The Syntheses and Photochromic Properties of Several Substituted and Condensed Benzo[e]dimethylidihydropyrenes

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ABSTRACT

The symmetric multistate photo-switchable molecule 72, which contains two DHP units with a dibenzocyclophane as a spacer, was successfully synthesized by different routes using aryne-furan type Diels-Alder reactions. In the course of making 72, the intermediate furan 79 was synthesized, which upon deoxygenation gave photo-switchable furan 82.

In a study of substitution effects on benzo[e]pyrene 21, the substituents phenyl, acetyl, nitro and phenylethynyl were attached to the 4,5-positions. The acetyl and nitro groups were introduced by direct substitution of 21, while coupling methodology were used for the phenyl and phenylethynyl groups. In the later case, a Suzuki coupling was used on bromide 69, followed by bromination, or a Sonogashira coupling was used on the bromoiiodide 100, and then an aryne-furan Diels-Alder reaction and deoxygenation were used to give the final substituted benzo[e]pyrenes 105 and 103.

The successful synthesis of the phenylbenzo[e]pyrene 105 enabled us to access the monosubstituted tris-pyrene system 120 through the reaction of bromophenylpyrene 107 and furan 79.

The thermal return reactions (cyclophanediene to dihydropyrene) were studied on the benzo[e]pyrene derivatives and multistate photoswitch systems. Although the activation energies and enthalpies do not change much with substitution, the thermal return rates do appear to decrease with an electron withdrawing substituent.

Photochromic studies were performed on 72 and 120. They both opened in a stepwise manner with one DHP ring opening and then the other, though the intermediate could not be isolated.

A simple comparison of the photo opening and closing rates relative to benzo[e]pyrene 21 was performed under excess light conditions. All the derivatives of 21 synthesized in this thesis had faster visible opening rates than the parent 21; the UV closing rates did not change much however.
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List of Numbered Compounds

1 2 3 4 5 6 7
8 9 10 11 12 13 14 15
16 17 18 19 20 21
22 23 24 25 26
27 28 29 30
31 32 33
CH₃\(\text{SMe}\)CH\(\text{F}_2\text{C}_2\text{H}_5\)CH₃ \(\text{Me}^1\) (\(\text{C}_2\text{H}_5\)\(\text{N}\)) \(\text{N}(\text{C}_2\text{H}_5)\)₂

\(\text{NO}_2\) \(\text{CHO}\) \(\text{CHO}\) \(\text{CHO}\) \(\text{CHO}\) \(\text{CHO}\) \(\text{CHO}\) \(\text{CHO}\)

\(\text{COCH}_3\) \(\text{COCH}_3\) \(\text{CO}_2\text{H}_5\) \(\text{CO}_2\text{H}_5\) \(\text{CO}_2\text{H}_5\) \(\text{CO}_2\text{H}_5\)

\(\text{COCH}_3\) \(\text{COCH}_3\) \(\text{COCH}_3\) \(\text{COCH}_3\) \(\text{COCH}_3\) \(\text{COCH}_3\) \(\text{COCH}_3\)

\(\text{O}\) \(\text{O}\) \(\text{O}\) \(\text{O}\) \(\text{O}\) \(\text{O}\) \(\text{O}\)

\(\text{R}_1\text{R}_2\text{R}_3\) \(\text{R}_1\text{R}_2\text{R}_3\) \(\text{R}_1\text{R}_2\text{R}_3\) \(\text{R}_1\text{R}_2\text{R}_3\) \(\text{R}_1\text{R}_2\text{R}_3\)
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>Ar</td>
<td>arene</td>
</tr>
<tr>
<td>BLE</td>
<td>bond localization energy</td>
</tr>
<tr>
<td>CI</td>
<td>chemical ionization</td>
</tr>
<tr>
<td>CPD</td>
<td>metacyclophanediene</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift in ppm from standard</td>
</tr>
<tr>
<td>dec.</td>
<td>decomposition</td>
</tr>
<tr>
<td>DHP</td>
<td>dimethyldihydropyrene</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectrum</td>
</tr>
<tr>
<td>IR</td>
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</tr>
<tr>
<td>KO'Bu</td>
<td>potassium t-butoxide</td>
</tr>
<tr>
<td>LSIMS</td>
<td>liquid secondary ion mass spectrometry</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrum</td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>bs</td>
<td>broad singlet</td>
</tr>
<tr>
<td>s</td>
<td>second, singlet</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>dd</td>
<td>doublet of doublet</td>
</tr>
<tr>
<td>m</td>
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</tr>
<tr>
<td>ppm</td>
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<td>resonance energy</td>
</tr>
<tr>
<td>sd</td>
<td>standard deviation</td>
</tr>
<tr>
<td>sub</td>
<td>sublime</td>
</tr>
<tr>
<td>t</td>
<td>tertiary group</td>
</tr>
<tr>
<td>TBA</td>
<td>tetra-(n)-butylammonium cation</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet and visible spectrum</td>
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</table>
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To my husband, Jian Pu and my sons, Cullen and Gavin
Chapter One  Introduction

1.1 Aromaticity

The chemistry of aromatic compounds began with the discovery of benzene by Faraday\(^1\) in 1825. Kekule\(^2\) first suggested the cyclic structure of benzene in 1865 and applied the term aromatic to compounds containing a benzene ring. A year later, Erlenmeyer\(^3\) designated as aromatic compounds, those which had chemical reactivities similar to benzene. At that time, all unsaturated systems with cyclic conjugation were considered to be aromatic, until Willstaetter\(^4\) showed that cyclooctatetraene had no chemical similarity to benzene.

Later, the 19\(^{th}\)-century concept of the oscillation of double and single bonds in benzene was replaced by the concept of resonance between canonical structures. Huckel's molecular orbital (HMO) theory made the first successful attempt to account for such stability based on \(\pi\)-electron configurations.\(^5\) Huckel suggested that amongst fully conjugated, planar, monocyclic polyolefins, only those possessing \((4n + 2)\) \(\pi\)-electrons \((n\) is an integer) have special stability.

Although Huckel's work appeared in 1931, it was overlooked by many organic chemists for nearly 20 years until the 1950s, when there was an explosion of work based on the ideas that he presented, and in particular to prepare appropriate compounds to test their validity.

A series of annulenes were prepared. [14]Annulene 1 and [18]annulene 2 were shown to have properties that classified them as aromatic.\(^6\) As well, dehydroannulenes,
such as the cyclopolyenyne 3, were also prepared and shown to have properties appropriate for a conjugated \((4n + 2)\) \(\pi\)-electron system.

Huckel's rule thus provided a theoretical basis for aromaticity, even though it did not cover all cases, and was still questioned by many chemists. However, it generated interest to find further experimental evidence to describe aromaticity.

1.1.1 Estimation of Aromaticity

Aromaticity is often considered an elusive concept and the choice of criteria is controversial. Different individuals might have different ideas and feelings of exactly what they mean by the term. The one unifying basis for these ideas is that an aromatic compound is "benzene like". But how and in what way?

On looking at the chemical reactivity of benzene, the following properties should be considered.

- Thermal stability.
- Resistance of the ring to oxidation.
- Electrophilic substitution, rather than addition, reactions.

The problem with any criterion based on chemical properties is that it embraces a very wide range of different reactions and types of reactions, and different compounds
may resemble benzene in some way but may differ in others, and thus it is effectively
impossible to lay down a precise criterion.

Thermodynamic stability is another possible comparison basis, and it has been
proposed that cyclic conjugated systems may be considered to be aromatic if cyclic
delocalization makes a negative contribution to their heat of formation. Once again
there are problems in providing uniform standards. These include the difficulty often
involved in obtaining reliable data and in finding suitable reference compounds with
which they may be compared. Furthermore, although delocalization may be an
important factor in contributing to the overall stability of a conjugated cyclic polyene,
other contributing factors may sometimes nullify or override its effect.

Another criterion is based on physical evidence for delocalization of $\pi$-electrons, in
particular the equalizing of bond lengths of the aromatic ring. Complete cyclic
delocalization of $\pi$-electrons in a homocyclic ring should lead to all the bonds being of
equal length, as is the case in benzene, where all the bond distances are 1.397Å. In fact,
the C-C bond lengths in aromatic compounds should have values that are intermediate
between the length of a single C$_{sp^2}$-C$_{sp^2}$ bond (1.465Å in butadiene) and a C=C double
bond (1.337Å in ethylene). However, this criterion obviously does not easily apply to
heterocyclic and polycyclic systems because of their lower symmetry. More
importantly, X-ray data is needed for this method, and sometimes this is not easy to
obtain.

Perhaps the most useful criteria are magnetic criteria, which include diamagnetic
anisotropy, diamagnetic susceptibility exaltation and $^1$H NMR diatropism. The later is
currently the most favored one.
The majority of organic molecules do not have permanent magnetic moments and consequently are weakly diamagnetic, having negative magnetic susceptibilities. Most diamagnetic molecules are anisotropic; that is, the magnitudes of the diamagnetic susceptibility along the three perpendicular principle magnetic axes are not equal. The diamagnetic anisotropy is defined as \( \Delta \chi_m = \chi_z - \frac{1}{2}(\chi_x + \chi_y) \), where \( \chi_x \), \( \chi_y \), and \( \chi_z \) are the three principal components of the diamagnetic susceptibility. Direct measurement of the anisotropy of the molar diamagnetic susceptibilities \( \Delta \chi_m \), requires the growth of a monocrystal and an initial determination of the molecular orientation. Analysis shows that only a fraction of \( \Delta \chi_m \) for aromatic compounds, about one half for benzene,\(^8\) can be attributed to the ring current, whereas the other fraction is due to local anisotropy. The experimental difficulties and the need to separate the contributions of the local and non-local components limit the widespread use of the anisotropy of diamagnetic susceptibility as a criterion of aromaticity.

A property which is simpler to determine is the difference between the total molar magnetic susceptibility of an aromatic compound and that of an analogous hypothetical compound with localized bonds, \( \chi_M - \chi_M^{\text{loc}} \), this property is known as the exaltation of diamagnetic susceptibility \( (\Lambda)^9 \) or non-local magnetic susceptibility \( (\chi_M^{\text{nonloc}})^{10} \). The total molar magnetic susceptibility \( \chi_M \) of the compound under study is measured experimentally by determining the force at which the sample of the substance is repelled by a magnetic field of a given strength. The magnetic susceptibility of the hypothetical compound with localized bonds \( \chi_M^{\text{loc}} \) is calculated as the sum of the contributions of the separate structural elements of the molecule. Table 1 gives some examples of exaltation of diamagnetic susceptibility.
Table 1. Exaltation of diamagnetic susceptibility ($10^{-6} m^3 mol^{-1}$).¹¹

<table>
<thead>
<tr>
<th>Compound</th>
<th>Λ</th>
</tr>
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<tbody>
<tr>
<td>Benzene</td>
<td>13.7</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>30.5</td>
</tr>
<tr>
<td>Anthracene</td>
<td>48.6</td>
</tr>
<tr>
<td>Furan</td>
<td>8.9</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>-0.7</td>
</tr>
<tr>
<td>[16]Annulene</td>
<td>-5</td>
</tr>
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</table>

Again, the need for hypothetical compounds always provides a chance of obtaining misleading results.

