C}(33)-\mathrm{C}(34)$ | $1.557(11)$ |  |
| $\mathrm{O}(5)-\mathrm{C}(12)$ | $\mathrm{C}(33)-\mathrm{C}(32)$ | 0.9800 |  |
| $\mathrm{C}(13)-\mathrm{C}(15)$ | $1.458(8)$ | $1.529(11)$ |  |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.561(9)$ | 0.9600 |  |
| $\mathrm{C}(13)-\mathrm{C}(11)$ | $1.544(11)$ | $\mathrm{C}(29)-\mathrm{C}(33)$ | 0.9600 |
| $\mathrm{C}(13)-\mathrm{H}(13)$ | $1.594(11)$ | $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(11)-\mathrm{C}(10)$ | 0.9800 | $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(10)-\mathrm{C}(9)$ | $1.517(11)$ | $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(10)-\mathrm{C}(1)$ | $1.386(11)$ | $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | $1.525(11)$ |
| $\mathrm{C}(12)-\mathrm{C}(9)$ | $1.425(12)$ | $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~B})$ |  |
| $\mathrm{C}(12)-\mathrm{C}(14)$ | $1.508(12)$ | $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | $\mathrm{C}(28)$ |
|  | $1.583(11)$ |  |  |


| $\mathrm{C}(24)-\mathrm{C}(27)$ | 1.540(11) | $\mathrm{N}(1)-\mathrm{C}(15)$ | 1.372(11) |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 0.9600 | C(46)-C(43) | $1.445(15)$ |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(46)-\mathrm{H}(46 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 0.9600 | $\mathrm{C}(46)-\mathrm{H}(46 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(46)-\mathrm{H}(46 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~B})$ | 0.9600 | C(43)-C(47) | 1.523(14) |
| $\mathrm{C}(27)-\mathrm{H}(27 \mathrm{C})$ | 0.9600 | $\mathrm{C}(47)-\mathrm{H}(47 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(32)-\mathrm{C}(35)$ | 1.504(12) | $\mathrm{C}(47)-\mathrm{H}(47 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(32)-\mathrm{C}(31)$ | 1.568(11) | $\mathrm{C}(47)-\mathrm{H}(47 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(32)-\mathrm{H}(32)$ | 0.9800 | $\mathrm{C}(21)-\mathrm{C}(18)$ | $1.507(11)$ |
| $\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(28)-\mathrm{H}(28 \mathrm{C})$ | 0.9600 | $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(18)-\mathrm{C}(22)$ | $1.506(11)$ |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(18)-\mathrm{C}(23)$ | $1.517(11)$ |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{C})$ | 0.9600 | $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{C})$ | 0.9600 | $\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(23)-\mathrm{H}(23 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(38)-\mathrm{H}(38 \mathrm{C})$ | 0.9600 | $\mathrm{C}(40)-\mathrm{H}(40 \mathrm{~A})$ | 0.9600 |
| C(37)-C(40) | 1.494(11) | $\mathrm{C}(40)-\mathrm{H}(40 \mathrm{~B})$ | 0.9600 |
| $\mathrm{C}(37)-\mathrm{C}(42)$ | 1.529(11) | $\mathrm{C}(40)-\mathrm{H}(40 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(37)-\mathrm{C}(41)$ | 1.530(11) | $\mathrm{C}(15)-\mathrm{O}(1)$ | 1.184(12) |
| $\mathrm{C}(42)-\mathrm{H}(42 \mathrm{~A})$ | 0.9600 | $\mathrm{O}(2)-\mathrm{C}(34)$ | $1.186(10)$ |
| $\mathrm{C}(42)-\mathrm{H}(42 \mathrm{~B})$ | 0.9600 | $\mathrm{N}(2)-\mathrm{C}(35)$ | $1.389(11)$ |
| $\mathrm{C}(42)-\mathrm{H}(42 \mathrm{C})$ | 0.9600 | $\mathrm{N}(2)-\mathrm{C}(34)$ | 1.393(11) |
| $\mathrm{C}(41)-\mathrm{H}(41 \mathrm{~A})$ | 0.9600 | $\mathrm{N}(2)-\mathrm{C}(36)$ | $1.455(10)$ |
| $\mathrm{C}(41)-\mathrm{H}(41 \mathrm{~B})$ | 0.9600 | $\mathrm{O}(8)-\mathrm{C}(35)$ | $1.206(10)$ |
| $\mathrm{C}(41)-\mathrm{H}(41 \mathrm{C})$ | 0.9600 | $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 0.9600 |
| $\mathrm{C}(39)-\mathrm{H}(39 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~B})$ | 0.9600 |
| C(39)-H(39B) | 0.9600 | $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 0.9600 |
| $\mathrm{C}(39)-\mathrm{H}(39 \mathrm{C})$ | 0.9600 |  |  |
| $\mathrm{C}(48)-\mathrm{C}(43)$ | 1.514(11) | $\mathrm{C}(44)-\mathrm{Si}(1)-\mathrm{C}(45)$ | 109.4(6) |
| $\mathrm{C}(48)-\mathrm{H}(48 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(44)-\mathrm{Si}(1)-\mathrm{C}(43)$ | 111.4(5) |
| $\mathrm{C}(48)-\mathrm{H}(48 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(45)-\mathrm{Si}(1)-\mathrm{C}(43)$ | 108.4(5) |
| $\mathrm{C}(48)-\mathrm{H}(48 \mathrm{C})$ | 0.9600 | $\mathrm{C}(44)-\mathrm{Si}(1)-\mathrm{C}(30)$ | 109.9(5) |
| $\mathrm{C}(44)-\mathrm{H}(44 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(45)-\mathrm{Si}(1)-\mathrm{C}(30)$ | 105.5(5) |
| $\mathrm{C}(44)-\mathrm{H}(44 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(43)-\mathrm{Si}(1)-\mathrm{C}(30)$ | 112.0(4) |
| $\mathrm{C}(44)-\mathrm{H}(44 \mathrm{C})$ | 0.9600 | $\mathrm{C}(26)-\mathrm{Si}(2)-\mathrm{C}(25)$ | 111.9(4) |
| $\mathrm{C}(45)-\mathrm{H}(45 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(26)-\mathrm{Si}(2)-\mathrm{C}(24)$ | 108.7(4) |
| $\mathrm{C}(45)-\mathrm{H}(45 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(25)-\mathrm{Si}(2)-\mathrm{C}(24)$ | 108.5(4) |
| $\mathrm{C}(45)-\mathrm{H}(45 \mathrm{C})$ | 0.9600 | $\mathrm{C}(26)-\mathrm{Si}(2)-\mathrm{C}(11)$ | 107.4(4) |
| $\mathrm{C}(16)-\mathrm{O}(3)$ | $1.230(11)$ | $\mathrm{C}(25)-\mathrm{Si}(2)-\mathrm{C}(11)$ | 109.9(4) |
| $\mathrm{C}(16)-\mathrm{N}(1)$ | 1.367(12) | $\mathrm{C}(24)-\mathrm{Si}(2)-\mathrm{C}(11)$ | 110.5(4) |
| $\mathrm{C}(17)-\mathrm{N}(1)$ | 1.471(11) | $\mathrm{C}(39)-\mathrm{Si}(3)-\mathrm{C}(38)$ | 108.3(4) |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 0.9600 | $\mathrm{C}(39)-\mathrm{Si}(3)-\mathrm{C}(31)$ | 102.7(4) |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 0.9600 | $\mathrm{C}(38)-\mathrm{Si}(3)-\mathrm{C}(31)$ | 110.8(4) |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 0.9600 | $\mathrm{C}(39)-\mathrm{Si}(3)-\mathrm{C}(37)$ | 109.8(4) |


| $\mathrm{C}(38)-\mathrm{Si}(3)-\mathrm{C}(37)$ | 111.3(4) | $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(1)$ | 117.0(13) |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(31)-\mathrm{Si}(3)-\mathrm{C}(37)$ | 113.5(4) | $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(1)$ | 120.1(11) |
| $\mathrm{C}(19)-\mathrm{Si}(4)-\mathrm{C}(20)$ | 109.0(4) | $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 120.0(9) |
| $\mathrm{C}(19)-\mathrm{Si}(4)-\mathrm{C}(18)$ | 109.9(4) | $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(31)$ | 107.1(12) |
| $\mathrm{C}(20)-\mathrm{Si}(4)-\mathrm{C}(18)$ | 110.5(4) | $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(31)$ | 132.5(13) |
| $\mathrm{C}(19)-\mathrm{Si}(4)-\mathrm{C}(12)$ | 110.9(4) | $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 120.4(8) |
| $\mathrm{C}(20)-\mathrm{Si}(4)-\mathrm{C}(12)$ | 104.3(4) | $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{H}(3)$ | 119.8 |
| $\mathrm{C}(18)-\mathrm{Si}(4)-\mathrm{C}(12)$ | 112.1(4) | $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{H}(3)$ | 119.8 |
| $\mathrm{C}(30)-\mathrm{O}(6)-\mathrm{C}(31)$ | 101.3(5) | $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(1)$ | 122.1(9) |
| $\mathrm{C}(11)-\mathrm{O}(5)-\mathrm{C}(12)$ | 100.5(5) | $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2)$ | 118.9 |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(14)$ | 105.2(8) | $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2)$ | 118.9 |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(11)$ | 114.0(8) | $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | 120.7(9) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(11)$ | 102.8(7) | $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(30)$ | 106.9(12) |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{H}(13)$ | 111.4 | $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(30)$ | 132.2(14) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{H}(13)$ | 111.4 | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 117.9(8) |
| $\mathrm{C}(11)-\mathrm{C}(13)-\mathrm{H}(13)$ | 111.4 | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8)$ | 121.0 |
| $\mathrm{O}(5)-\mathrm{C}(11)-\mathrm{C}(10)$ | 99.5(8) | $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8)$ | 121.0 |
| $\mathrm{O}(5)-\mathrm{C}(11)-\mathrm{C}(13)$ | 98.2(7) | $\mathrm{C}(34)-\mathrm{C}(33)-\mathrm{C}(32)$ | 106.7(8) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(13)$ | 104.3(6) | $\mathrm{C}(34)-\mathrm{C}(33)-\mathrm{C}(30)$ | 115.0(8) |
| $\mathrm{O}(5)-\mathrm{C}(11)-\mathrm{Si}(2)$ | 106.2(6) | $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(30)$ | 102.3(7) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{Si}(2)$ | 125.6(8) | $\mathrm{C}(34)-\mathrm{C}(33)-\mathrm{H}(33)$ | 110.8 |
| $\mathrm{C}(13)-\mathrm{C}(11)-\mathrm{Si}(2)$ | 118.0(6) | $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{H}(33)$ | 110.8 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(1)$ | 121.9(9) | $\mathrm{C}(30)-\mathrm{C}(33)-\mathrm{H}(33)$ | 110.8 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 107.2(11) | $\mathrm{C}(24)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(10)-\mathrm{C}(11)$ | 130.1(13) | $\mathrm{C}(24)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(5)-\mathrm{C}(12)-\mathrm{C}(9)$ | 101.8(7) | $\mathrm{H}(29 \mathrm{~A})-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(5)-\mathrm{C}(12)-\mathrm{C}(14)$ | 98.6(7) | $\mathrm{C}(24)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(9)-\mathrm{C}(12)-\mathrm{C}(14)$ | 102.8(7) | $\mathrm{H}(29 \mathrm{~A})-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(5)-\mathrm{C}(12)-\mathrm{Si}(4)$ | 108.6(6) | $\mathrm{H}(29 \mathrm{~B})-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(9)-\mathrm{C}(12)-\mathrm{Si}(4)$ | 125.3(8) | $\mathrm{Si}(2)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(14)-\mathrm{C}(12)-\mathrm{Si}(4)$ | 115.7(6) | $\mathrm{Si}(2)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(16)-\mathrm{C}(14)-\mathrm{C}(13)$ | 104.2(9) | $\mathrm{H}(25 \mathrm{~A})-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(16)-\mathrm{C}(14)-\mathrm{C}(12)$ | 117.0(8) | $\mathrm{Si}(2)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(12)$ | 102.7(8) | $\mathrm{H}(25 \mathrm{~A})-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(16)-\mathrm{C}(14)-\mathrm{H}(14)$ | 110.8 | $\mathrm{H}(25 \mathrm{~B})-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14)$ | 110.8 | $\mathrm{C}(28)-\mathrm{C}(24)-\mathrm{C}(29)$ | 109.7(8) |
| $\mathrm{C}(12)-\mathrm{C}(14)-\mathrm{H}(14)$ | 110.8 | $\mathrm{C}(28)-\mathrm{C}(24)-\mathrm{C}(27)$ | 107.9(7) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | 119.8(9) | $\mathrm{C}(29)-\mathrm{C}(24)-\mathrm{C}(27)$ | 108.1(7) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(12)$ | 105.7(11) | $\mathrm{C}(28)-\mathrm{C}(24)-\mathrm{Si}(2)$ | 112.2(6) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(12)$ | 134.2(12) | $\mathrm{C}(29)-\mathrm{C}(24)-\mathrm{Si}(2)$ | 112.2(6) |
| $\mathrm{O}(6)-\mathrm{C}(30)-\mathrm{C}(4)$ | 101.3(7) | $\mathrm{C}(27)-\mathrm{C}(24)-\mathrm{Si}(2)$ | 106.6(6) |
| $\mathrm{O}(6)-\mathrm{C}(30)-\mathrm{C}(33)$ | 96.5(7) | $\mathrm{Si}(2)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(4)-\mathrm{C}(30)-\mathrm{C}(33)$ | 105.2(6) | $\mathrm{Si}(2)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(6)-\mathrm{C}(30)-\mathrm{Si}(1)$ | 109.5(7) | H(26A)-C(26)-H(26B) | 109.5 |
| $\mathrm{C}(4)-\mathrm{C}(30)-\mathrm{Si}(1)$ | 125.1(8) | $\mathrm{Si}(2)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(33)-\mathrm{C}(30)-\mathrm{Si}(1)$ | 114.8(6) | $\mathrm{H}(26 \mathrm{~A})-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(6)$ | 124.7(10) | $\mathrm{H}(26 \mathrm{~B})-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7)$ | 117.6 | $\mathrm{C}(24)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7)$ | 117.6 | $\mathrm{C}(24)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(5)$ | 122.8(13) | $\mathrm{H}(27 \mathrm{~A})-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~B})$ | 109.5 |