1.1.2 Ring Current and $^1$H NMR Spectroscopy

NMR spectroscopy is a popular method for the study of diamagnetic compounds. The proton chemical shifts in a NMR spectrum can be related to the diatropicity and paratropicity of the system and hence can serve as a criterion for assessment of their aromatic nature.

Proton chemical shifts for the conjugated π systems drawn in next page are shown in Table 2.

Benzene 4, which is considered as the "prototype" aromatic molecule, shows a proton chemical shift at δ 7.27, which is about 1.5 ppm downfield from a normal alkene. The additional deshielding can be explained by the induced ring current, which will be discussed later. In [14]annulene 1, the inner protons are shielded due to the ring current
and appear at $\delta -0.61$. In the isoelectronic bridged annulene 17, the internal methyl protons appear at $\delta -4.25$. Any deviation from planarity leads to a reduction of ring current. The bridged $[10]$annulene 12 has a bent geometry, with the internal methylene group pointing away from the $\pi$ network, the bridge protons appear at $\delta -0.52$ and are less shielded compared to 17. When an annulene suffers a total lack of planarity, the delocalization is disrupted. As a result, there is no ring current and hence it is atropic.

Cyclooctatetraene 8, is tub shaped and its protons appear at $\delta 5.7$. Since the proton chemical shift falls in the normal alkene range, this suggests there is no special ring current in this molecule. On the other hand, in the near planar $[12]$annulene 15, the inner protons are more strongly deshielded than those in normal alkenes. This paratropic
behavior is even more dramatic in the case of dianion 18, whose internal methyl protons appear at δ 21.

Table 2. $^1$H NMR Chemical shifts (δ) of selected π systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\pi$ electrons</th>
<th>δ outer protons</th>
<th>δ inner protons</th>
<th>reference</th>
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<tbody>
<tr>
<td>4</td>
<td>6</td>
<td>7.27</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>11.10</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>5.60</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>9.20</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>5.70</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>5.70</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>8.50 – 7.46</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>7.70 – 6.05</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>7.27 – 6.95</td>
<td>-0.52</td>
<td>17</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>8.23 – 6.50</td>
<td>0.65 to -0.40</td>
<td>18</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>6.80 – 5.40</td>
<td>-0.70 &amp; -1.20</td>
<td>19</td>
</tr>
<tr>
<td>15</td>
<td>12</td>
<td>5.50 – 5.20</td>
<td>6.06</td>
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</tr>
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<td>14</td>
<td>7.88</td>
<td>-0.61</td>
<td>21</td>
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<tr>
<td>16</td>
<td>14</td>
<td>9.50 – 8.70</td>
<td>-3.75 &amp; -3.80</td>
<td>22</td>
</tr>
<tr>
<td>17</td>
<td>14</td>
<td>8.67 – 7.98</td>
<td>-4.25</td>
<td>23</td>
</tr>
<tr>
<td>18</td>
<td>16</td>
<td>-3.19 to -3.96</td>
<td>21.00</td>
<td>24</td>
</tr>
</tbody>
</table>

The protons of cyclopropenium cation 5, resonate downfield at δ 11.1. In this case, the positive charge also deshields the protons. By the same token, an upfield shift...
is experienced by protons in a negatively charged system. This is manifested in the
proton chemical shift of the aromatic cyclooctatetraenyl dianion 9, which is the same as
that of the non-aromatic cyclooctatetraene.

In heterocycles, the proton chemical shifts are affected not only by the ring current,
which is similar to that in their benzenoid analogs, but also by the charge density on the
atom to which the proton is bound. Pyrrole 11, is more electron-rich than pyridine 10; the
dipole moment of pyrrole points away from the nitrogen, and towards the nitrogen in
case of pyridine. The non-ring current factors make the protons in pyridine more
deshielded than those in pyrrole.

Vogler²⁵ has derived an equation relating the observed total shielding effect (σ) to
the shielding due to ring current and other factors. This is given in the following
equation:

\[ \sigma = \sigma^{RC} + \sigma^{LA} + \sigma_{\mu}^0 + \sigma_\nu^q \]

Where

- \( \sigma^{RC} \) = Shielding due to ring current
- \( \sigma^{LA} \) = Shielding due to the local anisotropy
- \( \sigma_{\mu}^0 \) = Zero of the chemical shift scale
- \( \sigma_\nu^q \) = Shielding due to excess \( \pi \)-electron density

Therefore, interpretation of the chemical shifts has to be carried out with extreme
cautions, especially in the case of charged systems and heterocycles, where the shielding
arising from local anisotropic contributions and excess \( \pi \)-electron density are of equal
importance.²⁶

The ring current model, although proposed by Pauling²⁷ in 1936, was first applied
to proton chemical shifts by Pople²⁸ in 1956. According to this model the benzene ring
is looked upon as a conduction loop in which the $\pi$-electrons circulate perpendicularly to the direction of the external magnetic field $H_0$. A secondary magnetic field is induced opposing the external one. This is illustrated in Figure 1.

**Figure 1. Induced ring current and proton magnetic deshielding in benzene.**

Although there is no proof that ring current exists, the ring current theory does adequately explain the chemical shifts of annulenes, and it has become a widely accepted concept. Haddon’s work on the calculation of ring currents for annulenes is quite remarkable. As for the calculation of resonance energy, a reference compound has to be chosen to obtain the model chemical shift (MCS). The reference proton should experience the same magnetic environment as the proton of interest, but without the magnetic contribution from the ring current. Ring current chemical shift (RCCS) = Observed chemical shift (OCS) - Model chemical shift (MCS). Ring current (RC) is calculated by $\text{RCCS}_i = RC \times \text{RCGF}_i$ (i = 1,..., n). RCGF is the ring current geometric factor; n is the number of distinct chemical shifts in the observed molecule. Because chemical shift is affected by so many factors other than the ring current, the reference
proton chemical shift is almost impossible to estimate for molecules other than annulenes. Haddon’s ring current calculation thus mostly applies to annulenes.

A novel comparison was designed by Mitchell using a probe molecule to measure relative aromaticity with respect to benzene. The selected probe is dimethyldihydropyrene (DHP) 17, in which the internal methyl protons are shielded quite dramatically ($\delta \sim 4.25$). This chemical shift is remarkably affected by fusion of an aromatic ring on the side, but not much by substituents. This phenomenon can be explained by a bond localization effect.

When a benzene ring is fused to the [14]annulene 17 to give compound 19, the ring current in the DHP ring changes profoundly. Because of the $\pi$ electron delocalization in the benzo moiety, all bonds are partially localized. The complete delocalization in DHP ring is broken; thus, the induced ring current is dramatically reduced. The competition of the ring currents between DHP and benzene depends on their relative resonance energies. The manifestation of the ring current is best shown by the internal proton chemical shifts in such annulenes. An intrinsic relationship exists between proton chemical shift and resonance energy. If different aromatic moieties are fused to DHP, and the internal methyl proton chemical shifts are compared, the resonance energy (or more strictly, the bond localization energy, BLE) of the fused molecule can be determined relative to benzene.
The series with [e]-fused aromatics 20-23 is one of the most recently series studied. There is a near linear relationship between BLE (here Dewar resonance energies are used) and the internal methyl proton chemical shift $\delta$(Me).

$$\text{BLE} = \frac{3.39 + \delta(\text{Me})}{2.24}$$

Table 3. Comparison of calculated and actual BLE values (benzene units)\(^a\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$(Me)</th>
<th>calculated BLE</th>
<th>Actual BLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-4.06</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>21</td>
<td>-1.58</td>
<td>1.08</td>
<td>1.00</td>
</tr>
<tr>
<td>22</td>
<td>-0.54</td>
<td>1.54</td>
<td>1.52</td>
</tr>
<tr>
<td>23</td>
<td>0.00</td>
<td>1.78</td>
<td>1.84(^a)</td>
</tr>
</tbody>
</table>

\(^a\)Dewar RE (anthracene) = 1.600 eV = 1.84 benzene units;

1 benzene unit = RE(benzene) = 0.869 eV.

The calculated BLEs in Table 3 are from the above equation. We can see the discrepancies are rather small for all the compounds.

This work gives an experimental determined resonance energy relative to benzene, No reference molecule is needed in calculating the relative resonance energy to benzene.
1.2 Photochromism

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra.\(^{32}\)

\[
\begin{align*}
A & \xrightleftharpoons[\text{Thermal}]{hv_2} B \\
A & \xrightarrow{hv_1} B
\end{align*}
\]

There are two types of photochromism. One is when the back reaction occurs thermally, which is called type T; if the back reaction occurs photochemically, it is called type P. Usually the thermodynamically stable form A is colorless or light yellow and form B is colored, and this is then referred to as positive photochromism. When the maximal absorption wavelength of A is longer than B, then the photochromism is negative or inverse. We will see later that our dimethyldihydropyrene (DHP) system is an example of negative photochromism.

In order to be put to practical use, a photochromic compound must have the following properties:\(^{33}\)

1. Thermal stability of both isomers;
2. Low fatigue (can be cycled many times without significant loss of performance);
3. High sensitivity and rapid response;

Among these requirements, the most important ones are the thermal stability of both isomers and the fatigue resistance.
1.3 Examples of Organic Photochromic Compounds

For photochromic compounds, the chemical processes involved mostly belong to the following five types.

(1) *cis-trans* Isomerization;

(2) Electrocyclic reaction;

(3) Heterolytic cleavage;

(4) Tautomerism;

(5) Homolytic cleavage.

The examples hereafter are followed the five types to illustrate different photochromic compounds.

1.3.1 *cis-trans* Isomerization

(a) Stilbenes

\[
\begin{align*}
24 & \xrightarrow{h\nu_1} 24' \\
\text{hv}_1 & \text{hv}_2 / \Delta
\end{align*}
\]

The *cis-trans* isomerization of stilbene is an early example of a photochromic conversion and now primarily is only of theoretical and historical interest. Henry\textsuperscript{34} was the first to delineate with clarity the several processes occurring when stilbenes are irradiated with light.
The ultraviolet absorption spectrum in solution shows that the first absorption maximum of the \textit{trans}-isomer 24 (294 nm) is at lower energy than that of the \textit{cis}-isomer \textit{24*} (272 nm).\footnote{35} This implies that the \textit{cis}-isomer is less planar.

Monosubstitution by halogen at the \textit{para} position does not alter the absorption spectra of the stilbenes appreciably.\footnote{36,37} The introduction of groups more polar than halogen, shifts the absorption slightly to the red: \textit{trans}-4-nitro or 4-dimethylaminostilbenes have absorption maxima at \(\sim\) 350 nm, whereas the \textit{cis}-isomers have \(\lambda_{\text{max}} \sim 310\) nm.\footnote{38}

(b) Azobenzenes

\begin{center}
\begin{tikzpicture}

\node (A) at (0,0) {\textbf{25}};
\node (B) at (1.5,0) {\textbf{25'}};
\node (C) at (1.5,0.75) {\textbf{25'}};

\draw[->] (A) -- (B) node[midway,above] {$h v_1$};
\draw[->] (B) -- (C) node[midway,above] {$h v_2 / \Delta$};
\end{tikzpicture}
\end{center}

Azobenzene and nearly all its mono-substituted derivatives have their principal absorption bands (\(\pi-\pi^*\)) in the ultraviolet region and their yellow color is caused by a weak \(\pi-\pi^*\) absorption near 450 nm.\footnote{39} On conversion to the \textit{cis}-isomer 25', the \(\pi-\pi^*\) band shifts to shorter wavelengths and there is an increase in the strength of the \(\pi-\pi^*\) absorption, often accompanied by a shift in absorption maximum.

Substitution of positions \textit{ortho} or \textit{para} to the azo function with a strongly electron-donating group such as amino or dimethylamino shifts the main absorption band into the visible spectrum, sometimes causing it to overlap the \(\pi-\pi^*\) band.\footnote{40}
1.3.2 Electro cyclic Reaction

(a) cis-Stilbene to dihydrophenanthrene

\[
\text{hv}_1 \quad \text{hv}_2 \quad [\text{O}]
\]

Two photochromic reactions occur for stilbene: cis-trans isomerization and photocyclization. They compete with each other. In the presence of air, the dihydrophenanthrene 24" irreversibly converts to phenanthrene 26 through hydrogen elimination by reaction with oxygen as shown above. When the 2 (or 6) and 2' (or 6') positions of the above phenyl rings were substituted with methyl groups, the elimination reaction was suppressed and the compound underwent a reversible photocyclization reaction, that is, a photochromic reaction, even in the presence of oxygen. However, the lifetime of the colored dihydrophenanthrene was very short; in the dark, the yellow color disappeared in 3 min at 30°C.

(b) Diarylethenes

Diarylethenes are derivatives of stilbenes. For the parent compounds stilbenes, there are several problems which limit their application as switches: the cis-trans isomerization competing with the photocyclization, and the oxidation of the photocyclized product to form phenanthrene.

A third problem is the thermal return reaction. The lifetime of the dihydro intermediate of stilbene derivatives is not long enough for practical applications. In the course of searching for thermally irreversible stilbene-like compounds suitable for
photocyclization, Irie\textsuperscript{43} has developed a series of diarylethenes involving heterocycles. The following examples were the first thermally irreversible diarylethenes.

![Chemical structures](image)

The dicyano and maleic anhydride groups were selected to shift the absorption maxima of the dihydro-type isomers to longer wavelengths. The maleic anhydride group also prohibits the \textit{cis-trans} photoisomerization. The photogenerated dihydro-type isomers of the above two compounds are thermally inert in the dark for more than three months, even at 80°C, but readily regenerated the open ring isomers by irradiation with visible light (\(\lambda > 450\text{ nm}\)).

A theoretical study by Nakamura and Irie\textsuperscript{44} produced a guide for the synthesis of thermally irreversible photochromic diarylethenes. This can be summarized as follows:

The activation energy barrier for the forward and reverse reactions correlates with the ground state energy difference between the open- and the closed-ring isomers. The barrier becomes large when the energy difference is small, and vise versa. When the energy barrier is small the cycloreversion reaction readily takes place. On the other hand, the aromatic stabilization energy of the aryl groups correlates well with the ground
state energy difference. For the simple diarylethenes, the highest energy difference was from phenyl group and the lowest was from the thienyl group.

Following the above principle, various diarylethenes with different aryl groups, ethene links and suitable substitutions were synthesized. Most of the closed ring forms are stable with a lifetime over 12 h at 80°C and can undergo $\sim 10^4$ cycles of opening and closing.

For application to optical memory, it is desirable to develop photochromic compounds that have sensitivity in the wavelength region 650-830 nm. The absorption spectra of closed ring isomers are affected by substituents on the aryl groups while the upper cycloalkene structure affects the absorption spectra of open ring isomers. The above picture gives a few successful structures with promising absorption maxima.

Unfortunately, compound 33 with the longest absorption wavelength of the closed ring isomer was thermally unstable, returning to the open isomer in 186 min at 60°C.
Another requirement of photochromic compounds for application, is to have high molar absorption coefficients (ε).

\[
\begin{align*}
&\text{34} & \text{35} & \text{36} \\
&5.0 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} & 1.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} & 1.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}
\end{align*}
\]

The ε value of the parent dithienylperfluorocyclopentene 34 was doubled by introducing phenyl rings at the 5 and 5' positions of the thiophene rings. This further increased to \(1.8 \times 10^4\) L mol\(^{-1}\) cm\(^{-1}\) when electron donating \(N,N\)-diethylamino groups were substituted at the para position of the phenyl rings. Research showed that introduction of electron rich substituents or large π-conjugation systems is effective at increasing ε values. Electron withdrawing substituents did not affect the ε value, although, they increased the absorption maxima.\(^{33}\)

(c) Dimethyldihydroxyrenes

\[
\text{17} \xrightarrow{\text{hv}_1/\Delta} \text{17'}
\]

This is one of the very few negative photochromic systems, where the closed form (DHP) 17, is the colored stable state, and the open form metacyclophanediene (CPD) 17', is the thermally unstable colorless state. Irradiation of DHP with visible light converts it
to the CPD; irradiation with ultraviolet light closes it back to the green DHP. This latter reaction also occurs thermally.

For the following chapters, as for compounds 17 and 17', the prime indicates the fully opened photo isomer. The thermal return reaction refers to the reaction in which the open isomer converts to the closed isomer.

Early studies on the parent 17, and many of its simple substituted derivatives were carried out by Blattmann. These results suggested that the quantum yield for the UV closing 17' to 17, was close to one, while that for the visible light opening of 17 to 17', was only about 0.02. The difference in enthalpy between DHP and CDP is about 3 kcal mol$^{-1}$ regardless of substituents. Electron withdrawing groups at the 2 position, such as, 37 and 38, increased the photo opening quantum yield for the DHP to CPD reaction to 0.3-0.4, however, they also speeded up the thermal return rate (Table 4).

![Diagram of compounds](image)

Table 4. Rate data (k) at 30°C and activation energies ($E_{act}$) for thermal return reactions$^{45}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>k (min$^{-1}$)</th>
<th>$E_{act}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>0.001</td>
<td>23.0</td>
</tr>
<tr>
<td>37</td>
<td>0.069</td>
<td>20.5</td>
</tr>
<tr>
<td>38</td>
<td>0.052</td>
<td>19.7</td>
</tr>
</tbody>
</table>
The substituent effect was also tested at the 4-position of the di-\(t\)-butyl compound 20.\textsuperscript{45,47} It was found that electron withdrawing groups decreased the thermal return rate. For example, the thermal rates for CPD to DHP conversion of compounds 39 to 42 were 0.0018, 0.0028, 0.0016, 0.0012 min\(^{-1}\) at 40\(^\circ\)C, respectively, while the parent 20 had a rate of 0.0031 min\(^{-1}\) at 40\(^\circ\)C.

\[
\begin{align*}
20 & \quad R = \text{H} \\
39 & \quad R = \text{NO}_2 \\
40 & \quad R = \text{COC}_6\text{H}_{5} \\
41 & \quad R = \text{COCH}_3 \\
42 & \quad R = \text{COC}_2\text{H}_5
\end{align*}
\]

Increasing the size of the internal alkyl group had little effect on the quantum yield, but increased the thermal return rate.\textsuperscript{45,47} For example, the thermal return rates of 43', 44', and 45' were 0.0044, 0.0047, and 0.012 min\(^{-1}\) at 40\(^\circ\)C.

\[
\begin{align*}
43 & \quad R_1 = \text{CH}_3, \quad R_2 = \text{C}_2\text{H}_5 \\
44 & \quad R_1 = \text{CH}_3, \quad R_2 = \text{CH}_2\text{Br} \\
45 & \quad R_1 = R_2 = \text{C}_2\text{H}_5
\end{align*}
\]

Such compounds are also thermally much less stable, due to internal group migration.

Annellation of an aromatic ring had a much larger effect on both quantum yield and thermal return rate.\textsuperscript{48,49}
Compound 19 readily converts to 19' quantitatively with projector lamp light. Irradiation with UV light quantitatively converts 19' back to 19. This process occurs thermally at a rate of 0.0004 min$^{-1}$ at 30°C, which is much slower than for the parent 17' to 17 (0.001 min$^{-1}$) under the same conditions. Photochromic studies were also conducted on the series of 21 to 23.$^{30}$ the thermal return rate of 21' is 0.0020 min$^{-1}$ at 46°C, which is three times slower than that of 20', while the quantum yield of visible light opening reaction increased by 25 times. However, fusion of naphtho- or anthro-groups increases the thermal return rate. The compounds 22' and 23' had thermal return rates of 0.0101 and 0.0344 min$^{-1}$ at 46°C, respectively.

It is worth mentioning at this point that when the benzo ring of 21 is replaced by a furan as in 47, the thermal return rate was found to be the slowest so far, 0.000183 min$^{-1}$ at 46°C.$^{31,51}$
Unfortunately, this compound decomposes quickly during the photochromic processes.

One interesting system is the bis benzene annelated 48/48'.

![Diagram showing the transformation of 48 to 48']

Because of the large resonance stabilization energy of the four benzene rings of 48', the thermally stable state is the open CPD form. The thermal return rate of 48 to 48' is very fast. The half-life of 48 is only 3 min at -10°C. The activation energy of the thermal reaction was determined at low temperature as 20 kcal mol⁻¹.

Fusion of a benzene ring at the [a]- rather than the [e]-position of the parent as in 49/49' increased the thermal return rate.

![Diagram showing the transformation of 49 to 49']

Visible light irradiation of 49 at room temperature gave no detectable 49'. Low temperature study has not yet been done to establish the kinetics of this reaction. However, laser flash experiments suggest that the ring opening proceeded.
Photochromic studies on systems with more than one DHP unit were first carried out by Ward.\textsuperscript{50,53}

Compound 50 opened quickly to 50' using visible light. When the latter was irradiated with UV light, the mono closed 50'' was first formed before complete return to the bis-closed 50. This was determined by both \textsuperscript{1}H NMR spectroscopy and UV/Vis spectroscopy. The overall kinetics of the thermal reaction of 50' to 50 was followed by NMR spectroscopy. The thermal return rate at 46°C was determined to be 0.0057 min\textsuperscript{-1} and the activation energy was 24.3 kcal mol\textsuperscript{-1}.