| $\mathrm{C}(24)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{C})$ | 109.5 | $\mathrm{H}(42 \mathrm{~B})-\mathrm{C}(42)-\mathrm{H}(42 \mathrm{C})$ | 109.5 |
| :---: | :---: | :---: | :---: |
| $\mathrm{H}(27 \mathrm{~A})-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{C})$ | 109.5 | $\mathrm{C}(37)-\mathrm{C}(41)-\mathrm{H}(41 \mathrm{~A})$ | 109.5 |
| $\mathrm{H}(27 \mathrm{~B})-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{C})$ | 109.5 | $\mathrm{C}(37)-\mathrm{C}(41)-\mathrm{H}(41 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(35)-\mathrm{C}(32)-\mathrm{C}(33)$ | 104.3(8) | $\mathrm{H}(41 \mathrm{~A})-\mathrm{C}(41)-\mathrm{H}(41 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(35)-\mathrm{C}(32)-\mathrm{C}(31)$ | 116.1(8) | $\mathrm{C}(37)-\mathrm{C}(41)-\mathrm{H}(41 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{C}(31)$ | 102.7(7) | $\mathrm{H}(41 \mathrm{~A})-\mathrm{C}(41)-\mathrm{H}(41 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(35)-\mathrm{C}(32)-\mathrm{H}(32)$ | 111.1 | $\mathrm{H}(41 \mathrm{~B})-\mathrm{C}(41)-\mathrm{H}(41 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{H}(32)$ | 111.1 | $\mathrm{Si}(3)-\mathrm{C}(39)-\mathrm{H}(39 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{H}(32)$ | 111.1 | Si(3)-C(39)-H(39B) | 109.5 |
| $\mathrm{C}(24)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~A})$ | 109.5 | H(39A)-C(39)-H(39B) | 109.5 |
| $\mathrm{C}(24)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 109.5 | $\mathrm{Si}(3)-\mathrm{C}(39)-\mathrm{H}(39 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(28 \mathrm{~A})-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 109.5 | H(39A)-C(39)-H(39C) | 109.5 |
| $\mathrm{C}(24)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{C})$ | 109.5 | H(39B)-C(39)-H(39C) | 109.5 |
| $\mathrm{H}(28 \mathrm{~A})-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{C})$ | 109.5 | $\mathrm{C}(43)-\mathrm{C}(48)-\mathrm{H}(48 \mathrm{~A})$ | 109.5 |
| $\mathrm{H}(28 \mathrm{~B})-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{C})$ | 109.5 | $\mathrm{C}(43)-\mathrm{C}(48)-\mathrm{H}(48 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(6)-\mathrm{C}(31)-\mathrm{C}(5)$ | 97.9(8) | $\mathrm{H}(48 \mathrm{~A})-\mathrm{C}(48)-\mathrm{H}(48 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(6)-\mathrm{C}(31)-\mathrm{C}(32)$ | 99.3(7) | $\mathrm{C}(43)-\mathrm{C}(48)-\mathrm{H}(48 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(31)-\mathrm{C}(32)$ | 103.3(6) | $\mathrm{H}(48 \mathrm{~A})-\mathrm{C}(48)-\mathrm{H}(48 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(6)-\mathrm{C}(31)-\mathrm{Si}(3)$ | 105.0(6) | H(48B)-C(48)-H(48C) | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(31)-\mathrm{Si}(3)$ | 130.3(8) | $\mathrm{Si}(1)-\mathrm{C}(44)-\mathrm{H}(44 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{Si}(3)$ | 115.4(6) | $\mathrm{Si}(1)-\mathrm{C}(44)-\mathrm{H}(44 \mathrm{~B})$ | 109.5 |
| $\mathrm{Si}(4)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 109.5 | $\mathrm{H}(44 \mathrm{~A})-\mathrm{C}(44)-\mathrm{H}(44 \mathrm{~B})$ | 109.5 |
| $\mathrm{Si}(4)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 109.5 | $\mathrm{Si}(1)-\mathrm{C}(44)-\mathrm{H}(44 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{~A})-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 109.5 | $\mathrm{H}(44 \mathrm{~A})-\mathrm{C}(44)-\mathrm{H}(44 \mathrm{C})$ | 109.5 |
| $\mathrm{Si}(4)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{C})$ | 109.5 | H(44B)-C(44)-H(44C) | 109.5 |
| $\mathrm{H}(20 \mathrm{~A})-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{C})$ | 109.5 | $\mathrm{Si}(1)-\mathrm{C}(45)-\mathrm{H}(45 \mathrm{~A})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{~B})-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{C})$ | 109.5 | $\mathrm{Si}(1)-\mathrm{C}(45)-\mathrm{H}(45 \mathrm{~B})$ | 109.5 |
| Si(4)-C(19)-H(19A) | 109.5 | $\mathrm{H}(45 \mathrm{~A})-\mathrm{C}(45)-\mathrm{H}(45 \mathrm{~B})$ | 109.5 |
| $\mathrm{Si}(4)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~B})$ | 109.5 | $\mathrm{Si}(1)-\mathrm{C}(45)-\mathrm{H}(45 \mathrm{C})$ | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 | $\mathrm{H}(45 \mathrm{~A})-\mathrm{C}(45)-\mathrm{H}(45 \mathrm{C})$ | 109.5 |
| $\mathrm{Si}(4)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{C})$ | 109.5 | $\mathrm{H}(45 \mathrm{~B})-\mathrm{C}(45)-\mathrm{H}(45 \mathrm{C})$ | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 | $\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{N}(1)$ | 125.5(11) |
| $\mathrm{H}(19 \mathrm{~B})-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{C})$ | 109.5 | $\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(14)$ | 125.7(13) |
| $\mathrm{Si}(3)-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~A})$ | 109.5 | $\mathrm{N}(1)-\mathrm{C}(16)-\mathrm{C}(14)$ | 108.7(10) |
| $\mathrm{Si}(3)-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~B})$ | 109.5 | $\mathrm{N}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 109.5 |
| $\mathrm{H}(38 \mathrm{~A})-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~B})$ | 109.5 | $\mathrm{N}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 109.5 |
| $\mathrm{Si}(3)-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{C})$ | 109.5 | H(17A)-C(17)-H(17B) | 109.5 |
| $\mathrm{H}(38 \mathrm{~A})-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{C})$ | 109.5 | $\mathrm{N}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(38 \mathrm{~B})-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{C})$ | 109.5 | $\mathrm{H}(17 \mathrm{~A})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(40)-\mathrm{C}(37)-\mathrm{C}(42)$ | 108.6(7) | $\mathrm{H}(17 \mathrm{~B})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(40)-\mathrm{C}(37)-\mathrm{C}(41)$ | 108.0(8) | $\mathrm{C}(16)-\mathrm{N}(1)-\mathrm{C}(15)$ | 115.0(10) |
| $\mathrm{C}(42)-\mathrm{C}(37)-\mathrm{C}(41)$ | 106.7(7) | $\mathrm{C}(16)-\mathrm{N}(1)-\mathrm{C}(17)$ | 120.7(11) |
| $\mathrm{C}(40)-\mathrm{C}(37)-\mathrm{Si}(3)$ | 111.7(6) | $\mathrm{C}(15)-\mathrm{N}(1)-\mathrm{C}(17)$ | 124.3(11) |
| $\mathrm{C}(42)-\mathrm{C}(37)-\mathrm{Si}(3)$ | 107.3(6) | $\mathrm{C}(43)-\mathrm{C}(46)-\mathrm{H}(46 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(41)-\mathrm{C}(37)-\mathrm{Si}(3)$ | 114.3(6) | $\mathrm{C}(43)-\mathrm{C}(46)-\mathrm{H}(46 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(37)-\mathrm{C}(42)-\mathrm{H}(42 \mathrm{~A})$ | 109.5 | $\mathrm{H}(46 \mathrm{~A})-\mathrm{C}(46)-\mathrm{H}(46 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(37)-\mathrm{C}(42)-\mathrm{H}(42 \mathrm{~B})$ | 109.5 | $\mathrm{C}(43)-\mathrm{C}(46)-\mathrm{H}(46 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(42 \mathrm{~A})-\mathrm{C}(42)-\mathrm{H}(42 \mathrm{~B})$ | 109.5 | $\mathrm{H}(46 \mathrm{~A})-\mathrm{C}(46)-\mathrm{H}(46 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(37)-\mathrm{C}(42)-\mathrm{H}(42 \mathrm{C})$ | 109.5 | $\mathrm{H}(46 \mathrm{~B})-\mathrm{C}(46)-\mathrm{H}(46 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(42 \mathrm{~A})-\mathrm{C}(42)-\mathrm{H}(42 \mathrm{C})$ | 109.5 | $\mathrm{C}(46)-\mathrm{C}(43)-\mathrm{C}(48)$ | 107.7(9) |


| $\mathrm{C}(46)-\mathrm{C}(43)-\mathrm{C}(47)$ | $111.6(13)$ | $\mathrm{H}(23 \mathrm{~A})-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~B})$ | 109.5 |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(48)-\mathrm{C}(43)-\mathrm{C}(47)$ | $102.9(9)$ | $\mathrm{C}(18)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(46)-\mathrm{C}(43)-\mathrm{Si}(1)$ | $113.9(8)$ | $\mathrm{H}(23 \mathrm{~A})-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(48)-\mathrm{C}(43)-\mathrm{Si}(1)$ | $111.3(7)$ | $\mathrm{H}(23 \mathrm{~B})-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(47)-\mathrm{C}(43)-\mathrm{Si}(1)$ | $108.8(7)$ | $\mathrm{C}(37)-\mathrm{C}(40)-\mathrm{H}(40 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(43)-\mathrm{C}(47)-\mathrm{H}(47 \mathrm{~A})$ | 109.5 | $\mathrm{C}(37)-\mathrm{C}(40)-\mathrm{H}(40 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(43)-\mathrm{C}(47)-\mathrm{H}(47 \mathrm{~B})$ | 109.5 | $\mathrm{H}(40 \mathrm{~A})-\mathrm{C}(40)-\mathrm{H}(40 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(47 \mathrm{~A})-\mathrm{C}(47)-\mathrm{H}(47 \mathrm{~B})$ | 109.5 | $\mathrm{C}(37)-\mathrm{C}(40)-\mathrm{H}(40 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(43)-\mathrm{C}(47)-\mathrm{H}(47 \mathrm{C})$ | 109.5 | $\mathrm{H}(40 \mathrm{~A})-\mathrm{C}(40)-\mathrm{H}(40 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(47 \mathrm{~A})-\mathrm{C}(47)-\mathrm{H}(47 \mathrm{C})$ | 109.5 | $\mathrm{H}(40 \mathrm{~B})-\mathrm{C}(40)-\mathrm{H}(40 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(47 \mathrm{~B})-\mathrm{C}(47)-\mathrm{H}(47 \mathrm{C})$ | 109.5 | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{N}(1)$ | $124.7(12)$ |
| $\mathrm{C}(18)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 109.5 | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(13)$ | $128.5(12)$ |
| $\mathrm{C}(18)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 109.5 | $\mathrm{~N}(1)-\mathrm{C}(15)-\mathrm{C}(13)$ | $106.7(11)$ |
| $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 109.5 | $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(10)$ | $126.6(13)$ |
| $\mathrm{C}(18)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 109.5 | $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | $116.1(12)$ |
| $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 109.5 | $\mathrm{C}(10)-\mathrm{C}(1)-\mathrm{C}(6)$ | $117.3(12)$ |
| $\mathrm{H}(21 \mathrm{~B})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{C})$ | 109.5 | $\mathrm{C}(35)-\mathrm{N}(2)-\mathrm{C}(34)$ | $116.3(8)$ |
| $\mathrm{C}(22)-\mathrm{C}(18)-\mathrm{C}(21)$ | $107.8(8)$ | $\mathrm{C}(35)-\mathrm{N}(2)-\mathrm{C}(36)$ | $121.8(10)$ |
| $\mathrm{C}(22)-\mathrm{C}(18)-\mathrm{C}(23)$ | $107.7(8)$ | $\mathrm{C}(34)-\mathrm{N}(2)-\mathrm{C}(36)$ | $121.9(10)$ |
| $\mathrm{C}(21)-\mathrm{C}(18)-\mathrm{C}(23)$ | $107.0(8)$ | $\mathrm{O}(2)-\mathrm{C}(34)-\mathrm{N}(2)$ | $123.1(11)$ |
| $\mathrm{C}(22)-\mathrm{C}(18)-\mathrm{Si}(4)$ | $112.8(7)$ | $\mathrm{O}(2)-\mathrm{C}(34)-\mathrm{C}(33)$ | $131.7(11)$ |
| $\mathrm{C}(21)-\mathrm{C}(18)-\mathrm{Si}(4)$ | $\mathrm{N}(2)-\mathrm{C}(34)-\mathrm{C}(33)$ | $105.1(9)$ |  |
| $\mathrm{C}(23)-\mathrm{C}(18)-\mathrm{Si}(4)$ | $\mathrm{N}(2)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 109.5 |  |
| $\mathrm{C}(18)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | $111.7(7)$ | $\mathrm{N}(2)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(18)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 109.5 | $\mathrm{H}(36 \mathrm{~A})-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 109.5 | $\mathrm{~N}(2)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(18)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 | $\mathrm{H}(36 \mathrm{~A})-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 | $\mathrm{H}(36 \mathrm{~B})-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~B})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 | $\mathrm{O}(8)-\mathrm{C}(35)-\mathrm{N}(2)$ | $125.5(11)$ |
| $\mathrm{C}(18)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 109.5 | $\mathrm{O}(8)-\mathrm{C}(35)-\mathrm{C}(32)$ | $127.5(11)$ |
| $\mathrm{C}(18)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~B})$ | 109.5 | $\mathrm{~N}(2)-\mathrm{C}(35)-\mathrm{C}(32)$ | $106.9(1$ |

Symmetry transformations used to generate equivalent atoms:

Table A4- 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 50.

| Atom | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Si}(1)$ | $33(2)$ | $36(2)$ | $39(2)$ | $-3(2)$ | $3(2)$ | $5(2)$ |
| $\mathrm{Si}(2)$ | $29(2)$ | $39(2)$ | $34(2)$ | $6(2)$ | $3(1)$ | $-2(1)$ |
| $\mathrm{Si}(3)$ | $26(2)$ | $25(2)$ | $37(2)$ | $4(1)$ | $6(1)$ | $0(1)$ |
| $\mathrm{Si}(4)$ | $26(2)$ | $33(2)$ | $36(2)$ | $5(2)$ | $1(1)$ | $7(2)$ |
| $\mathrm{O}(6)$ | $16(4)$ | $11(3)$ | $29(4)$ | $5(3)$ | $8(3)$ | $-5(4)$ |
| $\mathrm{O}(5)$ | $18(4)$ | $22(4)$ | $29(4)$ | $7(3)$ | $-1(3)$ | $6(3)$ |
| $\mathrm{C}(13)$ | $47(9)$ | $30(7)$ | $30(7)$ | $10(6)$ | $-9(8)$ | $-29(6)$ |
| $\mathrm{C}(11)$ | $14(7)$ | $17(7)$ | $23(6)$ | $-5(6)$ | $-9(5)$ | $-5(5)$ |
| $\mathrm{C}(10)$ | $18(9)$ | $12(8)$ | $24(8)$ | $20(7)$ | $-20(8)$ | $5(7)$ |



| $\mathrm{C}(35)$ | $22(10)$ | $16(12)$ | $42(7)$ | $17(7)$ | $-12(7)$ | $-24(8)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Table A4- 5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 50.

| Atom | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | :--- |
|  |  |  |  |  |
|  |  |  | 1544 | 43 |
| $\mathrm{H}(13)$ | 3515 | 4441 | 1225 | 40 |
| H(14) | 5182 | 4261 | 542 | 31 |
| H(7) | 4670 | 8766 | 1460 | 37 |
| H(3) | 745 | 8821 | 1617 | 24 |
| H(2) | 1853 | 7421 | 682 | 27 |
| H(8) | 5888 | 7403 | 390 | 31 |
| H(33) | 505 | 10901 | 2877 | 67 |
| H(29A) | 5450 | 5358 | 2771 | 67 |
| H(29B) | 4969 | 6483 | 2446 | 67 |
| H(29C) | 5602 | 5815 | 2238 | 63 |
| H(25A) | 2534 | 7885 | 2306 | 63 |
| H(25B) | 3848 | 7855 | 2648 | 63 |
| H(25C) | 3024 | 7503 | 2271 | 56 |
| H(26A) | 1218 | 5952 | 2192 | 56 |
| H(26B) | 1743 | 4828 | 1835 | 56 |
| H(26C) | 1530 | 5607 | 3127 | 76 |
| H(27A) | 3621 | 4822 | 2854 | 76 |
| H(27B) | 2542 | 4813 | 3011 | 76 |
| H(27C) | 3029 | 5892 | 45 | 37 |
| H(32) | 2092 | 10495 | 2180 | 73 |
| H(28A) | 4732 | 4177 | 2298 | 73 |
| H(28B) | 3493 | 3858 | 7606 | 73 |
| H(28C) | 4481 | 3720 | 60 |  |
| H(20A) | 8084 | 4280 | 1718 | 60 |
| H(20B) | 6892 | 3874 | 1579 | 60 |
| H(20C) | 6991 | 4620 | 1951 | 60 |
| H(19A) | 7649 | 5922 | 691 | 65 |
| H(19B) | 7306 | 4731 | 752 | 65 |
| H(19C) | 8508 | 5126 | 885 | 65 |
| H(38A) | 5547 | 9946 | 80 | 53 |
| H(38B) | 5103 | 10789 | -226 | 53 |
| H(38C) | 4354 | 9802 | -118 | 53 |
| H(42A) | 5806 | 12838 | 542 | 64 |
| H(42B) | 6447 | 11859 | 362 | 64 |
| H(42C) | 6780 | 12290 | 784 | 64 |
| H(41A) | 6479 | 10715 | 1159 | 65 |
| H(41B) | 6384 | 10153 | 744 | 65 |
| H(41C) | 5447 | 9970 | 1068 | 65 |
| H(39A) | 3116 | 12134 | -34 | 46 |
| H(39B) | 4185 | 12777 | 102 | 46 |
|  |  | 143 |  |  |
|  |  |  |  |  |


| H(39C) | 3146 | 12659 | 389 | 46 |
| :---: | :---: | :---: | :---: | :---: |
| H(48A) | 431 | 12592 | 2238 | 91 |
| H(48B) | -572 | 12270 | 1956 | 91 |
| H(48C) | 187 | 13253 | 1851 | 91 |
| H(44A) | -919 | 10193 | 1472 | 122 |
| H(44B) | -1312 | 10622 | 1056 | 122 |
| H(44C) | -1525 | 11297 | 1441 | 122 |
| H(45A) | -193 | 12491 | 693 | 119 |
| H(45B) | 888 | 12986 | 891 | 119 |
| H(45C) | -308 | 13169 | 1082 | 119 |
| H(17A) | 3045 | 6110 | 224 | 64 |
| H(17B) | 2044 | 5352 | 340 | 64 |
| H(17C) | 3121 | 4895 | 127 | 64 |
| H(46A) | 2023 | 12873 | 1480 | 278 |
| H(46B) | 2638 | 11868 | 1651 | 278 |
| H(46C) | 2207 | 12755 | 1941 | 278 |
| H(47A) | 1743 | 10481 | 1932 | 232 |
| H(47B) | 417 | 10408 | 1947 | 232 |
| H(47C) | 1072 | 11068 | 2270 | 232 |
| H(21A) | 7472 | 6513 | 2153 | 86 |
| H(21B) | 6709 | 7374 | 1949 | 86 |
| H(21C) | 7935 | 7668 | 2091 | 86 |
| H(22A) | 7126 | 7978 | 1272 | 94 |
| H(22B) | 8238 | 7598 | 1060 | 94 |
| $\mathrm{H}(22 \mathrm{C})$ | 8312 | 8335 | 1435 | 94 |
| H(23A) | 9564 | 7094 | 1757 | 82 |
| H(23B) | 9506 | 6339 | 1386 | 82 |
| H(23C) | 9217 | 5902 | 1812 | 82 |
| H(40A) | 4264 | 11504 | 1276 | 74 |
| H(40B) | 4339 | 12583 | 1045 | 74 |
| H(40C) | 5343 | 12222 | 1319 | 74 |
| H(36A) | 992 | 7107 | 64 | 56 |
| H(36B) | -246 | 7419 | 187 | 56 |
| H(36C) | 633 | 7079 | 514 | 56 |