Compound 51 was the first three way photochromic switch in the DHP system,\textsuperscript{50,53} in which all three states are clearly separable.
Irradiation of 51 with visible light opened the DHP and gave the colorless 51', which on UV irradiation or thermally returned back to 51. The bis closed system 51'' was obtained using a 355 nm laser flash, and this returned back to 51 very rapidly thermally. The thermal return rate and activation energy of 51' to 51 was found to be very close to that for the CPD form of benzopyrene 21 to its DHP form: the rate at 46°C for 51' was 0.00224 min$^{-1}$ and $E_{\text{act}}$ was 24.1 kcal mol$^{-1}$.

It is worth mentioning that an electrically conducting main chain photochromic conjugated polymer incorporating DHP units has been reported recently.$^{54}$ It was the first example of electrical conductivity in a backbone photochromic conjugated polymer.
The photochromic process of 52 and 52' still occurred, but slower than for the monomer. The solution phase of an optoelectronic redox switch was also demonstrated. This study indicates the possibility of making solid state photochromic switches on a molecular level.

(d) Fulgides

Fulgides were first synthesized and studied early this century\textsuperscript{55}. However, the mechanism of the photochromic process remained unclear for a long time. Until the 1960s, the coloration was believed to occur by \textit{cis-trans} isomerization about a double bond.\textsuperscript{56} In 1968, Santiago and Becker\textsuperscript{57} first recognized that the mechanism was the photochemical 6π-electron cyclization of the hexatriene moiety of 53 to generate 53'.

Initially fulgides were not very good photochromic compounds because of a number of thermal and side reactions of the colored form 53'.\textsuperscript{55} Besides the thermal ring opening, the major thermal reactions are hydrogen rearrangement and (or followed by) dehydrogenative aromatization.
This changed when the important fulgide 57 was reported by Heller\textsuperscript{55,58} in 1981.

\[
\begin{array}{c}
\text{57''} \xrightarrow{\text{UV}} \text{57} \xrightarrow{\text{UV}} \text{57'} \\
\text{57'} \xrightarrow{\text{Vis, UV}} \text{57''}
\end{array}
\]

Because there are no \(\alpha\)-hydrogens on the furan ring, the sigmatropic proton shifts are prevented. In addition, the vicinal methyl groups on the ring closing carbon atoms prevented the thermal ring opening of 57'. This was thus the first thermally irreversible photochromic molecule in the long history of fulgides. Furthermore, 57' had a small molar absorption coefficient at 366 nm, whereas 57 had a large absorption, and the photochemical back reaction from 57' to 57 upon irradiation with 366 nm light was negligible. Therefore, the conversion of 57 to 57' was close to 100%.

Since the discovery of compound 57, much effort was put into improvement of the photochromism. Replacement of \(R_1\) by a bulkier group, such as, ethyl, \(n\)-propyl, \textit{iso}-propyl or \textit{tert}-butyl significantly slowed down the \textit{cis}-\textit{trans} isomerisation.\textsuperscript{55} Heller\textsuperscript{58,59} found that the adamantylidene group, instead of isopropylidene increased the ring-opening quantum yield of visible irradiation. After 1990, the main interest switched to the development of new fulgide derivatives,\textsuperscript{60} which include using different aromatic rings, such as, pyrrole, indole, and different substituents onto the aromatic ring as well.

### 1.3.3 Heterolytic Cleavage

The photochromic reactions of spiropyrans and the closed related spirooxazines are the reversible cleavage of the C-O bond in the spiropyran or spirooxazine rings.\textsuperscript{61} Two typical examples are shown below:
The photochromic properties of spiropyrans were first studied by Fisher and Hirshberg in 1950. The closed forms are usually a nicely crystalline colorless or pale yellow solid. Solutions are colorless or weakly colored, and upon irradiation with ultraviolet light develop color or become more intensely colored. The colored solution fades thermally to their original state.

The open structure is essentially that of a merocyanine dye. Since the thermal fading of the colored forms is relatively fast, it is usually difficult to obtain a UV-Vis spectrum of a pure merocyanine form. However, the merocyanine form has a very strong tendency to associate into aggregates with a stack-like arrangement of the merocyanine molecules. When the molecular dipoles are arranged in a parallel structure, their absorption spectra are shifted to the red. In the case of antiparallel dipole arrangement, the spectra are shifted to the blue. The tendency for merocyanine aggregation is so strong that the aggregates are formed on irradiation of a spiropyran in a methacrylate polymer and even on swelling of the polymer film in a solvent.
1.3.4 Tautomerism

Some anils with structures similar to 60 have been shown to be photochromic. The mechanism was thought to be that a six-membered ring hydrogen transfer to form a colored quinoid structure.\textsuperscript{63} The photo generated colors fade with warming.

\[
\begin{array}{c}
\text{Ph} - \\
\text{N} \quad \text{Ph} \\
\text{Ph} - \\
\text{N} \quad \text{Ph}
\end{array} \quad \xrightarrow{h \nu 1} \quad \text{Ph} \\
\text{N} \quad \text{Ph} \\
\text{Ph} - \\
\text{N} \quad \text{Ph}
\]

The thermal return usually is very fast. Thus, photochemical studies have been done mostly at low temperatures.

1.3.5 Homolytic Cleavage

\[
\begin{array}{c}
\text{Ph} - \\
\text{N} \quad \text{Ph} \\
\text{Ph} - \\
\text{N} \quad \text{Ph}
\end{array} \quad \xrightarrow{h \nu} \quad \text{Ph} \\
\text{N} \quad \text{Ph} \\
\text{Ph} - \\
\text{N} \quad \text{Ph}
\]

A yellow benzene solution of compound 61, upon irradiation with sunlight at 15°C turned to reddish purple.\textsuperscript{63} The color disappeared in the dark. This can also be observed in the crystalline state. The structure of 61' was confirmed by ESR study. However, this type of system is rarely used in modern photochromic studies.

1.4 Thesis Motivations and Objectives

The dimethyldihydropyrene system has proven to be a promising photochromic system. However, with the low quantum yield of visible light opening and fast thermal
return rate, the parent compound 20 does not possess the desired properties to be a molecular photoswitch. The [e]-annelated compound, benzopyrene 21, made by one previous graduate student in our group, Dr. Ward, shows the best photoswitching properties so far. My research goals were thus as follows:

1. To synthesize more complicated systems with more than one DHP unit (multistate photoswitches).

2. To explore how the photochromic properties of various substituted benzopyrenes change on substitution.

3. As a result of our work above, to attach a substituent on one side of the DHP units in a multistate photoswitch in order to differentiate both ends.

4. To study the thermal kinetics and photoisomerization of the derivatives of benzopyrene 21 so obtained.
Chapter Two  Syntheses

2.1 Syntheses of Annelated Dimethyldihydropyrenes with Benzene as a Spacer

The only system known in which the thermally stable form contained two closed DHP units, 50, was made by Ward.\textsuperscript{50,53} In this system, the spacer was the polycyclic chrysene. We were interested to determine whether a simpler spacer such as benzene to give 62 could be made, and whether it would change the photoswitching properties.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Structures of 50, 62, and 19.}
\end{figure}

Although \textsuperscript{[e]} position annelated dimethyldihydropyrenes have better photoswitching properties than their \textsuperscript{[a]} analogues, the synthesis of the parent 19 was a long process with 9 steps and a 9% overall yield.\textsuperscript{64}

Zhou\textsuperscript{30,65} found an alternative route to annelate DHPs which did not necessitate going back to a new thiacyclophane synthesis for each new compound.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Synthesis of 65 from 63.}
\end{figure}
This involved reaction of an intermediate aryne, which was not isolated, with a furan in a Diels-Alder reaction.

To obtain the parent benzopyrene system 19 by this route, the aryne intermediate at the 4,5-positions is required, which in turn requires the bromide 66.

However, only the 2,7-positions of the parent 17, are brominated, so these need to be blocked to introduce a bromine at the 4-position. Thus 2,7-di-t-butyl-dimethylidihydropyrene, 20, was selected as the best starting material, with the bonus that it is much easier to synthesize than the parent 17.\textsuperscript{46,70} Ward\textsuperscript{31} showed this route to be successful for benzo[e]pyrene 21.

2.1.1 A System Containing Two Dimethyldihydropyrene Units

In order to synthesize 62, the aryne 67, would need to be trapped by the isofuran 47\textsuperscript{31} which should give the adduct 68 as a mixture of isomers, (for the subsequent use, isomers indicate diastereomers, unless otherwise stated).
Bromination of 20 with NBS in DMF and CH$_2$Cl$_2$ gave bromide 69 in greater than 90% yield.\textsuperscript{31}

The bromide was first converted to yield the adduct 70, which on reaction with the tetrazine 71 underwent a retro Diels-Alder reaction to yield the isofuran 47 in 60% overall yield.\textsuperscript{31} This was then again reacted with aryne 67, generated from bromide 69 in dry THF using excess NaNH$_2$, in a Diels-Alder reaction to yield adduct 68.

This reaction usually finished within a few hours on the milligram scale. However, the compound was difficult to purify because it decomposed during column chromatography on SiGel which was sluggish due to poor solubility. So for synthetic purposes, the crude product was washed several times with a small amount of pentane, to give residual 68 of about 95% purity.

In theory, two diastereomers of 68 could be obtained, one of which is chiral and one is a meso form.
In 68A, which has Cs symmetry, there should be two methyl signals and two t-butyl signals (which are illustrated in the same color). Isomer 68B, also has two methyl signals and two t-butyl signals. In fact, both isomers of 68 are obtained in equal amounts and four internal methyl signals could be seen in the $^1$H NMR spectrum at $\delta$ -3.40, -3.44, -4.37, -4.38, as well as four t-butyl signals at $\delta$ 1.66, 1.70, 1.71, 1.73. The two protons on the oxygen bridge head are identical for the isomer 68B at $\delta$ 7.924 and different for the isomer 68A at $\delta$ 7.976 and 7.918 as two doublets with a small coupling constant of 0.64 Hz. The strong deshielding of these protons is caused by the two DHP rings. Partial $^1$H NMR spectra of 68 with unequal amount of isomers is shown in Figure 2.

The $^{13}$C NMR spectrum confirmed this analysis, i.e. the bridge head carbon signal was a single peak at $\delta$ 81.09 for isomer 68B and two peaks at $\delta$ 80.82 and 81.53 for isomer 68A. The compound gave a correct molecular weight by mass spectrometry (LSIMS) at m/z 727.5 (MH+) and a satisfactory elemental analysis.

In our group, furan adducts have normally been deoxygenated with Fe$_2$(CO)$_9$, and so this was tried first to convert 68 to 62. After 68 and Fe$_2$(CO)$_9$ were refluxed in benzene for 1 h, the cooled reaction mixture was filtered through alumina and after the solvent was evaporated, the residual was chromatographed over alumina using benzene/hexanes (1:6). Much green material did not move, but a small amount was eluted and gave a complicated NMR spectrum. There were 3 to 5 peaks in the internal methyl region around $\delta$ -1.07 depending upon resolution. Further column chromatography did not reduce the number of peaks. The t-butyl region was rather complex and so the mixture was refluxed with Me$_3$NO in benzene for 1 h to ensure any
iron complex, but the NMR spectrum of the residual was similar in pattern, and the signals were smaller. Either the impurities in the product were not iron metal complexes or Me$_3$NO did not decomplex them.