Table A5- 1. Crystal data and structure refinement for $\mathbf{8 4 a}$

| Identification code | 84a |
| :---: | :---: |
| Empirical formula | C23 H20 O6 |
| Formula weight | 392.39 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{c}$ |
| Unit cell dimensions | $a=14.2500(13) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=7.8987(7) \AA \quad \beta=95.7520(10)^{\circ}$. |
|  | $\mathrm{c}=16.1812(15) \AA \quad \gamma=90^{\circ}$. |
| Volume | 1812.1(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.438 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.104 \mathrm{~mm}^{-1}$ |
| F(000) | 824 |
| Crystal size | $0.33 \times 0.19 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.53 to $27.42^{\circ}$. |
| Index ranges | $-18<=\mathrm{h}<=18,-10<=\mathrm{k}<=10,-20<=1<=20$ |
| Reflections collected | 19966 |
| Independent reflections | $4116[\mathrm{R}(\mathrm{int})=0.0484]$ |
| Completeness to theta $=25.25^{\circ}$ | 99.9 \% |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4116 / 0 / 283 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.037 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0579, \mathrm{wR} 2=0.1490$ |
| R indices (all data) | $\mathrm{R} 1=0.0981, \mathrm{wR} 2=0.1744$ |
| Largest diff. peak and hole | 0.603 and -0.218 e. $\AA^{-3}$ |

Table A5- 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{8 4 a}$. U(eq) is defined as one third of the trace of the orthogonalized $\mathrm{U}^{i j}$ tensor.

| Atom | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | ---: |
|  |  |  |  |  |
| $\mathrm{O}(1)$ | $263(1)$ | $1276(2)$ | $8254(1)$ | $45(1)$ |
| $\mathrm{O}(2)$ | $4691(1)$ | $837(2)$ | $11773(1)$ | $43(1)$ |
| $\mathrm{O}(3)$ | $2692(1)$ | $4937(2)$ | $12154(1)$ | $53(1)$ |
| O(4) | $2252(1)$ | $5394(3)$ | $8002(1)$ | $60(1)$ |
| C(5) | $2446(1)$ | $1937(2)$ | $9584(1)$ | $27(1)$ |
| C(6) | $2515(1)$ | $1773(2)$ | $10472(1)$ | $26(1)$ |
| C(7) | $3439(1)$ | $1679(3)$ | $10876(1)$ | $28(1)$ |
| C(8) | $4225(1)$ | $1787(3)$ | $10454(1)$ | $30(1)$ |
| C(10) | $3274(2)$ | $2033(3)$ | $9168(1)$ | $34(1)$ |
| C(12) | $3807(2)$ | $1705(3)$ | $11787(1)$ | $36(1)$ |
| C(19) | $3358(2)$ | $4785(3)$ | $11760(1)$ | $40(1)$ |
| C(9) | $4159(1)$ | $1984(3)$ | $9593(1)$ | $33(1)$ |
| C(11) | $5041(2)$ | $1863(3)$ | $11129(1)$ | $39(1)$ |
| C(14) | $4148(2)$ | $3557(3)$ | $11987(1)$ | $41(1)$ |
| C(13) | $5045(2)$ | $3629(3)$ | $11523(2)$ | $47(1)$ |
| C(1) | $1692(1)$ | $1720(3)$ | $10894(1)$ | $31(1)$ |
| C(2) | $809(1)$ | $1836(3)$ | $10475(1)$ | $31(1)$ |
| C(4) | $1525(1)$ | $1976(3)$ | $9180(1)$ | $29(1)$ |
| C(18) | $789(2)$ | $4031(3)$ | $8152(1)$ | $40(1)$ |
| C(3) | $738(1)$ | $1950(2)$ | $9607(1)$ | $30(1)$ |
| C(15) | $1147(2)$ | $2165(3)$ | $8275(1)$ | $37(1)$ |
| C(17) | $-87(2)$ | $4009(3)$ | $8644(2)$ | $42(1)$ |
| C(16) | $-84(2)$ | $2158(3)$ | $8944(1)$ | $37(1)$ |
| C(20) | $1566(2)$ | $5280(3)$ | $8377(2)$ | $44(1)$ |
| O(5A) | $1376(2)$ | $6338(4)$ | $9028(2)$ | $40(1)$ |
| O(6A) | $3404(2)$ | $5537(4)$ | $11033(2)$ | $35(1)$ |
| C(21A) | $2051(2)$ | $7672(4)$ | $9262(2)$ | $47(1)$ |
| C(22A) | $2870(2)$ | $7040(4)$ | $9843(2)$ | $44(1)$ |
| C(23A) | $2584(2)$ | $6436(4)$ | $10684(2)$ | $38(1)$ |
| O(6B) | $3650(9)$ | $5934(18)$ | $11155(8)$ | $65(5)$ |
| O(5B) | $1664(7)$ | $5758(13)$ | $9086(6)$ | $41(3)$ |
| C(21B) | $2535(9)$ | $6665(18)$ | $9361(9)$ | $54(4)$ |
| C(22B) | $2387(17)$ | $7260(40)$ | $10254(16)$ | $135(9)$ |
| C(23B) | $2965(19)$ | $7280(40)$ | $10936(15)$ | $138(9)$ |
|  |  |  |  |  |

Table A5- 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $\mathbf{8 4 a}$.

| $\mathrm{O}(1)-\mathrm{C}(15)$ | 1.440(3) | $\mathrm{C}(17)-\mathrm{C}(16)$ | 1.540(3) |
| :---: | :---: | :---: | :---: |
| $\mathrm{O}(1)-\mathrm{C}(16)$ | 1.443(3) | $\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~A})$ | 0.9900 |
| $\mathrm{O}(2)-\mathrm{C}(12)$ | 1.436(3) | $\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~B})$ | 0.9900 |
| $\mathrm{O}(2)-\mathrm{C}(11)$ | 1.447(3) | $\mathrm{C}(16)-\mathrm{H}(17)$ | 1.0000 |
| $\mathrm{O}(3)-\mathrm{C}(19)$ | 1.201(3) | $\mathrm{C}(20)-\mathrm{O}(5 \mathrm{~B})$ | 1.202(9) |
| $\mathrm{O}(4)-\mathrm{C}(20)$ | 1.205(3) | $\mathrm{C}(20)-\mathrm{O}(5 \mathrm{~A})$ | 1.392(4) |
| $\mathrm{C}(5)-\mathrm{C}(4)$ | 1.407(3) | $\mathrm{O}(5 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})$ | 1.451(4) |
| $\mathrm{C}(5)-\mathrm{C}(10)$ | 1.419(3) | $\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})$ | 1.434(4) |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.435(3) | $\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 1.509(5) |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.412(3) | $\mathrm{C}(21 \mathrm{~A}) \mathrm{H}(21 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(6)-\mathrm{C}(1)$ | 1.417(3) | $\mathrm{C}(21 \mathrm{~A}) \mathrm{H}(21 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.371(3) | $\mathrm{C}(22 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})$ | 1.535(5) |
| $\mathrm{C}(7)-\mathrm{C}(12)$ | 1.514(3) | $\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | $1.395(3)$ | $\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 0.9900 |
| C(8)-C(11) | 1.514(3) | $\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(10)-\mathrm{C}(9)$ | 1.375(3) | $\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(10)-\mathrm{H}(10)$ | 0.9500 | $\mathrm{O}(6 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})$ | 1.47 (3) |
| $\mathrm{C}(12)-\mathrm{C}(14)$ | 1.565(3) | $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | 1.463(16) |
| $\mathrm{C}(12)-\mathrm{H}(12)$ | 1.0000 | $\mathrm{C}(21 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | 1.55(3) |
| $\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~A})$ | 1.326 (3) | $\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{C})$ | 0.9900 |
| $\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~B})$ | 1.427(14) | $\mathrm{C}(21 \mathrm{~B})$ - $\mathrm{H}(21 \mathrm{D}$ ) | 0.9900 |
| $\mathrm{C}(19)-\mathrm{C}(14)$ | 1.503(3) | $\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})$ | 1.31(3) |
| $\mathrm{C}(9)-\mathrm{H}(9)$ | 0.9500 | $\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{C})$ | 0.9900 |
| $\mathrm{C}(11)-\mathrm{C}(13)$ | 1.534(3) | $\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{D})$ | 0.9900 |
| $\mathrm{C}(11)-\mathrm{H}(11)$ | 1.0000 | $\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{C})$ | 0.9900 |
| $\mathrm{C}(14)-\mathrm{C}(13)$ | 1.546(3) | $\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{D})$ | 0.9900 |
| $\mathrm{C}(14)-\mathrm{H}(14)$ | 1.0000 |  |  |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 0.9900 | $\mathrm{C}(15)-\mathrm{O}(1)-\mathrm{C}(16)$ | 96.50(16) |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 0.9900 | $\mathrm{C}(12)-\mathrm{O}(2)-\mathrm{C}(11)$ | 96.29(16) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.371(3) | $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(10)$ | 124.05(19) |
| $\mathrm{C}(1)-\mathrm{H}(1)$ | 0.9500 | $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 115.73(18) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.400(3) | $\mathrm{C}(10)-\mathrm{C}(5)-\mathrm{C}(6)$ | 120.22(18) |
| $\mathrm{C}(2)-\mathrm{H}(2)$ | 0.9500 | $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(1)$ | 123.60(18) |
| $\mathrm{C}(4)-\mathrm{C}(3)$ | 1.375(3) | $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(5)$ | 115.82(18) |
| $\mathrm{C}(4)-\mathrm{C}(15)$ | 1.517(3) | $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(5)$ | 120.57(18) |
| $\mathrm{C}(18)-\mathrm{C}(20)$ | 1.500(3) | $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(6)$ | 122.42(18) |
| $\mathrm{C}(18)-\mathrm{C}(17)$ | 1.546 (3) | $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(12)$ | 105.23(17) |
| $\mathrm{C}(18)-\mathrm{C}(15)$ | 1.566(3) | $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(12)$ | 131.79(18) |
| $\mathrm{C}(18)-\mathrm{H}(18)$ | 1.0000 | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 121.80(19) |
| $\mathrm{C}(3)-\mathrm{C}(16)$ | 1.516(3) | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(11)$ | 104.48(18) |
| $\mathrm{C}(15)-\mathrm{H}(16)$ | 1.0000 | $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(11)$ | 133.27(19) |


| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(5)$ | 121.67(19) | $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(15)$ | 104.96(17) |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10)$ | 119.2 | $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(15)$ | 132.50(19) |
| $\mathrm{C}(5)-\mathrm{C}(10)-\mathrm{H}(10)$ | 119.2 | $\mathrm{C}(20)-\mathrm{C}(18)-\mathrm{C}(17)$ | 119.8(2) |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(7)$ | 101.41(16) | $\mathrm{C}(20)-\mathrm{C}(18)-\mathrm{C}(15)$ | 111.36(18) |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(14)$ | 101.25(17) | $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(15)$ | 101.17(18) |
| $\mathrm{C}(7)-\mathrm{C}(12)-\mathrm{C}(14)$ | 106.52(18) | $\mathrm{C}(20)-\mathrm{C}(18)-\mathrm{H}(18)$ | 108.0 |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{H}(12)$ | 115.3 | $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{H}(18)$ | 108.0 |
| $\mathrm{C}(7)-\mathrm{C}(12)-\mathrm{H}(12)$ | 115.3 | $\mathrm{C}(15)-\mathrm{C}(18)-\mathrm{H}(18)$ | 108.0 |
| $\mathrm{C}(14)-\mathrm{C}(12)-\mathrm{H}(12)$ | 115.3 | $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | 121.62(18) |
| $\mathrm{O}(3)-\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~A})$ | 122.5(2) | $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(16)$ | 104.68(18) |
| $\mathrm{O}(3)-\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~B})$ | 126.9(6) | $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(16)$ | 133.6(2) |
| $\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~B})$ | 20.4(5) | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(4)$ | 101.51(17) |
| $\mathrm{O}(3)-\mathrm{C}(19)-\mathrm{C}(14)$ | 123.2(2) | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(18)$ | 100.51(17) |
| $\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(19)-\mathrm{C}(14)$ | 113.8(2) | $\mathrm{C}(4)-\mathrm{C}(15)-\mathrm{C}(18)$ | 107.15(18) |
| $\mathrm{O}(6 \mathrm{~B})-\mathrm{C}(19)-\mathrm{C}(14)$ | 108.4(6) | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{H}(16)$ | 115.3 |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | 118.02(19) | $\mathrm{C}(4)-\mathrm{C}(15)-\mathrm{H}(16)$ | 115.3 |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{H}(9)$ | 121.0 | $\mathrm{C}(18)-\mathrm{C}(15)-\mathrm{H}(16)$ | 115.3 |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{H}(9)$ | 121.0 | $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | 101.28(18) |
| $\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{C}(8)$ | 101.67(17) | $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~A})$ | 111.5 |
| $\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{C}(13)$ | 101.35(18) | $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~A})$ | 111.5 |
| $\mathrm{C}(8)-\mathrm{C}(11)-\mathrm{C}(13)$ | 107.83(18) | $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~B})$ | 111.5 |
| $\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{H}(11)$ | 114.8 | $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~B})$ | 111.5 |
| $\mathrm{C}(8)-\mathrm{C}(11)-\mathrm{H}(11)$ | 114.8 | $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(17)-\mathrm{H}(15 \mathrm{~B})$ | 109.3 |
| $\mathrm{C}(13)-\mathrm{C}(11)-\mathrm{H}(11)$ | 114.8 | $\mathrm{O}(1)-\mathrm{C}(16)-\mathrm{C}(3)$ | 101.28(17) |
| $\mathrm{C}(19)-\mathrm{C}(14)-\mathrm{C}(13)$ | 119.5(2) | $\mathrm{O}(1)-\mathrm{C}(16)-\mathrm{C}(17)$ | 101.86(18) |
| $\mathrm{C}(19)-\mathrm{C}(14)-\mathrm{C}(12)$ | 110.12(18) | $\mathrm{C}(3)-\mathrm{C}(16)-\mathrm{C}(17)$ | 107.67(17) |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(12)$ | 100.86(18) | $\mathrm{O}(1)-\mathrm{C}(16)-\mathrm{H}(17)$ | 114.8 |
| $\mathrm{C}(19)-\mathrm{C}(14)-\mathrm{H}(14)$ | 108.6 | $\mathrm{C}(3)-\mathrm{C}(16)-\mathrm{H}(17)$ | 114.8 |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14)$ | 108.6 | $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(17)$ | 114.8 |
| $\mathrm{C}(12)-\mathrm{C}(14)-\mathrm{H}(14)$ | 108.6 | $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(20)-\mathrm{O}(4)$ | 115.7(5) |
| $\mathrm{C}(11)-\mathrm{C}(13)-\mathrm{C}(14)$ | 101.49(18) | $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(20)-\mathrm{O}(5 \mathrm{~A})$ | 26.2(5) |
| $\mathrm{C}(11)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 111.5 | $\mathrm{O}(4)-\mathrm{C}(20)-\mathrm{O}(5 \mathrm{~A})$ | 124.4(2) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 111.5 | $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(20)-\mathrm{C}(18)$ | 116.8(5) |
| $\mathrm{C}(11)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 111.5 | $\mathrm{O}(4)-\mathrm{C}(20)-\mathrm{C}(18)$ | 122.9(2) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 111.5 | $\mathrm{O}(5 \mathrm{~A})-\mathrm{C}(20)-\mathrm{C}(18)$ | 112.6(2) |
| $\mathrm{H}(13 \mathrm{~A})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 109.3 | $\mathrm{C}(20)-\mathrm{O}(5 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})$ | 117.4(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 121.46(19) | $\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})$ | 117.4(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{H}(1)$ | 119.3 | $\mathrm{O}(5 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 111.9(3) |
| $\mathrm{C}(6)-\mathrm{C}(1)-\mathrm{H}(1)$ | 119.3 | $\mathrm{O}(5 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~A})$ | 109.2 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 118.10(19) | $\mathrm{C}(22 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~A})$ | 109.2 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2)$ | 121.0 | $\mathrm{O}(5 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~B})$ | 109.2 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2)$ | 121.0 | $\mathrm{C}(22 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~B})$ | 109.2 |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | 122.42(19) | $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~B})$ | 107.9 |


| $\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})$ | $113.4(3)$ | $\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{C})$ | 111.0 |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~A})$ | 108.9 | $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{D})$ | 111.0 |
| $\mathrm{C}(23 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~A})$ | 108.9 | $\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{D})$ | 111.0 |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 108.9 | $\mathrm{H}(21 \mathrm{C})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{D})$ | 109.0 |
| $\mathrm{C}(23 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 108.9 | $\mathrm{C}(23 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | $131(2)$ |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 107.7 | $\mathrm{C}(23 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{C})$ | 104.5 |
| $\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | $103.0(3)$ | $\mathrm{C}(21 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{C})$ | 104.5 |
| $\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~A})$ | 111.2 | $\mathrm{C}(23 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{D})$ | 104.5 |
| $\mathrm{C}(22 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~A})$ | 111.2 | $\mathrm{C}(21 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{D})$ | 104.5 |
| $\mathrm{O}(6 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~B})$ | 111.2 | $\mathrm{H}(22 \mathrm{C})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{D})$ | 105.7 |
| $\mathrm{C}(22 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~B})$ | 111.2 | $\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})-\mathrm{O}(6 \mathrm{~B})$ | $123(2)$ |
| $\mathrm{H}(23 \mathrm{~A})-\mathrm{C}(23 \mathrm{~A})-\mathrm{H}(23 \mathrm{~B})$ | 109.1 | $\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{C})$ | 106.7 |
| $\mathrm{C}(19)-\mathrm{O}(6 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})$ | $113.3(14)$ | $\mathrm{O}(6 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{C})$ | 106.7 |
| $\mathrm{C}(20)-\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | $117.3(9)$ | $\mathrm{C}(22 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{D})$ | 106.7 |
| $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | $103.9(13)$ | $\mathrm{O}(6 \mathrm{~B})-\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{D})$ | 106.7 |
| $\mathrm{O}(5 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{C})$ | 111.0 | $\mathrm{H}(23 \mathrm{C})-\mathrm{C}(23 \mathrm{~B})-\mathrm{H}(23 \mathrm{D})$ | 106.6 |