**Figure 2.** Partial $^1$H NMR spectra of both isomers of 68 (unequal amount).

When less than one equivalent of Fe$_2$(CO)$_9$ was used to deoxygenate the adduct 68, some starting material 68 was recovered, and the two isomers were present in unequal amounts. This made it possible to assign the $^1$H NMR spectra of different isomers, as shown above.
Next, the conversion of 68 to 62 was attempted using sodium in THF. Sodium was added into the solution of 68 in THF under argon, the mixture was stirred in room temperature. Unfortunately, most of the starting material decomposed and remained at the bottom of the plate during TLC. The very small amount that was obtained on chromatography with benzene/hexanes (1:6) gave an internal methyl proton signal at δ -1.07. (CH$_3$)$_3$Si$^{68}$, which was made in situ from (CH$_3$)$_3$SiCl and anhydrous NaI in CH$_3$CN, and worked well in making benzo[e]pyrene 21, was also tried, but was not successful. Ti(0)$^{69}$, which was generated from TiCl$_4$ and Zn in dry THF, and SmI$_2$$^{70}$ in dry THF under argon, were also attempted, but failed.

On the basis of its chemical shift, the peak at δ -1.07 suggests that 62 was obtained. However, more evidence is required to substantiate this claim.

2.1.2 A system containing three dimethyldihydropyrene units

When a DHP is benzannelated on both sides, the [e,l] positions, then the open CPD form is the thermally stable isomer.$^{52}$

Ward$^{50,53}$ made use of this property to prepare a three way switch 51, in which one DHP is closed, one is open. We thought we could prepare a system with two closed
DHPs utilising the open unit in the center, and thus we thought 72 would be a worthwhile target.

In 72, irradiation with visible light, should open both terminal DHPs to give 72', which should thermally or with UV light return to 72. Irradiation of 72 with UV light should close the central CPD to give the triple DHP 72'', which should revert to 72 thermally.

In order to synthesize 72, we thought we could make use of the bis-Diels-Alder reaction that was successful in converting dibromide 73 to bis-adduct 74.\textsuperscript{52}
In our case, isofuran 47 would be substituted for the furan. Thus reaction of the dibromide 73 and excess isofuran 47 (3 equivalents) in dry THF with a large excess of NaNH₂ and catalytic amount of KO'Bu, resulted in a brown mixture which was filtered through celite and the {\( ^1 \text{H} \)} NMR spectrum was taken.

Three groups of new internal methyl signals centered at \( \delta -3.43, -4.58 \) and -5.28 were found, indicating several isomers of adduct 75 to be present. Because of the poor solubility of the product, further purification was not successful. After the brown mixture was washed with pentane a few times, the residual was greenish and was directly carried on to next step, the deoxygenation.

Crude 75 was refluxed with Fe₂(CO)₉ in benzene and the reaction mixture turned dark brown. TLC indicated that a red spot moved in hexanes/benzene (6:1). Column chromatography was used to collect the red portion, which we hoped was 72.
Two major internal methyl proton peaks at $\delta$ -1.37 and -1.63 were observed and there were some smaller peaks in this region too, which could not be separated by chromatography.

In the Diels-Alder reaction of the dibromide 73 and furan, there was always some mono adduct 74a generated.\(^1\)

Similarly, the Diels-Alder reaction of 47 and 73 might give a similar product, which on deoxygenation might produce the small peaks.

In an attempt to avoid this, bisfuran 76\(^2\) was reacted with excess bromide 69 in the presence of NaNH\(_2\) and KO\(^t\)Bu. This should generate 75 without mono adduct.

However, surprisingly, after the product from the Diels-Alder reaction was deoxygenated with Fe\(_2\)(CO)\(_9\), only a small amount of material was obtained which showed the same internal methyl signal pattern as from the reaction of 47 and 73. As well, there were some peaks around $\delta$ -4.0, which could not be identified.

A stepwise route was thus designed.
Use of low temperature allowed the monoisofuran 77 to be isolated as the major product from the reaction of 74 and tetrazine\textsuperscript{71} 71. However, the yield of this reaction was generally low at about 30%. The product could be purified by column chromatography over alumina to give a beautiful red-orange solid, mp (dec) 182-183 °C. Some deep purple material remained on top of the column during chromatography, and was suspected to be compound 80.
The structure of 77 was indicated by its NMR spectrum. Two signals for the internal methyl protons at $\delta$ 0.373 and 0.137 and two t-butyl proton signals at $\delta$ 1.241 and 1.239 indicate an unsymmetrical structure because of the oxygen bridge.

In comparison of 77 and 81, the internal methyl proton chemical shifts in 77 are more downfield than in compound 81, which are at $\delta$ -0.98 and -1.20 (d$_8$-THF).

This can be explained in terms of the DHP ring current. Because the double bonds in a furan ring are more localized than those in a benzene ring, the ring current in the DHP ring of 77 is much smaller caused by furan fusion than in 81, due to increased bond fixation.

The $^{13}$C NMR spectrum of 77 shows two bridge head carbon peaks at $\delta$ 80.22, 80.15. The CI MS gave the appropriate ion for MH+ at $m/z$ 451. The HRMS confirmed the formula of C$_{32}$H$_{34}$O$_2$ with the exact mass peak at $m/z$ 450.2559 (M+); the calculated value is 450.2559.

Compound 77 was used in the next step as soon as possible and reacted with the arylene 67 derived from bromide 69 in a Diels-Alder reaction to give adduct 78 as a mixture of diastereomers in 72% yield. The reaction usually finished within a few hours.

In theory, there could be four isomers. Two have both oxygen bridges up(u) (78uuA and 78uuB) and two have one up one down(d) (78udA and 78udB).
Chromatography was used to separate the isomers into a 78uu group and a 78ud group. Further separation of isomers A and B within each group could not be achieved.

Because of the difference of the two DHP rings in 78, there should be four internal methyl signals in the $^1$H NMR spectrum of each isomer. As determined previously in compound 74, the uu isomer has the largest spread of chemical shift for the internal methyl protons, $\Delta \delta = 0.60$ ppm, so in 78 the uu isomers might be expected to have a larger range in chemical shift than the ud isomers. During chromatography, spectra were obtained with unequal amounts of the four isomers, and hence we could determine that the methyl signals for the uu group were at $\delta$ -4.70, -4.32, -3.47, -3.29 and 4.73, 4.31, 3.48, -3.26, while those of the ud isomers were at $\delta$ -4.43, -4.24, -3.77, -3.25 and -4.41, -4.23, -3.77 and -3.28.
The overall structure is supported by mass spectroscopy (LSIMS) which gave the correct molecular ion of MH+ at m/z 793.6 and satisfactory HRMS, found = 793.4987 (MH+), calc = 793.4985.

The Diels-Alder reaction of 78 and tetrazine 71 followed by a spontaneous retro-Diels-Alder reaction readily gave the furan 79 as a mixture of isomers in greater than 90% yield. Compound 79 was not stable on SiGel and slowly decomposed on alumina, with one isomer decomposing faster than the other. After a short alumina column, the less stable isomer in the tail part of the eluant was sometimes only 10% of the more stable isomer. Thus the identification of signals belonging to each isomer was possible.

In 79, two types of internal methyl proton signals should be present because of the different DHP rings. The internal methyl signals of the DHP attached to the furan should appear further downfield than those in the other DHP ring. In theory, each isomer should give four internal methyl signals. Seven peaks were observed at δ 0.45, -0.52, -0.54 and -3.68, -3.72, -4.02, -4.04, with the one at δ 0.45 being overlapped peaks of two isomers. The correct LSIMS at m/z 767.5 (MH+) and HRMS at 766.4737 confirmed that the structural formula of 79 was C$_{56}$H$_{62}$O$_2$ (calculated value, 766.4750).
Upon obtaining 79, the next step, the Diels-Alder reaction with aryne 67 derived from bromide 69 to give 75 should have been straightforward. However, the product 75 could not be properly purified due to its poor solubility.

Thus crude 75 was deoxygenated by refluxing with Fe$_2$(CO)$_9$ in benzene. Unexpectedly, the resulting deoxygenation product 72 contained the same impurities as before. After column chromatography over SiGel with hexanes/benzene (6:1) as eluant and then recrystallization from toluene, small dark red crystals were obtained, mp (dec) 176-181°C. Unfortunately, upon drying, the crystals broke apart and became a powder. It was thought that solvent was entrained within the crystals. However, crystallization was successful in purifying 72 since the small impurity peaks disappeared from the $^1$H NMR spectrum. The overall yield was about 7% from the bis adduct 74.

Theoretically, compound 72 could contain three isomers as illustrated above. Diastereomers 72A and 72B have Cs symmetry, so all the internal DHP methyl proton in each molecule are identical (they are marked in the same colors). Isomer 72C, however,
due to the CPD ring in the center, the two terminal DHP rings are not identical. There should be one signal for each DHP ring. Overall, four internal methyl proton signals are seen in the $^1$H NMR spectrum of 72A-C at $\delta$ -1.360, -1.364, -1.622, -1.626. Only one broad peak at $\delta$ 1.28 for the internal methyl protons of the central CPD ring is observed.

The structure of 72 was supported by mass spectrometry. An EI MS gave an ion $\text{MH}_2^+$ at $m/z$ 1078. The HRMS $m/z$ was 1077.7256. Calculated for $\text{C}_{82}\text{H}_{92} (\text{MH}^+) = 1077.7277$. In addition, the elemental analysis is satisfactory.

Although a large number of cyclophanes have been prepared, only a few have heterocycles on the bridges. After obtaining 79, compound 82 became an interesting target. So, the following reaction was performed.

When the reddish brown solid 79 and $\text{Fe}_2(\text{CO})_9$ were refluxed in benzene, the reaction mixture gradually turned to red. After chromatography, a red solid 82 was obtained in 80% yield as a mixture of two isomers.
In theory, there are two internal methyl proton signals and two \( \tau \)-butyl signals for the DHP ring, one from 82A, and one from 82B, and the same number of signals from the CPD ring. Indeed, the \( ^1 \text{H NMR} \) spectrum shows two internal methyl proton signals at \( \delta \) -1.66 and -1.37, which fall in the region of benzopyrene 21 derivatives. Also two \( \tau \)-butyl signals at \( \delta \) 1.53 and 1.49 indicate the present of a DHP ring. Only one slightly broad signal at \( \delta \) 1.03 for the internal methyl proton on the CPD is observed, however, two \( \tau \)-butyl signals at \( \delta \) 1.32 and 1.31 could been seen.

The NMR spectra of 82 and its benzo analogue 51\( ^{50} \) are extremely similar. The two internal methyl signals and two \( \tau \)-butyl signals from the DHP ring in 51 are at \( \delta \) -1.67, -1.37 and \( \delta \) 1.54, 1.50. The two \( \tau \)-butyl signals from the CPD are the same as in 82 at \( \delta \) 1.32 and 1.31. The greatest difference comes from the internal methyl protons of the CPD ring, which are singlets at \( \delta \) 1.18 for 51 and \( \delta \) 1.03 for 82. Clearly, a furan fused on the CPD ring does not alter the ring current of the DHP ring much.

LSI mass spectra gave the correct molecular ion at \( m/z \) 750.5 (M+) and HRMS gave an exact mass value of 751.4869 (MH+); \( C_{56}H_{62}O = 751.4879 \).
2.2 Derivatives of Benzo[e]dimethyldihydropyrene

Photochemical and photophysical studies have been done of substituent effects on the pyrenes 17 and 20. However, photochromic studies on substituted arene annelated dimethyl-dihydropyrenes have not been reported.

In terms of photoswitching properties and stability, benzo[e]pyrene 21 is the best candidate so far. We thus thought that study of substituent effects on compound 21 would be worthwhile. One of our research goals was thus to synthesize 83 with different X and Y groups.

![Chemical structure](image1)

Acetyl, nitro and formyl groups have been successfully introduced onto the parent 17, and acetyl and nitro groups onto the parent benzo system 19. For 20, acetyl and nitro groups have also been introduced at the 4-position.

The Friedel-Crafts reaction of 21 with Ac₂O and BF₃Et₂O as Lewis acid went smoothly and the yield of 84 was about 80%.
Compound **84** formed nice purple crystals in a mixed solvent of hexanes/CH$_2$Cl$_2$ (1:1) by slow evaporation, mp 173-174°C. Both internal methyl and t-butyl protons were differentiated by the acetyl group and appeared at δ -1.48, -1.55 and δ 1.51, 1.49, unlike the corresponding 2-acetyl benzopyrene **85**, in which the internal methyl signal appears as a singlet at δ -1.67. The acetyl methyl protons in **84** were a singlet at δ 2.73. In addition, the characteristic carbonyl carbon appeared at δ 201.16 in the $^{13}$C NMR spectrum. In the IR spectrum, the conjugated C=O stretching frequency was at 1670 cm$^{-1}$. The correct CI MS and elemental analysis were also obtained for **84**.

The next target was the nitropyrene **86**. Nitration of DHPs have previously been carried out with Cu(NO$_3$)$_2$.5H$_2$O in Ac$_2$O. However, extensive decomposition occurred during the nitration of **21**. The yield of **86** was only 28%, with about 10% of dinitrobenzopyrene **87** as by-product.

[Diagram of the reaction]

Compounds **86** and **87** were easily separated by column chromatography and both could be further purified by recrystallization in a mixed solvent of hexanes/CH$_2$Cl$_2$. **86** sublimed at 161-162°C, **87** decomposed at 195°C.

The structure of **86** was confirmed by its $^1$H NMR spectrum. Due to the strong electron-withdrawing effect of the nitro group, the internal methyl protons were deshielded from δ -1.58 in benzopyrene **21** to δ -1.28 and -1.35 in **86**, with the
differentiation of the two internal methyls indicating the unsymmetrical structure. The two \( t \)-butyl signals were also differentiated and appeared at \( \delta 1.53 \) and \( 1.47 \). The five aromatic protons on the DHP ring showed five distinct signals.

A correct molecular ion by CI MS at \( m/z \ 440 \ (MH^+) \) and satisfactory HRMS confirmed the formula of this compound as \( C_{30}H_{33}NO_2 \).

The nitro group in compound 88 produces a very different substitution effect for that of 86 on the chemical shifts of internal methyl protons.\(^6^8\) For 88 a singlet was observed at \( \delta -1.85 \) for the internal methyl protons, which is the same as in the parent benzopyrene 19. Why the substituent effects are so different for nitro groups in the 2- and 4-positions remains unclear.

The dinitrobenzo[e]pyrene 87 gave a simple NMR spectrum due to its symmetrical structure. The internal methyl protons were a singlet and were further deshielded to \( \delta -0.70 \). The \( t \)-butyl signal appeared a singlet at \( \delta 1.46 \). Only two DHP proton signals at \( \delta 8.10 \) and 7.98 were observed.

The experimental value for the exact mass of 87 was 484.2360, consistent with the theoretical value 484.2362. A CI MS also gave correct molecular ion at \( m/z \ 485 \ (MH^+) \).

In compound 89, the internal methyl proton signal appears as a singlet at \( \delta -1.60 \), which is deshielded by about 0.25 ppm from the parent benzopyrene 19.\(^6^8\) It is obvious
that the effect of nitro groups at the 2- or 2,7- positions is not nearly as large as that on 4- or 4,5- positions.

The TiCl₄ catalysed formylation reaction²⁴ to generate compound 90 was not successful. Instead, a mixture of mono- and di-chlorobenzo[e]pyrenes 91 and 92 was obtained.

The substituted benzopyrenes obtained above were all by direct substitution of 21. An alternative approach is first to introduce the substituent on to the more robust parent 20, and then construct the benzene ring later.

In the case of 93, generation of the aryne and reaction with furan should form adduct 94, which on deoxygenation should give the substituted benzopyrene 95. However, there are limitations to this route:

(1) The functional group X has to be stable under strong basic conditions.

(2) Substituent X should not promote any other reaction than the Diels-Alder reaction between the DHP aryne and furan.
Substituent X should not interfere with the deoxygenation reaction.

Since direct nitration did not work very well for the benzopyrene 21, it was chosen as the test reaction of the alternate route first.

The same conditions were used for the nitration of bromide 69 as for the parent 20. The resulting product was a mixture of the three compounds, 96, 97 and 98. The green colored 97 could be separated by chromatography on SiGel, mp (sub) 151°C, while the brown mixture of 96 and 98 was not separable.

The structure of 97 was easily confirmed from its $^1$H NMR spectrum. Only 97 showed an AB pattern for H-9,10, which appeared at $\delta$ 8.529 and 8.517, while H-1,3,6,8 were doublets with small coupling constants ($J = 1.2$ Hz). As would be expected for all the isomers, both internal methyl and $t$-butyl groups were differentiated by the unsymmetrical substitution. The internal methyl proton signals for 97 appeared at $\delta$ -3.68 and -3.70 and $t$-butyl proton signals were at $\delta$1.69 and 1.63.

Compounds 96 and 98 showed slightly different solubility in pentane. After carefully washing the solid mixture, the residual contained 90% of one isomer. This was only necessary for characterization since in the subsequent Diels-Alder reaction both isomers should yield adduct 99.
The less soluble isomer, showed a single $t$-butyl peak at $\delta$ 1.68 (the methyls were at $\delta$ -3.65 and -3.68), and we believe this is isomer 96, since isomer 98 with both substituents at one end of the molecule should differentiate the $t$-butyl groups most. The $t$-butyl signals of the other isomer were at $\delta$ 1.72 and 1.65.

The mass spectrum of 97 showed a characteristic bromine pattern with 1:1 peaks at $m/z$ 467 (M$^+$, $^{79}$Br) and 469 (M$^+$, $^{81}$Br) by CI MS. The HRMS was satisfactory with a $m/z$ value 467.1464, calculated value 467.1460 ($^{79}$Br, MH$^+$).

However, in the subsequent Diels-Alder reaction, 96 and furan in the presence of NaNH$_2$ gave no detectable adduct 99, and all starting material was consumed.

Since the above reaction failed, it suggested that an electron withdrawing group was not a good choice in this stepwise route to generate a substituted benzo[e]pyrene. Instead, we decided that an arylethyne substituent would be a better test of this idea since phenylethynyl has been attached to the parent DHP 20 through bromide 69 by Sheepwash. This reaction required a relatively high temperature, as it was carried out in DMF. In theory, a Sonogashira coupling should be easier with an iodide rather than a bromide. Thus, compound 100 was chosen as the starting material for the sequence to give 103.
The iodination reagent was generated by reacting I$_2$ with Ag(collidine)$_2$PF$_6$ and was used in situ.$^{78}$ However, iodination of bromide 69 was very slow at low temperature, and even at room temperature took overnight to complete. Besides the 4,9-isomer 100, a lesser amount of the 4,10-isomer 104 was also obtained, in about a 3:1 ratio. However, for synthetic purposes, both 100 and 104 should give the same product 102 after the Diels-Alder reaction with furan. Thus, separation of 100 and 104 was only carried out for characterization purposes.

Again, compounds 100 and 104 could not be separated by column chromatography, but their solubilities were slightly different in pentane. After carefully washing of the product mixture a few times with pentane, the $^1$H NMR spectrum of the residual showed a single internal methyl signal at δ -3.86, the $t$-butyl signals were two slightly separated siglets at δ 1.68 and 1.67, this was believed to be the 4,9-isomer 100. The signals of the more soluble isomer had a bigger separation of the two $t$-butyl signals, which appeared
at $\delta$ 1.70 and 1.66, and the internal methyl showed two peaks at $\delta$ -3.93 and -3.95, this isomer was thus believed to be the 4,10-isomer, since with the two substituents on the same side, both $t$-butyl and internal methyl groups should differentiate more.

The green colored 100 sublimed at 162°C. In the $^1$H NMR spectrum of 100, the internal methyl protons showed as a singlet at $\delta$ -3.86, the six DHP aromatic protons as six signals at $\delta$ 8.90, 8.82, 8.65, 8.64, 8.48, 8.45, but the $t$-butyl groups were two singlets at $\delta$ 1.68 and 1.67. The mass spectrum gave correct isotope pattern 1:1 at $m/z$ 549 (MH+, $^{79}$Br) and 551 (MH+, $^{81}$Br), also satisfactory HRMS results. Evidently, an iodine and bromine do not differentiate the methyls of the DHP proton much.

The Sonogashira coupling of 100 and phenylacetylene went smoothly under mild conditions. Pd(PPh$_3$)$_2$Cl$_2$ and Cul were used as catalysts, Et$_3$NH as the base. The purity of the product depended on the starting material. When a mixture of 100 and 104 was used, the product was also a mixture of 4,10- and 4,9-isomers. However, for synthetic purposes, there was no need to separate the isomers since they would give the same Diels-Alder reaction product after the next step. A small amount of 100, purified by washing with pentane, was used to make some pure 101 for characterization purposes.

The $^1$H NMR spectrum of 101 showed two multiplets at $\delta$ 7.77-7.73 and $\delta$ 7.47-7.38 with integration of 2:3, which was the characteristic pattern of a mono
substituted phenyl group. Both internal methyls and t-butyl signals were differentiated by the unsymmetrical structure and their proton signals appeared at $\delta$ -3.75, -3.77 and $\delta$ 1.71, 1.69, respectively. The $^{13}$C NMR spectrum showed the acetylene carbons at $\delta$ 95.25 and 89.89. The IR spectrum had a peak at 2196 cm$^{-1}$, indicating the presence of a triple bond.