Symmetry transformations used to generate equivalent atoms:
Table A5- 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 84 a.

| Atom | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :---: | :---: | :---: |
| $\mathrm{O}(1)$ | $44(1)$ | $45(1)$ | $42(1)$ | $-8(1)$ | $-10(1)$ | $-4(1)$ |
| $\mathrm{O}(2)$ | $34(1)$ | $53(1)$ | $42(1)$ | $9(1)$ | $-2(1)$ | $6(1)$ |
| $\mathrm{O}(3)$ | $50(1)$ | $60(1)$ | $53(1)$ | $-6(1)$ | $24(1)$ | $5(1)$ |
| $\mathrm{O}(4)$ | $52(1)$ | $62(1)$ | $69(1)$ | $16(1)$ | $23(1)$ | $1(1)$ |
| $\mathrm{C}(5)$ | $30(1)$ | $23(1)$ | $28(1)$ | $1(1)$ | $2(1)$ | $4(1)$ |
| $\mathrm{C}(6)$ | $29(1)$ | $22(1)$ | $26(1)$ | $-1(1)$ | $3(1)$ | $-1(1)$ |
| $\mathrm{C}(7)$ | $28(1)$ | $28(1)$ | $28(1)$ | $0(1)$ | $3(1)$ | $1(1)$ |
| $\mathrm{C}(8)$ | $28(1)$ | $27(1)$ | $35(1)$ | $-3(1)$ | $4(1)$ | $1(1)$ |
| $\mathrm{C}(10)$ | $39(1)$ | $37(1)$ | $27(1)$ | $5(1)$ | $9(1)$ | $5(1)$ |
| $\mathrm{C}(12)$ | $29(1)$ | $47(1)$ | $31(1)$ | $1(1)$ | $0(1)$ | $1(1)$ |
| $\mathrm{C}(19)$ | $38(1)$ | $42(1)$ | $40(1)$ | $-14(1)$ | $10(1)$ | $-8(1)$ |
| $\mathrm{C}(9)$ | $28(1)$ | $36(1)$ | $37(1)$ | $3(1)$ | $12(1)$ | $4(1)$ |
| $\mathrm{C}(11)$ | $26(1)$ | $47(1)$ | $43(1)$ | $-2(1)$ | $1(1)$ | $3(1)$ |
| $\mathrm{C}(14)$ | $35(1)$ | $53(2)$ | $35(1)$ | $-12(1)$ | $0(1)$ | $-6(1)$ |
| $\mathrm{C}(13)$ | $28(1)$ | $56(2)$ | $56(2)$ | $-14(1)$ | $2(1)$ | $-8(1)$ |
| $\mathrm{C}(1)$ | $32(1)$ | $33(1)$ | $27(1)$ | $-1(1)$ | $6(1)$ | $-3(1)$ |
| $\mathrm{C}(2)$ | $28(1)$ | $29(1)$ | $38(1)$ | $0(1)$ | $9(1)$ | $-3(1)$ |
| $\mathrm{C}(4)$ | $34(1)$ | $24(1)$ | $29(1)$ | $-1(1)$ | $2(1)$ | $3(1)$ |
| $\mathrm{C}(18)$ | $39(1)$ | $42(1)$ | $36(1)$ | $9(1)$ | $-4(1)$ | $7(1)$ |
| $\mathrm{C}(3)$ | $27(1)$ | $22(1)$ | $39(1)$ | $0(1)$ | $-1(1)$ | $-1(1)$ |
|  |  |  |  | 149 |  |  |


| $\mathrm{C}(15)$ | $36(1)$ | $43(1)$ | $32(1)$ | $-2(1)$ | $-4(1)$ | $5(1)$ |
| :--- | :--- | :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}(17)$ | $31(1)$ | $41(1)$ | $52(2)$ | $9(1)$ | $-2(1)$ | $5(1)$ |
| $\mathrm{C}(16)$ | $30(1)$ | $37(1)$ | $44(1)$ | $0(1)$ | $-3(1)$ | $-4(1)$ |
| $\mathrm{C}(20)$ | $43(1)$ | $43(1)$ | $45(1)$ | $16(1)$ | $5(1)$ | $3(1)$ |
| $\mathrm{O}(5 \mathrm{~A})$ | $39(1)$ | $30(1)$ | $53(1)$ | $4(1)$ | $13(1)$ | $-1(1)$ |
| $\mathrm{O}(6 \mathrm{~A})$ | $29(1)$ | $38(1)$ | $38(1)$ | $-4(1)$ | $11(1)$ | $-7(1)$ |
| $\mathrm{C}(21 \mathrm{~A})$ | $44(2)$ | $27(2)$ | $71(2)$ | $5(2)$ | $16(2)$ | $-2(1)$ |
| $\mathrm{C}(22 \mathrm{~A})$ | $42(2)$ | $42(2)$ | $51(2)$ | $7(2)$ | $12(2)$ | $-7(2)$ |
| $\mathrm{C}(23 \mathrm{~A})$ | $37(2)$ | $30(2)$ | $47(2)$ | $2(1)$ | $6(1)$ | $-10(1)$ |

Table A5- 5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 84a.

| Atom | $x$ | $y$ | $z$ | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | ---: |
| H(10) | 3216 | 2135 | 8580 | 41 |
| H(12) | 3372 | 1221 | 12173 | 43 |
| H(9) | 4709 | 2081 | 9310 | 40 |
| H(11) | 5661 | 1491 | 10953 | 46 |
| H(14) | 4339 | 3646 | 12597 | 49 |
| H(13A) | 4999 | 4530 | 11096 | 56 |
| H(13B) | 5617 | 3813 | 11912 | 56 |
| H(1) | 1752 | 1600 | 11481 | 37 |
| H(2) | 261 | 1841 | 10765 | 37 |
| H(18) | 566 | 4190 | 7551 | 47 |
| H(16) | 1579 | 1767 | 7865 | 45 |
| H(15A) | -17 | 4809 | 9117 | 50 |
| H(15B) | -670 | 4279 | 8284 | 50 |
| H(17) | -703 | 1740 | 9103 | 45 |
| H(21A) | 1730 | 8598 | 9535 | 56 |
| H(21B) | 2291 | 8139 | 8755 | 56 |
| H(22A) | 3340 | 7961 | 9939 | 53 |
| H(22B) | 3177 | 6092 | 9573 | 53 |
| H(23A) | 2442 | 7406 | 11038 | 45 |
| H(23B) | 2027 | 5682 | 10610 | 45 |
| H(21C) | 2625 | 7645 | 8996 | 65 |
| H(21D) | 3089 | 5908 | 9366 | 65 |
| H(22C) | 2161 | 8438 | 10185 | 162 |
| H(22D) | 1838 | 6594 | 10402 | 162 |
| H(23C) | 2570 | 7378 | 11403 | 166 |
| H(23D) | 3328 | 8351 | 10927 | 166 |

## Appendix 2: Cartesian Coordinates for Calculated Structures

## ISE Calculations from Chapter 2

Table A6- 1. Cartesian Coordinates for 2-Methylfuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.398125 | -0.734035 | 0.000010 |
| 2 | 8 | -0.072388 | -1.064657 | -0.000016 |
| 3 | 6 | 0.639154 | 0.106674 | -0.000031 |
| 4 | 6 | -0.222605 | 1.163959 | -0.000010 |
| 5 | 6 | -1.549912 | 0.616603 | 0.000019 |
| 6 | 6 | 2.123406 | -0.013568 | 0.000016 |
| 7 | 1 | -2.087000 | -1.564989 | 0.000036 |
| 8 | 1 | 0.053303 | 2.209671 | 0.000023 |
| 9 | 1 | -2.484386 | 1.160575 | -0.000037 |
| 10 | 1 | 2.484591 | -0.554022 | -0.883876 |
| 11 | 1 | 2.576523 | 0.981672 | -0.000315 |
| 12 | 1 | 2.484567 | -0.553451 | 0.884266 |

Table A6- 2. Cartesian Coordinates for 2-Methylene-2,5-dihydrofuran

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 1.389641 | -0.710819 | 0.000017 |
| 2 | 8 | 0.009369 | -1.101545 | -0.000040 |
| 3 | 6 | -0.786942 | 0.024608 | -0.000005 |
| 4 | 6 | 0.086115 | 1.197306 | -0.000027 |
| 5 | 6 | 1.361476 | 0.791370 | 0.000016 |
| 6 | 6 | -2.125666 | -0.039826 | 0.000027 |
| 7 | 1 | 1.883012 | -1.134183 | 0.887678 |
| 8 | 1 | -0.282880 | 2.215694 | -0.000044 |
| 9 | 1 | 2.251567 | 1.409502 | 0.000038 |
| 10 | 1 | -2.712645 | 0.870588 | 0.000014 |
| 11 | 1 | -2.644846 | -0.990839 | 0.000043 |
| 12 | 1 | 1.883097 | $-1.134229$ | -0.887571 |

Table A6- 3. Cartesian Coordinates for 3-Methylene-2,3-dihydrofuran
Center Atomic Coordinates (Angstroms)

| Number | Number | X | Y | Z |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 6 | 1.355720 | 0.723614 | -0.000048 |
| 2 | 8 | 1.465956 | -0.632234 | -0.000129 |
| 3 | 6 | 0.112422 | -1.157347 | 0.000124 |
| 4 | 6 | -0.811048 | 0.054709 | 0.000025 |
| 5 | 6 | 0.096559 | 1.196259 | 0.000104 |
| 6 | 1 | 2.302469 | 1.250006 | -0.000108 |
| 7 | 6 | -2.152232 | 0.031420 | -0.000097 |
| 8 | 1 | -0.195370 | 2.237491 | 0.000173 |
| 9 | 1 | -0.000401 | -1.785679 | 0.890463 |
| 10 | 1 | -2.711450 | -0.899928 | -0.000197 |
| 11 | 1 | -2.730833 | 0.950172 | -0.000075 |
| 12 | 1 | -0.000595 | -1.786117 | -0.889869 |

Table A6- 4. Cartesian Coordinates for 3-Methylfuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 1.475007 | 0.647328 | -0.000029 |
| 2 | 8 | 1.452944 | -0.715311 | -0.000012 |
| 3 | 6 | 0.136714 | -1.081695 | 0.000028 |
| 4 | 6 | -0.678962 | 0.009969 | 0.000008 |
| 5 | 6 | 0.209793 | 1.144740 | 0.000039 |
| 6 | 1 | 2.455188 | 1.099794 | -0.000049 |
| 7 | 6 | -2.178770 | 0.026412 | -0.000023 |
| 8 | 1 | -0.071243 | 2.189600 | 0.000054 |
| 9 | 1 | -0.053136 | -2.144800 | 0.000047 |
| 10 | 1 | -2.575554 | 0.542990 | 0.882815 |
| 11 | 1 | -2.586028 | -0.989866 | -0.000757 |
| 12 | 1 | -2.575462 | 0.544249 | -0.882155 |

Table A6- 5. Cartesian Coordinates for 1-Methylene-1,4-dihydroisobenzofuran

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 0.798863 | 1.707958 | -0.000002 |
| 2 | 8 | 1.988384 | 1.008840 | -0.000006 |
| 3 | 6 | 1.670579 | -0.348639 | -0.000004 |
| 4 | 6 | 0.208547 | -0.455838 | 0.000001 |
| 5 | 6 | -0.289097 | 0.915129 | 0.000004 |
| 6 | 6 | -0.627687 | -1.524974 | -0.000001 |
| 7 | 6 | -2.063934 | -1.287562 | -0.000003 |
| 8 | 6 | -2.596425 | -0.049322 | 0.000002 |
|  |  |  |  | 152 |


| 9 | 6 |  | -1.767889 | 1.219102 |
| :---: | :---: | ---: | ---: | ---: |
|  | 0.000015 |  |  |  |
| 10 | 6 |  | 2.640686 | -1.273073 |$-0.000006$

Table A6- 6. Cartesian Coordinates for 1-Methylene-1,6-dihydroisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 0.875644 | 1.712904 | 0.000133 |
| 2 | 8 | 2.031386 | 0.959351 | 0.000087 |
| 3 | 6 | 1.660369 | -0.387475 | -0.000028 |
| 4 | 6 | 0.187671 | -0.435971 | -0.000008 |
| 5 | 6 | -0.244519 | 0.963810 | 0.000051 |
| 6 | 6 | -0.685455 | -1.458835 | -0.000033 |
| 7 | 6 | -2.173320 | -1.206531 | 0.000220 |
| 8 | 6 | -2.552628 | 0.256583 | -0.000170 |
| 9 | 6 | -1.660549 | 1.263394 | -0.000148 |
| 10 | 6 | 2.591552 | -1.347123 | -0.000136 |
| 11 | 1 | 1.035913 | 2.782099 | 0.000196 |
| 12 | 1 | -0.347084 | -2.492810 | -0.000156 |
| 13 | 1 | -2.636598 | -1.706617 | 0.869497 |
| 14 | 1 | -3.617241 | 0.480255 | -0.000423 |
| 15 | 1 | -1.991004 | 2.299213 | -0.000383 |
| 16 | 1 | 3.647197 | -1.102871 | -0.000124 |
| 17 | 1 | 2.302266 | -2.391312 | -0.000225 |
| 18 | 1 | -2.637124 | -1.707300 | -0.868357 |

Table A6- 7. Cartesian Coordinates for 1-Methylisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 0.686859 | 1.798575 | -0.000008 |
| 2 | 8 | 1.838440 | 1.071966 | -0.000029 |
| 3 | 6 | 1.531573 | -0.255841 | -0.000025 |
| 4 | 6 | 0.158250 | -0.395647 | -0.000030 |
| 5 | 6 | -0.394212 | 0.950584 | 0.000001 |
| 6 | 6 | -0.720527 | -1.522018 | -0.000046 |


| 7 | 6 | -2.070575 | -1.300392 | -0.000015 |
| :---: | :---: | ---: | ---: | :---: |
| 8 | 6 | -2.615703 | 0.030802 | 0.000031 |
| 9 | 6 | -1.811304 | 1.137123 | 0.000039 |
| 10 | 6 | 2.668146 | -1.25571 | 0.000058 |
| 11 | 1 | 0.805632 | 2.870763 | -0.000074 |
| 12 | 1 | -0.321114 | -2.532918 | -0.000069 |
| 13 | 1 | -2.756599 | -2.143141 | -0.000020 |
| 14 | 1 | -3.696002 | 0.149333 | 0.000056 |
| 15 | 1 | -2.234026 | 2.138174 | 0.000059 |
| 16 | 1 | 3.305850 | -1.091396 | 0.884711 |
| 17 | 1 | 2.287587 | -2.241000 | -0.000092 |
| 18 | 1 | 3.306117 | -1.091231 | -0.884379 |

Table A6- 8. Cartesian Coordinates for 4-Methylene-1,4-dihydroisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 2.176595 | 0.691121 | 0.000085 |
| 2 | 8 | 2.427220 | -0.740405 | 0.000028 |
| 3 | 6 | 1.220613 | -1.361198 | -0.000018 |
| 4 | 6 | 0.146869 | -0.528968 | -0.000009 |
| 5 | 6 | 0.675797 | 0.825537 | 0.000042 |
| 6 | 6 | -1.303419 | -0.775507 | -0.000048 |
| 7 | 6 | -2.109601 | 0.446159 | -0.000052 |
| 8 | 6 | -1.566456 | 1.689987 | -0.000007 |
| 9 | 6 | -0.132270 | 1.910735 | 0.000044 |
| 10 | 6 | -1.877093 | -2.003390 | -0.000074 |
| 11 | 1 | 2.660946 | 1.111494 | -0.889032 |
| 12 | 1 | 1.277495 | -2.442545 | -0.000058 |
| 13 | 1 | -3.189778 | 0.324572 | -0.000088 |
| 14 | 1 | -2.220137 | 2.558520 | -0.000009 |
| 15 | 1 | -1.294324 | -2.919400 | -0.000063 |
| 16 | 1 | -2.957099 | -2.112173 | -0.000106 |
| 17 | 1 | 0.258054 | 2.924515 | 0.000078 |
| 18 | 1 | 2.660882 | 1.111410 | 0.889275 |