The mass spectra showed a correct molecular ion and isotope pattern for one bromine. The HRMS signal found at $m/z$ 522.1920 (M+, $^{79}$Br), was consistent with the calculated value of 522.1922.

The Diels-Alder reaction of 101 (in fact 101 and the isomer derived from 104 were used), and furan in the presence of the strong base NaNH$_2$ to produce 102 went well. The green product was purified over deactivated SiGel using hexanes/EtOAc (6:1) as eluant to give 73% of 102 as a mixture of two diastereomers. Further separation was not attempted.

The $^1$H NMR spectrum showed four signals for the internal methyls at $\delta$ -3.158, -3.162, -3.416, -3.424, and four signals for the t-butyl groups at $\delta$ 1.656, 1.653, 1.608 and 1.604. A weak peak at 2191 cm$^{-1}$ in the IR spectrum showed the presence of a triple bond.
The correct molecular ion at \( m/z \) 511 (MH+) and satisfactory HRMS analysis confirmed the molecular formula as C_{33}H_{38}O.

The deoxygenation of 102 with Fe\(_2\)(CO)\(_9\) in benzene gave the expected product 103, together with some unidentified side product. With prolonged reaction time, the NMR signals of the product became smaller. So, TMSI\(^68\) was tested, however, 5 peaks at δ -1.30, -1.40, -1.42, -1.55, -1.60 were present in the DHP region and the products could not be separated by TLC. Searching for clean and effective deoxygenation methods is desirable in the future.

On some occasions, while making the adduct 102, the phenylethynylbenzopyrene 103 was generated at the same time. In the Diels-Alder reaction of the bromide 101 and furan in two out of five trials, 103 was obtained in a ratio of 103/102 of 20:80 and 50:10 respectively. Different batches of NaNH\(_2\) and KO'Bu had been used. Thus, the freshness of the base may affect this reaction.

The phenylethynyl group further deshielded the internal methyl signals and differentiated them at δ -1.40 and -1.42. Also, there were two signals at δ 1.54 and 1.48 which belong to the \( \tau \)-butyl groups. Due to the overlapping of the benzo and phenyl groups, the \(^1\)H NMR spectrum was complicated. The total number of aromatic protons was 14 relative to the 6 internal methyl protons. Four distinct doublets with coupling
constant about 1.0 Hz indicated the 4 protons on the DHP ring, the other proton H-6 was buried in the multiplet of the phenyl proton signals.

The $^{13}$C NMR spectrum had two signals at $\delta$ 94.61 and 89.94 for the acetylene carbons, and the IR showed a vibration peak at 2189 cm$^{-1}$, which indicated the triple bond in the molecule.

The CI MS gave a correct molecular ion at $m/z$ 495 (MH$^+$), and a HRMS of 494.2980 is very close to the calculated value of 494.2974.

The successful route to the arene-yne 103 by a coupling reaction suggested that the simple aryl substituted derivative 105 would be a good target.

Thus the phenyl group was introduced first to the parent 20 by Suzuki coupling of bromide 69 with commercially available phenyl boronic acid using aqueous Na$_2$CO$_3$ as base and Pd(PPh$_3$)$_2$Cl$_2$ as catalyst. The reaction completed within two hours under reflux in THF, and gave 87% of 106.
This was purified by column chromatography over SiGel using hexanes/benzene (6:1) as eluant, and gave green crystals, mp 162-163°C. The $^1$H NMR spectrum showed the unsymmetrical structure of 106 with two internal methyl signals and two $t$-butyl signals at δ -3.84, -3.86 and δ 1.68, 1.59. The phenyl group appeared as three multiplets with integration of 2:2:1. NOESY experiments showed that the protons close to the DHP on the phenyl ring had through space interaction with H-3 and H-5 on the DHP ring.

Mass spectrometry (methane Cl) supported the molecular composition with $m/z$ 421 (MH$^+$), and the elemental analysis was satisfactory.

The bromination of 106 was carried out at -78°C in dry ice/acetone. By $^1$H NMR, the product contained a mixture of mostly the 4,9-isomer 107 (85%) and 12% of the 4,10-isomer 108 and 3% of starting material 106.

For characterization, the mixture was washed with a small amount of pentane a few times and then the residual contained 95% of the 4,9-isomer 107. However, for synthetic purposes, both 107 and 108 should give the same Diels-Alder reaction product.

The bromine in 107 deshielded the internal methyl proton signals to δ -3.72, -3.75 from δ -3.84, -3.86 in 106. The phenyl group showed three multiplets with integration of 2:2:1. The $t$-butyl groups showed two signals at δ 1.69 and 1.56. More importantly, the
mass spectrum displayed a 1:1 bromine pattern at \( m/z \) 499 (MH+, \(^{79}\text{Br}\)) and 501 (MH+, \(^{81}\text{Br}\)). The exact mass also confirmed the molecular formula as \( \text{C}_{32}\text{H}_{35}\text{Br} \).

Reaction of 107 with furan and NaNH$_2$ in THF gave the green adduct 109 as a mixture of two equal amount isomers. Like most furan adducts, the product was not stable in halogenated solvents on SiGel, and showed limited solubility in saturated hydrocarbon solvents. Purification of 109 was achieved over deactivated SiGel, and the NMR spectra were taken in CDCl$_3$ which was filtered through alumina before use. For synthetic purposes, 109 was washed with pentane a few times and usually the purity was over 85%, so no column chromatography was needed.

Four internal methyl and four \( t \)-butyl signals were expected in the $^1\text{H}$ NMR spectrum of 109. Indeed, four singlets in the internal methyl region at \( \delta \) -2.88, -2.90, -3.13, -3.17 and four singlets for the \( t \)-butyl groups at \( \delta \) 1.602,1.599, 1.502 and 1.496
were observed. The $^{13}$C NMR spectrum confirmed the unsymmetrical structures by showing four oxygen bridge head carbon resonances at δ 81.08, 81.06, 80.76 and 80.65.

Mass spectrometry gave the correct molecular ion at m/z 486 (M+) by electron impact. Elemental analysis also gave the appropriate percentage of carbon and hydrogen.

The aromatization of adduct 109 was successful with Fe$_2$(CO)$_9$ in benzene, and gave 81% of 105 as a bright red solid, mp 180-181°C.

The structure of 105 was confirmed by its $^1$H NMR spectrum, which showed the internal methyl groups and the $\tau$-butyl groups at δ -1.453, -1.456, and δ 1.49, 1.39. Since the methyl protons of parent 21 are at δ -1.58, the effect of substitution of a DHP ring by a phenyl group is much smaller than a fused benzene ring. The protons of the fused benzene moiety still appeared as an approximate AA'XX' pattern. Some of the DHP proton signals were buried under the phenyl proton signals, but the total integration of aromatic protons was in correct ratio to that of the internal methyl protons.

The mass spectrum showed the correct molecular ion at m/z 471 (MH+) by methane chemical ionization. A HRMS gave the exact mass as 470.2974; the calculated value was also 470.2974.
2.3 Diels-Alder Reactions of Isopyrofuran 47

Extensive use of isofuran 47 has been made in the synthesis of molecules containing more than one dimethyldihydropyrene unit by way of aryne-furan Diels-Alder reactions. Ward^{51} also used 47 with other dienophiles such as, dimethyl acetylenedicarboxylate and fumaronitrile. Both of the reactions worked very well with nearly quantitative yields. However, he was unable to aromatize either adduct to generate useful photoswitching molecules.

The following reactions have been known for many years:^{80}

\[
\begin{align*}
\text{CO}_2\text{Me} & + \text{C} \rightarrow \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} & + \text{O} \rightarrow 110 \\
111 & \rightarrow 112, 113 \\
110 & \rightarrow 111 \\
111 & \rightarrow 112, 113
\end{align*}
\]

After the first step, the adduct 111 reacts further with excess furan to generate the bis adducts 112 or 113 depending upon reaction temperature. On this basis, we thought that the bis adduct 114 might be generated at high temperature by reacting isofuran 47 and the adduct 70.
Indeed, when isofuran 47 and adduct 70 were refluxed overnight in toluene, the resultant green product had rather limited solubility in many solvents, including THF, CH₂Cl₂ and EtOAc. The reaction was very moisture and air sensitive. The reaction vessel used must be oven dried and held in a dessicator while cooling. Only a small amount of toluene was required, but 1.2 equivalents of isofuran 47 were used. Excess 47 was used because it had much better solubility in hexanes than 70 and was easily removed afterwards by washing with hexane. The yield of this reaction was then 50% to 75%. Further recrystallization from toluene gave fine green needles of 114, which decomposed at 219-224°C.

In theory, four cis-fused diastereomers could exist. Two have both oxygen bridges up (u) (114uuA, 114uuB) and two have one up and one down (d) (114udA, 114udB). Four internal methyl signals and four t-butyl signals should be found in the appropriate regions for each pair of isomers.
Due to limited solubility, the NMR spectra were taken at 40°C in CDCl₃. However, the ¹H NMR spectrum only showed half the expected number of signals, four internal methyl proton signals at δ -3.861, -3.866, -4.29 and -4.34, and four t-butyl signals at δ 1.710, 1.681, 1.679 and 1.659. The proton at the oxygen bridge head showed as four singlets at δ 6.667, 6.651, 6.640, 6.633 and likewise there were four carbon signals at δ 81.53, 81.49, 81.38 and 81.34 in the ¹³C NMR spectrum. In each of isomers 114uuB and 114udA, the two carbons on the CH-CH bridge in the middle of the two oxygen bridges are chemically equivalent and, thus only three signals should be observed in either the group A or group B isomers. Indeed, three signals appear at δ 54.14, 53.92 and 53.87 from the ¹³C NMR spectrum, and three signals at δ 2.503, 2.505 and 2.413 in the ¹H NMR spectrum, with the one at δ 2.505 being a singlet, while those at δ 2.503 and 2.413 are doublets each with a coupling constant 6.5 Hz.

From the information above, we deduced that only two isomers either 114uuA and 114uuB or 114udA and 114udB were obtained experimentally.

Compounds 115uu and 115ud are known. In the 115uu isomer with both oxygen bridges up, the coupling constants J_\text{ab} \equiv 0 \text{ Hz} and J_\text{bc} \equiv 0 \text{ Hz}, indicates the dihedral angles between Ha and Hb as well as between Hb and Hc are approximately 90°. In the 115ud isomer however the coupling constants J_\text{ab} \equiv 0 \text{ Hz} and J_\text{bc} \equiv 4.5 \text{ Hz} indicates the dihedral angles of approximately 90° between Ha and Hb, and 45° between Hb and Hc.
Figure 3. Partial $^1$H NMR spectra of isomers of 114.
In our case, the bridge head protons appeared as four singlets. The bridge protons on the CH group showed three signals, one singlet, and the other two coupling to each other with a coupling constant of 6.5 Hz. Clearly there is no coupling between the oxygen bridge head protons and the CH-CH bridge protons, which suggest that our isomers have the two oxygen bridges on the same side, i.e., 114uuA and 114uuB.