Table A6- 9. Cartesian Coordinates for 6-Methylene-1,6-dihydroisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 2.069811 | 0.935342 | -0.000054 |
| 2 | 8 | 2.773608 | -0.229179 | -0.000134 |
| 3 | 6 | 1.811199 | -1.320561 | 0.000093 |
| 4 | 6 | 0.457614 | -0.652014 | 0.000052 |
|  |  |  |  | 154 |


| 5 | 6 | 0.722378 | 0.777564 | 0.000040 |
| :---: | :---: | :---: | :---: | :---: |
| 6 | 6 | -0.795963 | -1.150194 | 0.000008 |
| 7 | 6 | -1.945048 | -0.241790 | -0.000008 |
| 8 | 6 | -1.650423 | 1.195032 | 0.000034 |
| 9 | 6 | -0.390552 | 1.692683 | 0.000048 |
| 10 | 1 | 2.679350 | 1.830330 | -0.000136 |
| 11 | 1 | 2.003829 | -1.931000 | 0.889766 |
| 12 | 6 | -3.222293 | -0.698301 | -0.000077 |
| 13 | 1 | -2.499831 | 1.873733 | 0.000058 |
| 14 | 1 | -0.213906 | 2.764917 | 0.000094 |
| 15 | 1 | -3.445508 | -1.761089 | $-0.000113$ |
| 16 | 1 | -4.068385 | -0.017827 | -0.000101 |
| 17 | 1 | -0.988556 | -2.220807 | -0.000006 |
| 18 | 1 | 2.003801 | -1.931388 | -0.889308 |

Table A6- 10. Cartesian Coordinates for 6-Methylisobenzofuran

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -2.236859 | 0.828360 | -0.000033 |
| 2 | 8 | -2.777251 | -0.417452 | -0.000026 |
| 3 | 6 | -1.767626 | -1.328527 | 0.000073 |
| 4 | 6 | -0.554443 | -0.680340 | -0.000012 |
| 5 | 6 | -0.864295 | 0.739826 | 0.000015 |
| 6 | 6 | 0.807537 | -1.112982 | -0.000045 |
| 7 | 6 | 1.812175 | -0.180825 | -0.000030 |
| 8 | 6 | 1.488164 | 1.228494 | 0.000010 |
| 9 | 6 | 0.202371 | 1.690102 | 0.000035 |
| 10 | 1 | -2.939085 | 1.647439 | -0.000072 |
| 11 | 1 | -2.068488 | -2.364533 | 0.000125 |
| 12 | 6 | 3.266425 | -0.585121 | 0.000005 |
| 13 | 1 | 2.311475 | 1.939456 | 0.000008 |
| 14 | 1 | -0.008299 | 2.756161 | 0.000037 |
| 15 | 1 | 1.041278 | -2.174878 | -0.000053 |
| 16 | 1 | 3.790258 | -0.191869 | -0.881145 |
| 17 | 1 | 3.380131 | -1.673592 | -0.000356 |
| 18 | 1 | 3.790042 | -0.192486 | 0.881561 |

## ASE Calculations from Chapter 2

Table A6- 11. Cartesian Coordinates for Isobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -3.633890 | -0.374338 | -0.000062 |
| 2 | 6 | -2.186616 | -0.374384 | 0.000147 |
| 3 | 6 | -1.470234 | 0.856064 | -0.000075 |
| 4 | 6 | -2.193926 | 2.030442 | 0.000205 |
| 5 | 6 | -3.626416 | 2.030489 | 0.000175 |
| 6 | 6 | -4.350187 | 0.856160 | 0.000285 |
| 7 | 6 | -4.013958 | -1.711288 | 0.000030 |
| 8 | 6 | -1.806637 | -1.711360 | -0.000035 |
| 9 | 1 | -0.383201 | 0.869532 | -0.000060 |
| 10 | 1 | -1.668623 | 2.981996 | 0.000168 |
| 11 | 1 | -4.151654 | 2.982078 | 0.000423 |
| 12 | 1 | -5.437219 | 0.869703 | 0.000332 |
| 13 | 1 | -4.962923 | -2.225429 | -0.000008 |
| 14 | 1 | -0.857706 | -2.225564 | -0.000044 |
| 15 | 8 | -2.910323 | -2.495842 | -0.000827 |

Table A6- 12. Cartesian Coordinates for 2 H -Indene

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y Z |  |
| 1 | 6 | -3.957917 | -1.257872 | 0.001474 |
| 2 | 6 | -2.510428 | -1.331748 | -0.273516 |
| 3 | 6 | -1.734229 | -0.118337 | -0.305118 |
| 4 | 6 | -2.371425 | 1.079528 | -0.121514 |
| 5 | 6 | -3.795485 | 1.152731 | 0.140220 |
| 6 | 6 | -4.577756 | 0.029903 | 0.183919 |
| 7 | 6 | -4.480762 | -2.528884 | 0.000661 |
| 8 | 6 | -3.371773 | -3.499281 | -0.268217 |
| 9 | 6 | -2.149208 | -2.648773 | -0.427799 |
| 10 | 1 | -0.664632 | -0.158390 | -0.498972 |
| 11 | 1 | -1.799383 | 2.003838 | -0.145113 |
| 12 | 1 | -4.248503 | 2.131310 | 0.279135 |
| 13 | 1 | -5.645434 | 0.099926 | 0.379838 |
| 14 | 1 | -5.517606 | -2.804018 | 0.162637 |
| 15 | 1 | -3.255361 | -4.217374 | 0.558081 |
| 16 | 1 | -1.153281 | -3.029078 | -0.629020 |
| 17 | 1 | -3.570269 | -4.094542 | -1.172770 |

Table A6- 13. Cartesian Coordinates for 2,7a-Dihydro-1H-indene

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -4.098963 | -1.225612 | -0.524076 |
| 2 | 6 | -2.589904 | -1.331447 | -0.395307 |
| 3 | 6 | -1.776400 | -0.152904 | -0.616534 |
| 4 | 6 | -2.367733 | 1.071961 | -0.521945 |
| 5 | 6 | -3.783843 | 1.205887 | -0.179485 |
| 6 | 6 | -4.609809 | 0.131381 | -0.137174 |
| 7 | 6 | -4.580861 | -2.426133 | 0.313529 |
| 8 | 6 | -3.448013 | -3.463560 | 0.143275 |
| 9 | 6 | -2.229764 | -2.590134 | -0.042525 |
| 10 | 1 | -0.703951 | -0.246288 | -0.775456 |
| 11 | 1 | -1.772791 | 1.973922 | -0.643895 |
| 12 | 1 | -4.166066 | 2.195629 | 0.059220 |
| 13 | 1 | -5.663816 | 0.251151 | 0.110046 |
| 14 | , | -4.633079 | -2.117086 | 1.364606 |
| 15 | 1 | -3.364214 | -4.154985 | 0.988157 |
| 16 | 1 | -1.205174 | -2.941047 | 0.054263 |
| 17 | 1 | -3.625513 | -4.069283 | -0.759372 |
| 18 | 1 | -4.365297 | -1.401115 | -1.585175 |
| 19 | 1 | -5.562837 | -2.799448 | 0.005397 |

Table A6- 14. Cartesian Coordinates for 1,7a-Dihydroisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -3.531399 | -0.285793 | 0.032550 |
| 2 | 6 | -2.127869 | -0.425059 | -0.528162 |
| 3 | 6 | -1.315284 | 0.809675 | -0.255283 |
| 4 | 6 | -1.951579 | 2.002134 | -0.130790 |
| 5 | 6 | -3.410017 | 2.107231 | -0.125013 |
| 6 | 6 | -4.190761 | 0.992997 | 0.002008 |
| 7 | 6 | -3.898503 | -1.501688 | 0.502593 |
| 8 | 6 | -1.687501 | -1.715879 | 0.163037 |
| 9 | 1 | -0.228072 | 0.753159 | -0.245738 |
| 10 | 1 | -1.370266 | 2.911461 | 0.004340 |
| 11 | 1 | -3.864974 | 3.094032 | -0.133187 |
| 12 | 1 | -5.267096 | 1.072912 | 0.138098 |
| 13 | 1 | -4.844432 | -1.844778 | 0.905217 |
| 14 | 1 | -1.218459 | -1.488373 | 1.130131 |
| 15 | 8 | -2.916846 | -2.447597 | 0.434683 |
|  |  |  |  | 157 |


| 16 | 1 | -1.046728 | -2.364701 | -0.434379 |
| :--- | :--- | :--- | :--- | :--- |
| 17 | 1 | -2.196589 | -0.581999 | -1.620756 |

Table A6- 15. Cartesian Coordinates for 2,3,3a,7a-Tetrahydro-1H-indene

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -3.951123 | -1.141071 | -0.518733 |
| 2 | 6 | -2.577198 | -1.305669 | 0.127130 |
| 3 | 6 | -1.678011 | -0.169356 | -0.264511 |
| 4 | 6 | -2.231338 | 1.065747 | -0.367923 |
| 5 | 6 | -3.669154 | 1.260470 | -0.142381 |
| 6 | 6 | -4.523525 | 0.206802 | -0.188995 |
| 7 | 6 | -4.673580 | -2.415342 | -0.077926 |
| 8 | 6 | -3.564612 | -3.507258 | -0.138224 |
| 9 | 6 | -2.211538 | -2.743480 | -0.245617 |
| 10 | 1 | -0.605122 | -0.316069 | -0.378353 |
| 11 | 1 | -1.613570 | 1.931760 | -0.594688 |
| 12 | 1 | -4.040708 | 2.266700 | 0.037865 |
| 13 | 1 | -5.597156 | 0.348137 | -0.075294 |
| 14 | 1 | -5.029671 | -2.287109 | 0.951320 |
| 15 | 1 | -3.591470 | -4.137436 | 0.755572 |
| 16 | 1 | -1.433764 | -3.169157 | 0.396096 |
| 17 | 1 | -3.707400 | -4.166895 | -0.999147 |
| 18 | 1 | -3.793531 | -1.184721 | -1.614816 |
| 19 | 1 | -5.538849 | -2.656735 | -0.703195 |
| 20 | 1 | -1.841468 | -2.762592 | -1.277742 |
| 21 | 1 | -2.733803 | -1.253080 | 1.222969 |

Table A6- 16. Cartesian Coordinates for 1,3,3a,7a-Tetrahydroisobenzofuran

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -3.360827 | 0.046935 | 0.700425 |
| 2 | 6 | -2.426168 | -0.530206 | -0.357562 |
| 3 | 6 | -1.323238 | 0.444865 | -0.643483 |
| 4 | 6 | -1.664853 | 1.758174 | -0.693471 |
| 5 | 6 | -3.045117 | 2.182662 | -0.425657 |
| 6 | 6 | -3.906202 | 1.362142 | 0.229538 |
| 7 | 6 | -4.262411 | -1.149672 | 0.954941 |
| 8 | 6 | -2.149476 | -1.901312 | 0.236593 |
| 9 | 1 | -0.318247 | 0.112120 | -0.895187 |
| 10 | 1 | -0.926770 | 2.511237 | -0.959027 |
| 11 | 1 | -3.358034 | 3.176302 | -0.737360 |
| 12 | 1 | -4.913228 | 1.686547 | 0.483974 |
| 13 | 1 | -5.050551 | -1.214511 | 0.192347 |
| 14 | 1 | -1.363132 | -1.844403 | 1.001669 |
| 15 | 8 | -3.393054 | -2.294540 | 0.850073 |
| 16 | 1 | -1.880047 | -2.658936 | -0.504368 |
| 17 | 1 | -3.022608 | -0.661183 | -1.279995 |
| 18 | 1 | -2.752375 | 0.227002 | 1.606607 |
| 19 | 1 | -4.718187 | -1.157381 | 1.948798 |

## FMO Calculations from Chapter 3

Table A6- 17. Cartesian Coordinates for Isobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.279157 | -0.685343 | 0.124600 |
| 2 | 8 | 0.013668 | -1.101284 | 0.124600 |
| 3 | 6 | 0.822719 | -0.010513 | 0.124600 |
| 4 | 6 | 0.060103 | 1.134645 | 0.124600 |
| 5 | 6 | -1.325714 | 0.689790 | 0.124600 |
| 6 | 6 | 0.357989 | 2.532273 | 0.124600 |
| 7 | 6 | -0.682145 | 3.420708 | 0.124600 |
| 8 | 6 | -2.051632 | 2.981204 | 0.124600 |
| 9 | 6 | -2.380950 | 1.653480 | 0.124600 |
| 10 | 1 | 1.389035 | 2.874962 | 0.124600 |
| 11 | 1 | -0.479836 | 4.488351 | 0.124600 |
| 12 | 1 | -2.837389 | 3.731807 | 0.124600 |
| 13 | 1 | -3.419022 | 1.332703 | 0.124600 |
| 14 | 1 | -2.025124 | -1.464715 | 0.124600 |
| 15 |  | 1.882953 | -0.209967 | 0.124600 |

Table A6- 18. Cartesian Coordinates for 1-Methylisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 0.394232 | 0.950579 | -0.000017 |
| 2 | 6 | -0.158236 | -0.395656 | -0.000038 |
| 3 | 6 | 0.720536 | -1.522013 | -0.000035 |
| 4 | 6 | 2.070589 | -1.300385 | 0.000002 |
| 5 | 6 | 2.615712 | 0.030795 | 0.000029 |
| 6 | 6 | 1.811298 | 1.137114 | 0.000017 |
| 7 | 6 | -0.686874 | 1.798553 | -0.000004 |
| 8 | 6 | -1.531575 | -0.255870 | -0.000013 |
| 9 | 1 | 0.321107 | -2.532913 | -0.000053 |
| 10 | 1 | 2.756626 | -2.143129 | 0.000019 |
| 11 | 1 | 3.696014 | 0.149318 | 0.000056 |
| 12 | 1 | 2.234017 | 2.138173 | 0.000013 |
| 13 | 1 | -0.805510 | 2.870756 | -0.000026 |
| 14 | 8 | -1.838419 | 1.071974 | -0.000001 |
| 15 | 6 | -2.668207 | -1.215536 | 0.000035 |
| 16 | 1 | -3.306068 | -1.091238 | -0.884490 |
| 17 | 1 | -2.287689 | -2.240981 | 0.000012 |
| 18 | 1 | -3.305993 | -1.091253 | 0.884620 |

Table A6- 19. Cartesian Coordinates for 1-Phenylisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 1.563271 | 2.059009 | 0.185250 |
| 2 | 8 | 0.223637 | 1.861835 | 0.173285 |
| 3 | 6 | -0.042892 | 0.523560 | 0.064545 |
| 4 | 6 | 1.170063 | -0.157227 | -0.008249 |
| 5 | 6 | 2.212716 | 0.850788 | 0.078759 |
| 6 | 6 | 1.540024 | -1.524839 | -0.178965 |
| 7 | 6 | 3.896377 | -0.853209 | -0.104707 |
| 8 | 6 | 3.588299 | 0.472594 | 0.035732 |
| 9 | 6 | -1.445699 | 0.139310 | 0.034280 |
| 10 | 6 | -2.438102 | 1.080544 | -0.305151 |
| 11 | 6 | -3.780260 | 0.714972 | -0.341867 |
| 12 | 6 | -4.166880 | -0.594867 | -0.046704 |
| 13 | 6 | -3.193531 | -1.533940 | 0.300053 |
| 14 | 6 | -1.849294 | -1.172809 | 0.348119 |
| 15 | 1 | 4.936139 | -1.166803 | -0.140362 |
| 16 | 1 | -2.144008 | 2.096887 | $-0.545393$ |
| 17 | 1 | -4.528999 | 1.456397 | -0.608461 |
| 18 | 1 | -1.111833 | -1.903058 | 0.663386 |
| 19 | , | -5.215161 | -0.878325 | -0.080347 |
| 20 | 1 | -3.482292 | -2.551884 | 0.548462 |
| 21 | 1 | 1.890634 | 3.082682 | 0.280733 |
| 22 | 1 | 4.367072 | 1.226682 | 0.109045 |
| 23 | 6 | 2.870846 | -1.849818 | -0.221605 |
| 24 | 1 | 3.165261 | -2.887154 | -0.355420 |
| 25 | , | 0.784463 | -2.294499 | -0.294857 |

Table A6- 20. Cartesian Coordinates for 1-(t-Butyldimethyl)isobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.577646 | -2.115099 | 0.014639 |
| 2 | 8 | -0.320956 | -1.615628 | 0.017787 |
| 3 | 6 | -0.359818 | -0.236086 | 0.008624 |
| 4 | 6 | -1.701145 | 0.133880 | 0.000066 |
| 5 | 6 | -2.490123 | -1.085486 | 0.003862 |
| 6 | 6 | -2.370693 | 1.395678 | -0.009042 |
| 7 | 6 | -3.740087 | 1.417539 | -0.014956 |
| 8 | 6 | -4.514258 | 0.207987 | -0.012251 |
| 9 | 6 | -3.916262 | -1.022943 | -0.002998 |
| 10 | 14 | 1.256837 | 0.739206 | 0.013420 |


| 11 | 6 | 1.255048 | 1.874330 | -1.507084 |
| ---: | ---: | ---: | ---: | ---: |
| 12 | 6 | 1.282477 | 1.824443 | 1.569528 |
| 13 | 6 | 2.769412 | -0.449954 | -0.017368 |
| 14 | 6 | 4.063644 | 0.395154 | -0.022112 |
| 15 | 6 | 2.776198 | -1.359566 | 1.230896 |
| 16 | 6 | 2.748655 | -1.331834 | -1.285117 |
| 17 | 1 | -1.661114 | -3.191398 | 0.020462 |
| 18 | 1 | -1.802662 | 2.321994 | -0.010481 |
| 19 | 1 | -4.263838 | 2.369713 | -0.021702 |
| 20 | 1 | -5.598319 | 0.282914 | -0.017440 |
| 21 | 1 | -4.507359 | -1.934757 | -0.000620 |
| 22 | 1 | 0.356906 | 2.503070 | -1.524906 |
| 23 | 1 | 1.268837 | 1.300489 | -2.440395 |
| 24 | 1 | 2.124124 | 2.543139 | -1.509610 |
| 25 | 1 | 1.293073 | 1.221409 | 2.484220 |
| 26 | 1 | 0.393699 | 2.465181 | 1.612159 |
| 27 | 1 | 2.161348 | 2.480120 | 1.587373 |
| 28 | 1 | 4.148629 | 1.027221 | 0.870318 |
| 29 | 1 | 4.129849 | 1.046176 | -0.902351 |
| 30 | 1 | 4.944050 | -0.263400 | -0.038454 |
| 31 | 1 | 1.887822 | -1.997574 | 1.273989 |
| 32 | 1 | 2.822280 | -0.779668 | 2.160794 |
| 33 | 1 | 3.657944 | -2.017065 | 1.214921 |
| 34 | 1 | 2.770821 | -0.731280 | -2.202691 |
| 35 | 1 | 3.632243 | -1.986693 | -1.304731 |
| 36 | 1 | 1.861198 | -1.971702 | -1.321150 |
| ----------------------------------------------------1 |  |  |  |  |

Table A6- 21. Cartesian Coordinates for 1-Cyanoisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 0.788863 | 0.929517 | 0.000001 |
| 2 | 6 | -0.005328 | -0.279862 | 0.000002 |
| 3 | 6 | 0.628423 | -1.553336 | 0.000004 |
| 4 | 6 | 1.998872 | -1.589644 | 0.000003 |
| 5 | 6 | 2.790237 | -0.392526 | 0.000001 |
| 6 | 6 | 2.212800 | 0.849165 | -0.000001 |
| 7 | 6 | -0.114226 | 1.974178 | -0.000004 |
| 8 | 6 | -1.331007 | 0.135960 | 0.000000 |
| 9 | 1 | 0.036307 | -2.463223 | 0.000006 |
| 10 | 1 | 2.509121 | -2.548700 | 0.000004 |
| 11 | 1 | 3.872495 | -0.484538 | 0.000000 |
| 12 | 1 | 2.816015 | 1.752230 | -0.000002 |
| 13 | 1 | -0.011108 | 3.048695 | -0.000003 |
| 14 | 8 | -1.376745 | 1.506399 | -0.000004 |
| 15 | 6 | -2.547979 | -0.571484 | -0.000001 |
| 16 | 7 | -3.533256 | -1.195353 | -0.000001 |
|  |  |  |  | 162 |

Table A6- 22. Cartesian Coordinates for 1,3-Dimethylisobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.218759 | -1.120154 | 0.053960 |
| 2 | 8 | 0.077184 | -1.538299 | 0.166252 |
| 3 | 6 | 0.907022 | -0.454775 | 0.233739 |
| 4 | 6 | 0.144356 | 0.691006 | 0.164691 |
| 5 | 6 | -1.239683 | 0.257827 | 0.047657 |
| 6 | 6 | 0.450647 | 2.086929 | 0.186516 |
| 7 | 6 | -0.576394 | 2.985743 | 0.095815 |
| 8 | 6 | -1.945251 | 2.557320 | -0.019959 |
| 9 | 6 | -2.281706 | 1.231760 | -0.044563 |
| 10 | 6 | 2.364425 | -0.722616 | 0.359569 |
| 11 | 6 | -2.266794 | -2.171697 | -0.032413 |
| 12 | 1 | 1.480575 | 2.423606 | 0.273612 |
| 13 | 1 | -0.364584 | 4.051570 | 0.110620 |
| 14 | 1 | -2.722738 | 3.313515 | -0.088881 |
| 15 | 1 | -3.319762 | 0.921244 | -0.132387 |
| 16 | 1 | 2.749900 | -1.297469 | -0.492685 |
| 17 | 1 | 2.911969 | 0.223435 | 0.402392 |
| 18 | 1 | 2.599232 | -1.290057 | 1.269661 |
| 19 | 1 | -2.274926 | -2.815593 | 0.856818 |
| 20 | 1 | -3.252417 | -1.705092 | -0.118872 |
| 21 | 1 | -2.123322 | -2.821835 | -0.905411 |

Table A6- 23. Cartesian Coordinates for 1,3-Diphenylisobenzofuran

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | 1.126509 | 0.118183 | -0.016869 |
| 2 | 8 | 0.036950 | -0.617802 | -0.382280 |
| 3 | 6 | -1.090924 | 0.150123 | -0.359582 |
| 4 | 6 | -0.730153 | 1.439406 | 0.027318 |
| 5 | 6 | 0.699795 | 1.414839 | 0.263753 |
| 6 | 6 | -1.449370 | 2.660634 | 0.180794 |
| 7 | 6 | -0.774770 | 3.777712 | 0.600819 |
| 8 | 6 | 0.625356 | 3.737578 | 0.894597 |
| 9 | 6 | 1.357789 | 2.590546 | 0.729594 |
| 10 | 6 | -2.331138 | -0.501226 | -0.745985 |
| 11 | 6 | 2.401106 | -0.578733 | 0.020955 |


| 12 | 1 | -2.508482 | 2.712015 | -0.047366 |
| ---: | ---: | ---: | ---: | ---: |
| 13 | 1 | -1.308931 | 4.716523 | 0.718461 |
| 14 | 1 | 1.112445 | 4.640317 | 1.252842 |
| 15 | 1 | 2.415992 | 2.575687 | 0.967059 |
| 16 | 6 | -2.308083 | -1.688541 | -1.505925 |
| 17 | 6 | -3.581830 | 0.025004 | -0.366883 |
| 18 | 6 | 3.620535 | 0.124181 | -0.040799 |
| 19 | 6 | 2.444073 | -1.985101 | 0.110621 |
| 20 | 6 | 4.835263 | -0.554671 | 0.008828 |
| 21 | 6 | 4.864909 | -1.947355 | 0.106748 |
| 22 | 6 | 3.661871 | -2.656793 | 0.150803 |
| 23 | 6 | -4.763350 | -0.601755 | -0.754289 |
| 24 | 6 | -4.727759 | -1.772466 | -1.514685 |
| 25 | 6 | -3.492887 | -2.313792 | -1.881582 |
| 26 | 1 | -1.352810 | -2.106976 | -1.805109 |
| 27 | 1 | -3.627629 | 0.906755 | 0.262993 |
| 28 | 1 | 3.616478 | 1.201708 | -0.164178 |
| 29 | 1 | 1.513593 | -2.541057 | 0.158266 |
| 30 | 1 | 5.763844 | 0.007682 | -0.043552 |
| 31 | 1 | 5.814255 | -2.474400 | 0.142383 |
| 32 | 1 | 3.671909 | -3.741186 | 0.223748 |
| 33 | 1 | -5.716976 | -0.179896 | -0.447895 |
| 34 | 1 | -5.651265 | -2.260739 | -1.813063 |
| 35 | 1 | -3.452099 | -3.226383 | -2.470518 |
| ------------------------------------------------------ |  |  |  |  |

Table A6- 24. Cartesian Coordinates for 1,3-Bis(t-butyl)isobenzofuran

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.135314 | 0.511780 | 0.443737 |
| 2 | 8 | -0.000003 | -0.229819 | 0.670534 |
| 3 | 6 | 1.135312 | 0.511781 | 0.443737 |
| 4 | 6 | 0.725576 | 1.781838 | 0.049836 |
| 5 | 6 | -0.725581 | 1.781837 | 0.049839 |
| 6 | 6 | 1.432044 | 2.967862 | -0.315070 |
| 7 | 6 | 0.716897 | 4.084171 | -0.658993 |
| 8 | 6 | -0.716908 | 4.084169 | -0.658991 |
| 9 | 6 | -1.432051 | 2.967859 | -0.315065 |
| 10 | 1 | 2.517561 | 2.981935 | -0.318349 |
| 11 | 1 | 1.239325 | 4.994999 | -0.939398 |
| 12 | , | -1.239339 | 4.994996 | -0.939394 |
| 13 | 1 | -2.517567 | 2.981931 | -0.318341 |
| 14 | 14 | -2.781242 | -0.362576 | 0.730263 |
| 15 | 14 | 2.781243 | -0.362574 | 0.730264 |
| 16 | 6 | 4.096603 | 0.940142 | 1.141617 |
| 17 | 6 | 2.554702 | -1.507375 | 2.221082 |
| 18 | 6 | 3.289944 | -1.363007 | -0.837987 |
|  |  |  |  |  |


| 19 | 6 | 4.665554 | -2.027364 | -0.613151 |
| :---: | :---: | :---: | :---: | :---: |
| 20 | 6 | 3.378703 | -0.423001 | -2.058792 |
| 21 | 6 | 2.243230 | -2.459448 | -1.124552 |
| 22 | 6 | -4.096605 | 0.940136 | 1.141616 |
| 23 | 6 | -2.554701 | -1.507376 | 2.221080 |
| 24 | 6 | -3.289938 | -1.363010 | -0.837987 |
| 25 | 6 | -4.665547 | -2.027372 | -0.613153 |
| 26 | 6 | -3.378700 | -0.423005 | -2.058793 |
| 27 | 6 | -2.243222 | -2.459448 | -1.124552 |
| 28 | 1 | 5.020603 | 0.454653 | 1.478070 |
| 29 | 1 | 4.354925 | 1.573133 | 0.285488 |
| 30 | 1 | 3.755230 | 1.595680 | 1.950777 |
| 31 | 1 | 3.450646 | -2.112691 | 2.402548 |
| 32 | 1 | 2.361198 | -0.920406 | 3.126488 |
| 33 | 1 | 1.708193 | -2.188046 | 2.083379 |
| 34 | 1 | 4.962813 | -2.599494 | -1.504227 |
| 35 | 1 | 5.454782 | -1.289386 | -0.424145 |
| 36 | 1 | 4.652384 | -2.728343 | 0.230620 |
| 37 | 1 | 3.655077 | -0.990527 | -2.959392 |
| 38 | 1 | 2.422372 | 0.073197 | -2.261791 |
| 39 | 1 | 4.137600 | 0.357556 | -1.923231 |
| 40 | 1 | 2.519077 | -3.026765 | -2.025680 |
| 41 | 1 | 2.164830 | -3.176809 | -0.298861 |
| 42 | 1 | 1.246225 | -2.036829 | -1.294492 |
| 43 | 1 | -5.020604 | 0.454643 | 1.478069 |
| 44 | 1 | -3.755236 | 1.595674 | 1.950775 |
| 45 | 1 | -4.354931 | 1.573124 | 0.285487 |
| 46 | 1 | -3.450646 | -2.112689 | 2.402549 |
| 47 | 1 | -1.708195 | -2.188052 | 2.083377 |
| 48 | 1 | -2.361192 | -0.920409 | 3.126487 |
| 49 | 1 | -4.962803 | -2.599502 | -1.504229 |
| 50 | 1 | -4.652376 | -2.728351 | 0.230618 |
| 51 | 1 | -5.454778 | -1.289397 | -0.424148 |
| 52 | 1 | -3.655073 | -0.990532 | -2.959393 |
| 53 | 1 | -4.137599 | 0.357550 | -1.923233 |
| 54 | 1 | -2.422371 | 0.073196 | -2.261792 |
| 55 | 1 | -2.519067 | -3.026765 | -2.025680 |
| 56 | 1 | -1.246217 | -2.036828 | -1.294491 |
| 57 | 1 | -2.164821 | -3.176810 | -0.298862 |

Table A6- 25. Cartesian Coordinates for 1,3-Dicyanoisobenzofuran

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -0.867119 | -1.124598 | 0.000000 |
| 2 | 8 | 0.425102 | -1.548198 | 0.000000 |


| 3 | 6 | 1.229684 | -0.451881 | 0.000000 |
| ---: | ---: | ---: | ---: | ---: |
| 4 | 6 | 0.458158 | 0.707243 | 0.000000 |
| 5 | 6 | -0.914039 | 0.266951 | 0.000000 |
| 6 | 6 | 0.768797 | 2.094138 | 0.000000 |
| 7 | 6 | -0.276112 | 2.982384 | 0.000000 |
| 8 | 6 | -1.641031 | 2.544394 | 0.000000 |
| 9 | 6 | -1.973800 | 1.213980 | 0.000000 |
| 10 | 6 | 2.625606 | -0.649790 | 0.000000 |
| 11 | 7 | 3.784787 | -0.768341 | 0.000000 |
| 12 | 6 | -1.887334 | -2.097674 | 0.000000 |
| 13 | 7 | -2.761171 | -2.868501 | 0.000000 |
| 14 | 1 | 1.801510 | 2.427975 | 0.000000 |
| 15 | 1 | -0.073046 | 4.049250 | 0.000000 |
| 16 | 1 | -2.427050 | 3.293815 | 0.000000 |
| 17 | 1 | -3.007943 | 0.884555 | 0.000000 |
| --------------------------------------------------------------1 |  |  |  |  |

## Calculated Models from Chapter 4

Table A6- 26. Cartesian Coordinates for 1,3,6,8-Tetrakis(tert-butyldimethylsilyl)naphtho[1,2-c:5,6-c]difuran, $\mathbf{2 5 c}$

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 14 | 5.141362 | 2.123563 | 0.595282 |
| 2 | 14 | 3.361936 | -2.978169 | 0.838450 |
| 3 | 6 | 2.356949 | 0.999860 | 0.189359 |
| 4 | 8 | 4.007923 | -0.371663 | 0.721832 |
| 5 | 6 | 2.874455 | -1.167862 | 0.645767 |
| 6 | 6 | 1.816160 | -0.330056 | 0.323191 |
| 7 | 6 | 3.699194 | 0.938862 | 0.446841 |
| 8 | 6 | -1.501715 | -2.087741 | 0.155493 |
| 9 | 1 | -1.853568 | -2.962224 | 0.269111 |
| 10 | 6 | -0.187108 | -1.852525 | 0.317648 |
| 11 | 1 | 0.379240 | -2.579750 | 0.547309 |
| 12 | 6 | 0.399459 | -0.548707 | 0.159133 |
| 13 | 6 | 3.542801 | -3.716121 | -0.892428 |
| 14 | 6 | 2.217784 | -3.642046 | -1.652064 |
| 15 | 1 | 2.345936 | -3.970888 | -2.566636 |
| 16 | 1 | 1.910033 | -2.711482 | -1.681131 |
| 17 | 1 | 1.547426 | -4.192684 | -1.196281 |
| 18 | 6 | 2.156378 | -3.993700 | 1.834429 |
| 19 | 1 | 2.644825 | -4.669268 | 2.349945 |
| 20 | 1 | 1.526108 | -4.438816 | 1.230171 |
| 21 | 1 | 1.663420 | -3.408936 | 2.447647 |
| 22 | 6 | 3.972185 | -5.181870 | -0.784297 |
| 23 | 1 | 3.295802 | -5.684674 | $-0.285171$ |
| 24 | 1 | 4.831334 | -5.236846 | $-0.316847$ |
| 25 | 1 | 4.065938 | -5.561604 | -1.683776 |
| 26 | 6 | 5.006766 | -2.954937 | 1.718084 |
| 27 | 1 | 4.889208 | -2.596604 | 2.621608 |
| 28 | 1 | 5.634376 | -2.389224 | 1.220273 |
| 29 | 1 | 5.360754 | -3.866911 | 1.770507 |
| 30 | 6 | 4.598467 | -2.939929 | -1.692375 |
| 31 | 1 | 5.462392 | -2.994176 | -1.232519 |
| 32 | 1 | 4.326369 | -2.000577 | -1.766260 |
| 33 | 1 | 4.679843 | -3.328358 | -2.587832 |
| 34 | 6 | 4.501343 | 3.870291 | 0.550773 |
| 35 | 1 | 3.801490 | 3.978702 | 1.229897 |
| 36 | 1 | 4.129644 | 4.058841 | -0.335289 |
| 37 | 1 | 5.236218 | 4.492144 | 0.735794 |
| 38 | 6 | 6.347083 | 1.804678 | -0.823519 |
| 39 | 6 | 7.501077 | 2.815157 | -0.784676 |
| 40 | 1 | 8.126125 | 2.627380 | -1.516755 |


| 41 | 1 | 7.970679 | 2.741413 | 0.072320 |
| :--- | :--- | ---: | ---: | :---: |
| 42 | 1 | 7.144526 | 3.721956 | -0.884508 |
| 43 | 6 | 6.931723 | 0.396086 | -0.705760 |
| 44 | 1 | 6.207382 | -0.262534 | -0.744938 |
| 45 | 1 | 7.405958 | 0.309827 | 0.146889 |
| 46 | 1 | 7.556150 | 0.238920 | -1.445429 |
| 47 | 6 | 5.935418 | 1.778452 | 2.241412 |
| 48 | 1 | 6.805418 | 2.227545 | 2.283845 |
| 49 | 1 | 6.061704 | 0.812560 | 2.347209 |
| 50 | 1 | 5.358833 | 2.113869 | 2.958234 |
| 51 | 6 | 5.619991 | 1.934746 | -2.159404 |
| 52 | 1 | 6.244555 | 1.751968 | -2.892361 |
| 53 | 1 | 5.264820 | 2.843466 | -2.251337 |
| 54 | 1 | 4.880804 | 1.292318 | -2.193853 |
| 55 | 14 | -5.141649 | -2.123163 | -0.595911 |
| 56 | 14 | -3.361756 | 2.978151 | -0.838299 |
| 57 | 6 | -2.357235 | -0.999460 | -0.189988 |
| 58 | 8 | -4.007743 | 0.371646 | -0.721681 |
| 59 | 6 | -2.874276 | 1.167844 | -0.645616 |
| 60 | 6 | -1.815980 | 0.330039 | -0.323040 |
| 61 | 6 | -3.699481 | -0.938462 | -0.447470 |
| 62 | 6 | 1.501895 | 2.087724 | -0.155342 |
| 63 | 1 | 1.853747 | 2.962207 | -0.268960 |
| 64 | 6 | 0.187287 | 1.852507 | -0.317497 |
| 65 | 1 | -0.379526 | 2.580150 | -0.547938 |
| 66 | 6 | -0.399703 | 0.547810 | -0.159201 |
| 67 | 6 | -3.542621 | 3.716104 | 0.892579 |
| 68 | 6 | -2.217605 | 3.642028 | 1.652215 |
| 69 | 1 | -2.346222 | 3.971288 | 2.566008 |
| 70 | 1 | -1.910276 | 2.710585 | 1.681063 |
| 71 | 1 | -1.548023 | 4.192895 | 1.197019 |
| 72 | 6 | -2.156199 | 3.993682 | -1.834278 |
| 73 | 1 | -2.644646 | 4.669251 | -2.349794 |
| 74 | 1 | -1.526705 | 4.439026 | -1.229434 |
| 75 | 1 | -1.664018 | 3.409147 | -2.446909 |
| 76 | 6 | -3.972005 | 5.181852 | 0.784448 |
| 77 | 1 | -3.295622 | 5.684656 | 0.285322 |
| 78 | 1 | -4.831620 | 5.237246 | 0.316218 |
| 79 | 1 | -4.066225 | 5.562004 | 1.683148 |
| 80 | 6 | -5.006586 | 2.954919 | -1.717933 |
| 81 | 1 | -4.889029 | 2.596586 | -2.621457 |
| 82 | 1 | -5.634663 | 2.389624 | -1.220901 |
| 83 | 1 | -5.361041 | 3.867312 | -1.771136 |
| 84 | 6 | -4.598288 | 2.939911 | 1.692526 |
| 85 | 1 | -5.462679 | 2.994576 | 1.231890 |
| 86 | 1 | -4.326655 | 2.000978 | 1.765631 |
| 87 | 1 | -4.679664 | 3.328341 | 2.587983 |
| 88 | 6 | -4.501164 | -3.870309 | -0.550622 |
| 89 | 1 | -3.802088 | -3.978492 | -1.229160 |
| 90 | 1 | -4.129464 | -4.058858 | 0.335440 |
|  |  |  |  | 168 |
|  |  |  |  |  |


| 91 | 1 | -5.236039 | -4.492161 | -0.735643 |
| :--- | :--- | ---: | ---: | ---: |
| 92 | 6 | -6.346904 | -1.804696 | 0.823670 |
| 93 | 6 | -7.500897 | -2.815175 | 0.784827 |
| 94 | 1 | -8.125946 | -2.627398 | 1.516906 |
| 95 | 1 | -7.971388 | -2.741892 | -0.073167 |
| 96 | 1 | -7.144347 | -3.721974 | 0.884659 |
| 97 | 6 | -6.931544 | -0.396104 | 0.705911 |
| 98 | 1 | -6.207203 | 0.262516 | 0.745089 |
| 99 | 1 | -7.405778 | -0.309844 | -0.146738 |
| 100 | 1 | -7.556437 | -0.238520 | 1.444800 |
| 101 | 6 | -5.936438 | -1.779122 | -2.240893 |
| 102 | 1 | -6.806128 | -2.228025 | -2.284692 |
| 103 | 1 | -6.061525 | -0.812577 | -2.347058 |
| 104 | 1 | -5.35653 | -2.113887 | -2.958083 |
| 105 | 6 | -5.619812 | -1.934763 | 2.159555 |
| 106 | 1 | -6.245264 | -1.752447 | 2.891514 |
| 107 | 1 | -5.265063 | -2.844363 | 2.251269 |
| 108 | 1 | -4.880624 | -1.292336 | 2.194004 |

Table A6- 27. Cartesian Coordinates for 4,14:7,11-Diepoxy-4,7,11,14-tetrahydro-2,9-propanonaphtho[1,2-f:5,6-f']diisoindole-1,3,8,10-tetrone, 3a,4,7,7a,10a,11,14,14a-octahydro(2R,3aR,4S,7R,7aS,9R,10aR,11S,14R,14aS)-rel- (9CI), 77a

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 8 | 2.069617 | 1.282181 | -2.492393 |
| 2 | 8 | 3.118023 | 1.790575 | 1.947438 |
| 3 | 8 | 4.077243 | -2.063911 | -0.200821 |
| 4 | 8 | -4.077247 | -2.063874 | 0.201346 |
| 5 | 8 | -3.117749 | 1.790030 | -1.947907 |
| 6 | 8 | -2.070026 | 1.283078 | 2.492242 |
| 7 | 7 | 2.414564 | 1.786092 | -0.260366 |
| 8 | 7 | -2.414647 | 1.786253 | 0.260008 |
| 9 | 6 | 2.636448 | 1.070390 | -1.438442 |
| 10 | 6 | 3.660052 | -0.009378 | -1.144599 |
| 11 | 1 | 4.487859 | 0.039940 | -1.855281 |
| 12 | 6 | 4.070678 | 0.198855 | 0.329068 |
| 13 | 1 | 5.123655 | 0.457859 | 0.464744 |
| 14 | 6 | 3.181363 | 1.336947 | 0.824168 |
| 15 | 6 | 3.106747 | -1.484184 | -1.094597 |
| 16 | 1 | 3.103546 | -2.007012 | -2.049607 |
| 17 | 6 | 3.782398 | -1.234027 | 0.939371 |
| 18 | 1 | 4.403589 | -1.508710 | 1.790227 |
| 19 | 6 | 2.281420 | -1.412194 | 1.057997 |
| 20 | 6 | 1.838513 | -1.532691 | -0.247005 |
| 21 | 6 | 0.458690 | -1.555803 | -0.560562 |
|  |  |  |  | 169 |


| 22 | 6 | -0.040518 | -1.491676 | -1.892088 |
| ---: | ---: | ---: | ---: | ---: |
| 23 | 1 | 0.666436 | -1.466726 | -2.715630 |
| 24 | 6 | -1.393284 | -1.382689 | -2.147294 |
| 25 | 1 | -1.757940 | -1.271755 | -3.163995 |
| 26 | 6 | -2.281363 | -1.412594 | -1.057630 |
| 27 | 6 | -1.838486 | -1.532631 | 0.247422 |
| 28 | 6 | -0.458660 | -1.555627 | 0.560973 |
| 29 | 6 | 0.040562 | -1.490959 | 1.892473 |
| 30 | 1 | -0.666379 | -1.465689 | 2.716011 |
| 31 | 6 | 1.393335 | -1.381856 | 2.147636 |
| 32 | 1 | 1.757970 | -1.270438 | 3.164291 |
| 33 | 6 | -3.782328 | -1.234361 | -0.939103 |
| 34 | 1 | -4.403538 | -1.509255 | -1.789884 |
| 35 | 6 | -3.106759 | -1.483911 | 1.094967 |
| 36 | 1 | -3.103559 | -2.006480 | 2.050115 |
| 37 | 6 | -3.181031 | 1.336544 | -0.824567 |
| 38 | 6 | -4.070522 | 0.198728 | -0.329225 |
| 39 | 1 | -5.123462 | 0.457735 | -0.465132 |
| 40 | 6 | -3.660077 | -0.009120 | 1.144543 |
| 41 | 1 | -4.487976 | 0.040329 | 1.855105 |
| 42 | 6 | -2.636669 | 1.070908 | 1.438275 |
| 43 | 6 | -1.300391 | 2.729871 | 0.127670 |
| 44 | 1 | -1.297522 | 3.369381 | 1.014908 |
| 45 | 1 | -1.499747 | 3.337523 | -0.758345 |
| 46 | 6 | -0.000101 | 1.927619 | -0.000463 |
| 47 | 1 | 0.090072 | 1.284982 | 0.879842 |
| 48 | 1 | -0.090375 | 1.285193 | -0.880923 |
| 49 | 6 | 1.300298 | 2.729740 | -0.128261 |
| 50 | 1 | 1.297715 | 3.369396 | -1.015405 |
| 51 | 1 | 1.499455 | 3.337263 | 0.757881 |
| ----------------------------------------------- |  |  |  |  |

Table A6- 28. Cartesian Coordinates for 5C-Biphenyl Rack, 78a

| Center Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 8 | 5.298703 | -2.151425 | 0.043507 |
| 2 | 6 | 4.418513 | -1.661156 | -0.988919 |
| 3 | 6 | 3.074779 | -1.679590 | -0.281154 |
| 4 | 6 | 3.382928 | -1.400771 | 1.058048 |
| 5 | 6 | 4.890055 | -1.232900 | 1.079116 |
| 6 | 6 | 5.256582 | 0.136745 | 0.390450 |
| 7 | 6 | 4.921602 | -0.168201 | -1.086853 |
| 8 | 6 | 3.883729 | 0.873364 | -1.482015 |
| 9 | 8 | 3.325975 | 0.989123 | -2.555177 |
| 10 | 7 | 3.652839 | 1.694889 | $-0.375347$ |
| 11 | 6 | 4.382965 | 1.328432 | 0.759835 |
| 12 | 8 | 4.302705 | 1.877039 | 1.840049 |
|  |  |  |  | 170 |


| 13 | 6 | 2.583550 | 2.698321 | -0.343483 |
| ---: | ---: | ---: | ---: | ---: |
| 14 | 6 | 1.237607 | 2.008033 | -0.099580 |
| 15 | 6 | -0.000018 | 2.911251 | 0.000107 |
| 16 | 6 | -1.237873 | 2.008163 | 0.098193 |
| 17 | 6 | -2.583522 | 2.698206 | 0.344348 |
| 18 | 7 | -3.652724 | 1.694689 | 0.376071 |
| 19 | 6 | -4.383171 | 1.328774 | -0.759091 |
| 20 | 8 | -4.303009 | 1.877787 | -1.839113 |
| 21 | 6 | -5.256579 | 0.136880 | -0.390076 |
| 22 | 6 | -4.890106 | -1.232550 | -1.079299 |
| 23 | 8 | -5.298756 | -2.151399 | -0.043967 |
| 24 | 6 | -4.418448 | -1.661559 | 0.988552 |
| 25 | 6 | -4.921371 | -0.168653 | 1.087087 |
| 26 | 6 | -3.883424 | 0.872802 | 1.482466 |
| 27 | 8 | -3.325580 | 0.988256 | 2.555613 |
| 28 | 6 | -3.074774 | -1.679866 | 0.280660 |
| 29 | 6 | -3.382995 | -1.400465 | -1.058397 |
| 30 | 6 | -2.371717 | -1.262490 | -1.994950 |
| 31 | 6 | -1.046477 | -1.399198 | -1.563124 |
| 32 | 6 | -0.712858 | -1.663617 | -0.220222 |
| 33 | 6 | -1.767172 | -1.820346 | 0.710385 |
| 34 | 6 | 0.712852 | -1.663709 | 0.219696 |
| 35 | 6 | 1.767202 | -1.819950 | -0.710965 |
| 36 | 6 | 1.046407 | -1.399954 | 1.562732 |
| 37 | 6 | 2.371639 | -1.263357 | 1.994652 |
| 38 | 1 | 4.527488 | -2.246657 | -1.900304 |
| 39 | 1 | 5.416574 | -1.440106 | 2.009177 |
| 40 | 1 | 6.308993 | 0.369138 | 0.570409 |
| 41 | 1 | 5.781871 | -0.117106 | -1.758531 |
| 42 | 1 | 2.833353 | 3.400732 | 0.455728 |
| 43 | 1 | 2.595790 | 3.223465 | -1.302736 |
| 44 | 1 | 1.320673 | 1.423090 | 0.823572 |
| 45 | 1 | 1.083694 | 1.288682 | -0.912176 |
| 46 | 1 | 0.075118 | 3.564892 | 0.880488 |
| 47 | 1 | -0.074988 | 3.566593 | -0.879017 |
| 48 | 1 | -1.083796 | 1.286971 | 0.909107 |
| 49 | 1 | -1.321499 | 1.425257 | -0.826207 |
| 50 | 1 | -2.594787 | 3.222024 | 1.304335 |
| 51 | 1 | -2.834131 | 3.401699 | -0.453665 |
| 52 | 1 | -6.309036 | 0.369195 | -0.569779 |
| 53 | 1 | -5.416774 | -1.439371 | -2.009366 |
| 54 | 1 | -4.527361 | -2.247410 | 1.899720 |
| 55 | 1 | -5.781556 | -0.117728 | 1.758884 |
| 56 | 1 | -2.584585 | -1.025953 | -3.033606 |
| 57 | 1 | -0.256947 | -1.247155 | -2.290870 |
| 58 | 1 | -1.557652 | -2.041709 | 1.751549 |
| 59 | 1 | 1.557710 | -2.040855 | -1.752229 |
| 60 | 1 | 0.256850 | -1.248373 | 2.290547 |
| 61 | 1 | 2.584465 | -1.027249 | 3.033422 |
| ---------------------------------------------- |  |  |  |  |
|  |  |  |  | 171 |

Table A6- 29. Cartesian Coordinates for $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy- $1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,9)chrysena- 3,7-dioxa-2,8-diona cyclooctaphane, 84a

| Center <br> Number | Atomic <br> Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 8 | -1.851470 | 1.816268 | -0.467409 |
| 2 | 8 | 3.881996 | -2.111531 | 0.197617 |
| 3 | 8 | -4.236838 | -1.635057 | 0.414832 |
| 4 | 8 | -2.344932 | 1.077737 | -2.545908 |
| 5 | 8 | 2.562963 | 1.663196 | 1.973898 |
| 6 | 8 | 2.377079 | 2.070495 | -0.245496 |
| 7 | 6 | 0.376560 | -1.217549 | 0.703945 |
| 8 | 6 | -0.654009 | -1.394847 | -0.295629 |
| 9 | 6 | -1.990182 | -1.253830 | 0.144078 |
| 10 | 6 | -2.304966 | -0.941479 | 1.453020 |
| 11 | 6 | 0.018213 | -0.897933 | 2.045210 |
| 12 |  | 0.808662 | -0.748873 | 2.774635 |
| 13 | 6 | -3.318527 | -1.193297 | -0.590569 |
| 14 | 1 | -3.438189 | -1.766823 | -1.508350 |
| 15 | 6 | -2.594613 | 1.129338 | -1.358844 |
| 16 | 6 | -1.303085 | -0.750533 | 2.422348 |
| 17 | 1 | -1.554976 | -0.490221 | 3.447169 |
| 18 | 6 | -3.809008 | -0.723679 | 1.450325 |
| 19 | 1 | -4.353304 | -0.916667 | 2.375167 |
| 20 | 6 | -3.717013 | 0.342424 | -0.710018 |
| 21 | 1 | -4.584955 | 0.410274 | -1.370430 |
| 22 | 6 | -4.093393 | 0.652787 | 0.767616 |
| 23 | 1 | -3.512597 | 1.469920 | 1.196517 |
| 24 | 1 | -5.157629 | 0.890815 | 0.848747 |
| 25 | 6 | -0.300696 | -1.669248 | -1.646953 |
| 26 | 1 | -1.091913 | -1.777419 | -2.382346 |
| 27 | 6 | 1.019694 | -1.782272 | -2.036904 |
| 28 | 1 | 1.272084 | -1.983509 | -3.074642 |
| 29 | 6 | 1.711571 | -1.365539 | 0.261696 |
| 30 | 6 | 3.687180 | 0.179321 | 0.465470 |
| 31 | 1 | 4.615551 | 0.310519 | 1.030260 |
| 32 | 6 | 2.019232 | -1.640902 | -1.058790 |
| 33 | 6 | 3.063013 | -1.195428 | 0.938484 |
| 34 | 1 | 3.136171 | -1.385063 | 2.007961 |
| 35 | 6 | 3.996598 | -0.133940 | -1.026363 |
| 36 |  | 5.069708 | -0.057594 | -1.222408 |
| 37 |  | 3.465995 | 0.517838 | -1.721695 |
| 38 | 6 | 3.535690 | -1.623466 | -1.117937 |
| 39 | 1 | 4.020368 | -2.225992 | -1.886464 |


| 40 | 6 | 0.116201 | 2.912398 | 0.287756 |
| :---: | :---: | :---: | :---: | :---: |
| 41 | 1 | -0.394033 | 3.823552 | 0.625742 |
| 42 | 1 | 0.052547 | 2.188856 | 1.105859 |
| 43 | 6 | -0.593490 | 2.348469 | -0.937291 |
| 44 | 1 | -0.783457 | 3.111262 | -1.700143 |
| 45 | 1 | -0.023628 | 1.538866 | -1.401523 |
| 46 | 6 | 1.583541 | 3.249961 | 0.042216 |
| 47 | 1 | 1.716583 | 3.884027 | -0.838912 |
| 48 | 1 | 2.006425 | 3.748883 | 0.916841 |
| 49 | 6 | 2.821524 | 1.370656 | 0.823426 |

Table A6- 30. Cartesian Coordinates for Symmetric Isomer of: $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy$1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,9)chrysena- 3,8 -dioxa-2,9-diona cyclononaphane, 84b

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.337125 | -1.203049 | 2.339839 |
| 2 | 6 | -0.021554 | -1.317430 | 1.934517 |
| 3 | 6 | 0.322229 | -1.446333 | 0.558948 |
| 4 | 6 | 1.650138 | -1.592185 | 0.093706 |
| 5 | 6 | 1.944808 | -1.696352 | -1.253891 |
| 6 | 6 | 0.941607 | -1.640182 | -2.237518 |
| 7 | 6 | -0.372200 | -1.519704 | -1.829825 |
| 8 | 6 | -0.714673 | -1.435357 | -0.450648 |
| 9 | 6 | -2.045938 | -1.336300 | 0.015166 |
| 10 | 6 | -2.346822 | -1.231946 | 1.360675 |
| 11 | 6 | 3.008468 | -1.610245 | 0.781833 |
| 12 | 6 | 3.724702 | -0.236912 | 0.504577 |
| 13 | 6 | 4.023049 | -0.350945 | -1.020242 |
| 14 | 6 | 3.459398 | -1.774938 | -1.318518 |
| 15 | 8 | 3.765802 | -2.469014 | -0.088229 |
| 16 | 6 | -3.855485 | -1.058358 | 1.410951 |
| 17 | 6 | -4.189691 | 0.392509 | 0.942716 |
| 18 | 6 | -3.844989 | 0.301592 | $-0.572367$ |
| 19 | 6 | -3.390154 | -1.209039 | -0.685410 |
| 20 | 8 | -4.275421 | -1.825361 | 0.260109 |
| 21 | 1 | -1.579703 | -1.098753 | 3.394234 |
| 22 | 1 | 0.776903 | -1.287847 | 2.668559 |
| 23 | 1 | 1.186611 | -1.700653 | -3.294723 |
| 24 | 1 | -1.166460 | -1.471407 | -2.567632 |
| 25 | 1 | 3.060438 | -1.960799 | 1.810882 |
| 26 | 1 | 4.666592 | -0.244558 | 1.066473 |


| 27 | 6 | 2.952022 | 0.960570 | 1.018407 |
| :---: | :---: | ---: | :---: | :---: |
| 28 | 1 | 5.099117 | -0.318501 | -1.211418 |
| 29 | 1 | 3.541795 | 0.429859 | -1.611115 |
| 30 | 1 | 3.903087 | -2.294197 | -2.168506 |
| 31 | 1 | -4.375369 | -1.400867 | 2.306126 |
| 32 | 1 | -3.613964 | 1.155045 | 1.467971 |
| 33 | 1 | -5.255111 | 0.593690 | 1.085373 |
| 34 | 6 | -2.798867 | 1.236138 | -1.150204 |
| 35 | 1 | -4.744718 | 0.421732 | -1.184629 |
| 36 | 1 | -3.506031 | -1.652169 | -1.672700 |
| 37 | 8 | -2.379847 | 2.174106 | -0.274372 |
| 38 | 8 | -2.385342 | 1.128259 | -2.287340 |
| 39 | 6 | -1.288949 | 3.037436 | -0.671764 |
| 40 | 6 | -0.013492 | 2.604871 | 0.045355 |
| 41 | 6 | 1.149284 | 3.572667 | -0.209236 |
| 42 | 6 | 2.402490 | 3.262551 | 0.603956 |
| 43 | 8 | 2.388805 | 0.971988 | 2.094357 |
| 44 | 8 | 3.009651 | 2.018379 | 0.177623 |
| 45 | 1 | -1.593242 | 4.044747 | -0.369816 |
| 46 | 1 | -1.183104 | 3.000538 | -1.758305 |
| 47 | 1 | -0.214850 | 2.538407 | 1.121375 |
| 48 | 1 | 0.254691 | 1.596767 | -0.288658 |
| 49 | 1 | 1.407699 | 3.587331 | -1.276265 |
| 50 | 1 | 0.846441 | 4.597086 | 0.053190 |
| 51 | 1 | 2.182477 | 3.197815 | 1.671908 |
| 52 | 1 | 3.167976 | 4.025534 | 0.434356 |
| ----------------------------------------------------------1 |  |  |  |  |

Table A6- 31. Cartesian Coordinates for Asymmetric Isomer of: $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy$1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,10)chrysena- 3,8-dioxa-2,9-diona cyclononaphane, 85b

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.184070 | -0.433417 | 2.033829 |
| 2 | 6 | 0.184438 | -0.391822 | 1.850322 |
| 3 | 6 | 0.811060 | -1.076970 | 0.770177 |
| 4 | 6 | 2.202595 | -1.039621 | 0.523130 |
| 5 | 6 | 2.779647 | -1.726985 | -0.529826 |
| 6 | 6 | 2.005509 | -2.480426 | -1.429896 |
| 7 | 6 | 0.640477 | -2.546676 | -1.227210 |
| 8 | 6 | 0.015242 | -1.865075 | -0.145483 |
| 9 | 6 | -1.376869 | -1.901638 | 0.098575 |
| 10 | 6 | -1.954384 | -1.200849 | 1.141214 |
|  |  |  |  | 174 |


| 11 | 6 | 3.362119 | -0.297649 | 1.171538 |
| :--- | :--- | ---: | ---: | ---: |
| 12 | 6 | 3.813608 | 0.868030 | 0.210890 |
| 13 | 6 | 4.461363 | 0.068069 | -0.955829 |
| 14 | 6 | 4.260395 | -1.392490 | -0.453334 |
| 15 | 8 | 4.443740 | -1.225465 | 0.972159 |
| 16 | 6 | -3.447863 | -1.411827 | 0.968621 |
| 17 | 6 | -3.921825 | -0.567352 | -0.278766 |
| 18 | 6 | -3.249549 | -1.353002 | -1.442308 |
| 19 | 6 | -2.551044 | -2.506520 | -0.654768 |
| 20 | 8 | -3.495532 | -2.735590 | 0.414810 |
| 21 | 1 | -1.651993 | 0.111550 | 2.849008 |
| 22 | 1 | 0.803803 | 0.190397 | 2.524856 |
| 23 | 1 | 2.465568 | -3.009117 | -2.260695 |
| 24 | 1 | 0.023143 | -3.135566 | -1.900044 |
| 25 | 1 | 3.278257 | -0.028331 | 2.222934 |
| 26 | 1 | 4.576730 | 1.450194 | 0.741413 |
| 27 | 6 | 2.745291 | 1.852589 | -0.228574 |
| 28 | 1 | 5.527650 | 0.291848 | -1.044075 |
| 29 | 1 | 3.980975 | 0.274462 | -1.914439 |
| 30 | 1 | 4.962532 | -2.130873 | -0.841597 |
| 31 | 1 | -4.084231 | -1.328142 | 1.848102 |
| 32 | 1 | -5.01196 | -0.666335 | -0.331627 |
| 33 | 6 | -3.652647 | 0.917591 | -0.121976 |
| 34 | 1 | -4.004243 | -1.762121 | -2.119747 |
| 35 | 1 | -2.383240 | -3.429257 | -1.210125 |
| 36 | 8 | -2.908984 | 1.440041 | -1.119458 |
| 37 | 8 | -4.087202 | 1.566212 | 0.809089 |
| 38 | 6 | -2.685950 | 2.872706 | -1.096555 |
| 39 | 6 | -1.573224 | 3.297743 | -0.141047 |
| 40 | 6 | -0.249768 | 2.553036 | -0.360583 |
| 41 | 6 | 0.859884 | 3.111412 | 0.532858 |
| 42 | 8 | 2.659596 | 2.342673 | -1.334417 |
| 43 | 8 | 1.919184 | 2.156289 | 0.795773 |
| 44 | 1 | -3.625153 | 3.366796 | -0.834777 |
| 45 | 1 | -2.424920 | 3.108215 | -2.131824 |
| 46 | 1 | -1.917039 | 3.155309 | 0.889518 |
| 47 | 1 | 0.062096 | 2.609256 | -1.408393 |
| 48 | 1 | -0.390428 | 1.495718 | -0.120597 |
| 49 | 1 | 1.302602 | 4.014984 | 0.102046 |
| 50 | 1 | 0.478214 | 3.343426 | 1.530812 |
| 51 | 1 | -2.550097 | -0.748627 | -2.021206 |
| 52 | 1 | -1.434212 | 4.379782 | -0.283176 |
|  |  |  |  |  |
|  |  |  |  |  |

Table A6- 32. Cartesian Coordinates for Symmetric Isomer of: $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy-
$1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,9)chrysena- 3,8 -dioxa-2,9-diona cyclonona-5-yn-phane, 84c

| Center <br> Number | Atomic Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.252828 | -1.330412 | -2.236689 |
| 2 | 6 | 0.081206 | -1.237245 | -1.888764 |
| 3 | 6 | 0.494283 | -1.209653 | -0.526548 |
| 4 | 6 | 1.848152 | -1.245489 | -0.119827 |
| 5 | 6 | 2.213600 | $-1.360660$ | 1.208804 |
| 6 | 6 | 1.252993 | $-1.330360$ | 2.236687 |
| 7 | 6 | -0.081049 | -1.237227 | 1.888768 |
| 8 | 6 | -0.494144 | -1.209640 | 0.526554 |
| 9 | 6 | -1.848016 | -1.245484 | 0.119829 |
| 10 | 6 | -2.213434 | -1.360723 | -1.208808 |
| 11 | 6 | 3.170502 | -1.194793 | -0.867488 |
| 12 | 6 | 3.890575 | 0.172354 | -0.540959 |
| 13 | 6 | 4.339422 | -0.062330 | 0.935919 |
| 14 | 6 | 3.732629 | -1.465811 | 1.196521 |
| 15 | 6 | -3.732445 | -1.465927 | -1.196541 |
| 16 | 6 | -4.339248 | -0.062443 | -0.935978 |
| 17 | 6 | -3.890697 | 0.172164 | 0.541002 |
| 18 | 6 | -3.170389 | -1.194883 | 0.867491 |
| 19 | 8 | -3.970103 | -2.100817 | 0.083802 |
| 20 | 1 | -1.545583 | -1.394056 | -3.281685 |
| 21 | 1 | 0.841568 | -1.219882 | -2.663517 |
| 22 | 1 | 1.545755 | -1.393974 | 3.281683 |
| 23 | 1 | -0.841405 | -1.219860 | 2.663527 |
| 24 | 6 | 3.101892 | 1.460192 | -0.686672 |
| 25 | 1 | 4.769438 | 0.258693 | -1.190646 |
| 26 | 1 | 3.971986 | 0.714464 | 1.608871 |
| 27 | 1 | 5.428634 | -0.105809 | 1.014904 |
| 28 | 1 | -5.428444 | -0.105927 | -1.015165 |
| 29 | 1 | -4.769712 | 0.258255 | 1.190508 |
| 30 | 6 | -3.102451 | 1.460223 | 0.687104 |
| 31 | 8 | -3.319687 | 2.466557 | 0.049606 |
| 32 | 8 | -2.125451 | 1.374104 | 1.624135 |
| 33 | 6 | -1.221740 | 2.510898 | 1.663476 |
| 34 | 6 | -0.353685 | 2.557282 | 0.490108 |
| 35 | 8 | 3.319733 | 2.466886 | -0.049948 |
| 36 | 8 | 2.125166 | 1.374115 | -1.623988 |
| 37 | 6 | 1.221475 | 2.510916 | -1.663481 |
| 38 | 6 | 0.353375 | 2.557297 | -0.490148 |
| 39 | 1 | -1.805164 | 3.432250 | 1.749309 |
| 40 | 1 | -0.642067 | 2.360228 | 2.577133 |


| 41 | 1 | 0.641878 | 2.360232 | -2.577184 |
| ---: | ---: | ---: | ---: | :---: |
| 42 | 1 | 1.804914 | 3.432262 | -1.749267 |
| 43 | 1 | -3.971699 | 0.714389 | -1.608828 |
| 44 | 8 | 3.970305 | -2.100674 | -0.083827 |
| 45 | 1 | 4.196650 | -2.043391 | 1.996763 |
| 46 | 1 | -4.196430 | -2.043517 | -1.996797 |
| 47 | 1 | -3.182664 | -1.487657 | 1.916363 |
| 48 | 1 | 3.182783 | -1.487522 | -1.916373 |
| ------------------------------------------------------------ |  |  |  |  |

Table A6- 33. Cartesian Coordinates for Asymmetric Isomer of: $1^{1}, 1^{4}, 1^{7}, 1^{10}$-Diepoxy$1^{1}, 1^{2}, 1^{3}, 1^{4}, 1^{7}, 1^{8}, 1^{9}, 1^{10}$-octahydro-1(2,10)chrysena- 3,8-dioxa-2,9-diona cyclonona-5-yn-phane, 85 c

| Center <br> Number | Atomic <br> Number | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | X | Y | Z |
| 1 | 6 | -1.255393 | -0.054904 | -1.908459 |
| 2 | 6 | 0.114002 | -0.092406 | -1.759801 |
| 3 | 6 | 0.731070 | -0.983600 | -0.838952 |
| 4 | 6 | 2.123964 | -1.018087 | -0.618653 |
| 5 | 6 | 2.704639 | -1.873963 | 0.298416 |
| 6 | 6 | 1.929150 | -2.762578 | 1.064226 |
| 7 | 6 | 0.560747 | -2.777508 | 0.869096 |
| 8 | 6 | -0.068593 | -1.905210 | -0.062554 |
| 9 | 6 | -1.466460 | -1.852993 | -0.271803 |
| 10 | 6 | -2.032611 | -0.942415 | -1.144567 |
| 11 | 6 | 3.273242 | -0.175754 | -1.142233 |
| 12 | 6 | 3.712583 | 0.826420 | -0.003669 |
| 13 | 6 | 4.348884 | -0.150662 | 1.024278 |
| 14 | 6 | 4.180256 | -1.512965 | 0.283873 |
| 15 | 8 | 4.365664 | -1.107775 | -1.093079 |
| 16 | 6 | -3.526821 | -1.085571 | -0.935072 |
| 17 | 6 | -3.871775 | -0.468372 | 0.473641 |
| 18 | 6 | -3.261302 | -1.537849 | 1.430934 |
| 19 | 6 | -2.651509 | -2.533450 | 0.400017 |
| 20 | 8 | -3.648909 | -2.488856 | -0.646582 |
| 21 | 1 | -1.721570 | 0.653856 | -2.585684 |
| 22 | 1 | 0.740188 | 0.589856 | -2.325829 |
| 23 | 1 | 2.389143 | -3.428556 | 1.789623 |
| 24 | 1 | -0.057328 | -3.465366 | 1.439696 |
| 25 | 1 | 3.185716 | 0.262153 | -2.135265 |
| 26 | 6 | 2.630485 | 1.722812 | 0.569614 |


| 27 | 1 | 4.472124 | 1.487005 | -0.436184 |
| :---: | :---: | ---: | :---: | :---: |
| 28 | 1 | 3.844605 | -0.115251 | 1.991770 |
| 29 | 1 | 5.409541 | 0.071834 | 1.169178 |
| 30 | 1 | 4.895945 | -2.291472 | 0.549143 |
| 31 | 1 | -4.190784 | -0.797555 | -1.749013 |
| 32 | 1 | -4.962944 | -0.441807 | 0.580523 |
| 33 | 1 | -4.041712 | -2.033873 | 2.013858 |
| 34 | 6 | -3.370206 | 0.936313 | 0.751605 |
| 35 | 1 | -2.521561 | -3.557965 | 0.749220 |
| 36 | 8 | -3.051284 | 1.359366 | 1.838425 |
| 37 | 8 | -3.360057 | 1.698151 | -0.377237 |
| 38 | 6 | -2.875841 | 3.052318 | -0.210813 |
| 39 | 6 | -1.415389 | 3.145345 | -0.152745 |
| 40 | 8 | 2.318668 | 1.800715 | 1.735065 |
| 41 | 8 | 2.084749 | 2.500068 | -0.410758 |
| 42 | 6 | 1.212639 | 3.569852 | 0.033872 |
| 43 | 6 | -0.214930 | 3.274391 | -0.087758 |
| 44 | 1 | -3.311536 | 3.475905 | 0.699255 |
| 45 | 1 | -3.267374 | 3.585784 | -1.081259 |
| 46 | 1 | 1.457969 | 3.805424 | 1.073146 |
| 47 | 1 | 1.473091 | 4.421623 | -0.602344 |
| 48 | 1 | -2.529159 | -1.109935 | 2.118528 |
| ---------------------------------------------------- |  |  |  |  |


[^0]:    ${ }^{\mathrm{i}}$ Value of $\beta$ is equal to one-half the $\pi$-electron energy in ethylene.

[^1]:    ${ }^{\text {ii }}$ While IBF is the most reactive isolable diene known o-xylylene is more reactive, but unisolable.

[^2]:    ${ }^{\text {iii }}$ Plotting $\log \left(\mathrm{SC}_{\text {ratio }}\right)$ vs $\log (\mathrm{k})$ results in a linear trend.

[^3]:    ${ }^{\text {iv }}$ Compound 32 exhibits a $43^{\circ}$ twist from end-to-end

[^4]:    ${ }^{v}$ B3LYP/6-31G(d) calculated structure

[^5]:    ${ }^{\text {vi }}$ Attempts to use excess NMM resulted in loss of spectrum quality to the point that accurate peak integrations could not be obtained.

[^6]:    ${ }^{\text {vii }}$ This polarization effect is seen in lower $S$ orbitals as well, but is most pronounced in the 5 S orbitals which is why they were used.

[^7]:    viii There is a small polarization on C 7 in the HOMO-1 towards the tether

[^8]:    ${ }^{\text {ix }}$ A RMSD between the calculated and experimental model was $0.3130 \AA$ for difuran $\mathbf{3}$. When the t-butyl and methyl substituents were removed the RMSD dropped to $0.09346 \AA$.