LSIMS gave the correct molecular ion at \( m/z \) 794.4 (M+) and a HRMS gave 794.5100; calculated as 794.5063.

Deoxygenation and aromatization of 114 was tried with several reagents: BH₃ with BF₃.Et₂O, Sml⁷₀, Ti (0)⁶⁹, Fe₂(CO)₉ with DDQ, and Na in THF, but, only P₂S₅ in CS₂ worked.

The adduct 114 and P₂S₅ was stirred in CS₂ for a few hours and the solution turned brown. After filtration and evaporation, chromatography was used to purify the product 116. Surprisingly, the first band which was eluted with hexanes was the red benzopyrene 21. How 21 was generated in this reaction is not clear. Eluted next was the green product 116 as a mixture of two isomers in about 30% yield.
There were two internal methyl and two t-butyl signals present in $^1$H NMR spectrum at $\delta$ -0.325, -0.310 and $\delta$ 1.474, 1.470 respectively. Due to the symmetry of the structures, there are only four types of aromatic protons within each isomer, and the most deshielded protons are from the naphtho spacer with chemical shifts at $\delta$ 9.196 and 9.190 from each isomer. LSIMS gave a correct $m/z$ at 760.6 (M$^+$); the exact mass was found as 761.5064. The calculated value for C$_{38}$H$_{64}$ (MH$^+$) was 761.5086.

The photochromism study of 116 was done in deaerated THF (due to its low solubility in cyclohexane). Various visible light sources, such as broad spectrum with/without cut-off filters, or monochromatic light were used. They all gave the same result that the signal of the UV-Vis absorption spectrum became smaller. This indicated that the sample decomposed under visible light irradiation.

Arynes generated from an aryl bromide and NaNH$_2$ usually react with furan at room temperature, and so they are fairly reactive. Indeed the aryne 67 generated from bromide 69 likewise proved to be a good dienophile, and reacts with furan at room temperature. We hoped the aryne from 9-bromophenanthrene 117 would be reactive enough to undergo the Diels-Alder reaction with isofuran 47.

In fact, the above reaction completed overnight and gave 85% of the adduct 118 as green crystals from toluene, mp 221-222°C. The $^1$H NMR spectrum showed two
singlets for both the internal methyl groups and the t-butyl groups at δ -3.14, -4.12 and δ 1.66, 1.63 respectively. The $^{13}$C NMR spectrum gave the bridge head carbons at δ 81.72 and 81.14. The CI MS gave a correct molecular ion at $m/z$ 561 (MH$^+$) and a correct elemental analysis was also obtained.

The deoxygenation of 118 was carried out with Fe$_2$(CO)$_9$ and was complete in a few hours. The resulting product 119 was obtained in about 86% yield and had poor solubility in hydrocarbon solvents, such as, hexane and benzene. It was purified by filtration through a short column of deactivated SiGel and crystallization from a mixed solvent of hexane/CH$_2$Cl$_2$.

![Diagram](image)

The $^1$H NMR spectrum of 119 showed singlets for both the internal methyl and the t-butyl protons at δ -1.07 and δ 1.55 respectively. The pattern of the proton spectrum on the DHP ring was similar to benzopyrene 21, with one sharp singlet for H-4,5, and two doublets each for H-3,6 and H-1,8. All the proton peaks could be assigned by COSY/NOESY spectra. The CI MS gave the correct molecular ion at $m/z$ 545 (MH$^+$), and a correct elemental analysis was also obtained.
2.4 An Unsymmetrical System Containing Three Dimethyl-dihydropyrene Units

The successful syntheses of compound 72 and of the substituted derivatives of benzopyrene 21 encouraged us to make a derivative of 72 which was substituted at one end of the DHP rings to differentiate the ends.

We tested first the direct acetylation of 72, however, as soon as BF$_3$Et$_2$O was added, the reaction mixture turned to black and $^1$H NMR spectrum showed that all the starting material was consumed. No product traveled on TLC which was DHP like.

We next tried an alternative route in which the central benzene rings were built last. Since a phenyl group had been successfully attached to the benzopyrene 21 by the stepwise route, we decided that the phenyl substituted tris-pyrene 120 was a suitable target through the following reactions.
The Diels-Alder reaction of 79 and the aryne derived from 107 was carried out in THF using NaNH$_2$ and gave the adduct 121. Due to its poor solubility and instability on both SiGel and alumina, the reaction mixture was just filtered through a short alumina column and then used directly in the subsequent deoxygenation reaction. A $^1$H NMR spectrum could be taken in C$_6$D$_6$, but decomposition occurred very quickly in CDCl$_3$ solution, even when previously filtered through alumina (which worked for other adducts). The crude $^1$H NMR spectrum showed three groups of peaks centered at $\delta$ -2.8, -4.2 and -5.0 suggested the product contained the correct DHP ring moieties. The crude yield of 121 was 23%.

Deoxygenation of 121 with Fe$_2$(CO)$_9$ gave product 120 as a mixture of four relatively stable isomers. Chromatography over alumina was used to purify the product.

![120A](image1.png) ![120B](image2.png) ![120C](image3.png) ![120D](image4.png)

The $^1$H NMR spectrum of 120 showed four broad internal methyl proton signals at $\delta$ -1.23, -1.36, -1.49 and -1.62. In comparison, the symmetric tris-pyrene 72 showed
only two signals at $\delta$ -1.37 and -1.63. The two signals at $\delta$ -1.36 and -1.62 of 120 were almost identical to those in 72, while the two newly generated signals of 120 at $\delta$ -1.23 and -1.49 are more deshielded by about 0.14 ppm from $\delta$ -1.37 and -1.63 in 72. As we know, the phenyl group reduces the ring current in the attached DHP ring through partial conjugation. Also, comparing the benzopyrene 21 and the phenyl substituted benzopyrene 105, the internal methyl protons are more deshielded by about 0.13 ppm from $\delta$ -1.58 in 21 to $\delta$ -1.45 in 105. Thus, we can conclude that two new signals of 120 at $\delta$ -1.23 and -1.49 were from the phenyl substituted DHP rings. The aromatic proton NMR pattern in 120 is similar to that in 72, except that more peaks are present consistent with the lower symmetry of 120.

The LSIMS showed a correct molecular ion at $m/z$ 1153.6 (MH+), the HRMS gave the exact mass as 1153.7576, while the calculated value was 1153.7590.
Chapter Three  Photochemical and Thermochemical Results and Discussion

3.1 Photochromism

The photochromism of the dimethyldihydropyrene system was first reported in 1965.46 In section 1.2, we reviewed some of the studies that have shown how substitution and annelation affect the photo opening reaction quantum yield and the rate of the thermal return reaction of the open form to the closed form. Very recently our group has made further reports.50 As we discussed earlier, arene annelation has the largest effect on photoswitching properties, and the benzene annelated dimethyldihydropyrene 21 is the best photoswitch in the dimethyldihydropyrene series so far.

3.1.1 The Tris-pyrene System 72

Ward studied the photochromic properties of the multistate photoswitches 50 and 51.50,51,53 In the case of 50, two DHP units were connected by means of a planar conjugated arene spacer. In 51, only one DHP unit is present in the thermally stable isomer, but on irradiation with UV light, two DHP units form. We thought the study of the photochromic property of the tris-pyrene 72 would be worthwhile, since in the thermally stable state, two DHP units are connected by a non-planar spacer, which on irradiation should form three planar DHP units.

In fact, visible light opening of the tris-pyrene 72 to its fully opened photoisomer 72' could be followed by means of UV-Vis spectroscopy. A deaerated solution of 72 in
cyclohexane, about 0.02 mg/mL, sealed in a quartz UV cell, was irradiated with a monochromatic light at 550 nm. A series of spectra were obtained at various time intervals shown in Figure 4.

Figure 4. The sequential UV-Vis spectra of photo openings of 72 at 550 nm.

On irradiation at 550 nm, the absorption bands which belonged to the closed isomer 72 at 409 nm and 389 nm decreased, while the 283 nm band increased. The spectrum of the open isomer 72' essentially consists of partially conjugated benzene rings and the UV-Vis absorption would be expected to be around 280 nm. Careful examination of the spectra, however, showed that an isosbestic point did not exist, suggesting that an intermediate isomer might form, such as 72'''. In order to confirm our observation, a $^1$H NMR study was performed. About 5 mg of 72 was dissolved in about 1 mL of CDCl$_3$ (which was filtered through alumina before use) and the solution was filtered
through alumina again to a NMR tube. The dark red solution was bubbled with argon for 30 min and was sealed with parafilm. The NMR tube was chilled in cold water and was irradiated with 500 W tungsten lamp with a 613 nm cut-off filter and monitored by a 300 MHz NMR spectrometer. After 30 min irradiation, the original internal methyl DHP proton signals at δ -1.359, -1.616 decreased, while new peaks at δ -1.373, -1.624 appeared. With longer irradiation, all peaks decreased, but the ratios of new peaks to the original ones were increased (see NMR spectra in Figure 5).

Figure 5. Sequential NMR spectra in the process of visible light opening of 72 at wavelength > 613 nm

When the conversion was near completion, some white solid started to precipitate out, which was thought to be due to the limited solubility of the fully opened isomer 72'. Complete disappearance of the peaks in the internal methyl DHP proton region took about 3 h.
Both the UV-Vis spectra and the $^1$H NMR spectra gave evidence that a third intermediate species, whose structure can only be $72'''$, was generated in the photo opening process, although this could not be isolated pure.

In the case of the bispyrenochrysene 50, no intermediate could be detected by $^1$H NMR in the photo opening process, and there was an isosbestic point when the opening was followed by UV-Vis spectroscopy. In 50, the thermally stable isomer is fully conjugated and planar and so, as the molecule absorbs a photon of energy, a double ring opening may occur.

In the case of 72, the cyclophane that connects the two DHP rings is not coplanar with the DHP rings, and so sufficient energy probably does not reach both ends of the molecule simultaneously, to open both ends without formation of the intermediate. Figure 6 shows the PCMODEL prediction of the structure of 72.
Figure 6. The predicted structure of 72 by PCMODEL.

Thus, photo opening of 72 is a two photon process, whereas 50 may be a one photon opening of both DHPs.

Figure 7. Sequential UV-Vis absorption spectra for the UV closing of 72' at different time intervals
Similarly, after 72 was fully opened to 72', the sample was irradiated with 350 nm UV light and this process was followed by both UV-Vis spectroscopy and NMR spectroscopy. The UV-Vis spectra are shown in Figure 7.

The UV closing spectra are very similar to visible opening ones shown in Figure 4, but in the opposite sequence. The colorless solution of 72' upon irradiation with 350 nm UV light became colored as the band at 283 nm decreased and the bands at 389 nm and 409 nm increased. Again there was no isosbestic point observed.

**Figure 8. Sequential NMR spectra in the UV closing reaction of 72' to 72 using 350 nm UV light.**

For the NMR study, the same solution used for the above photo opening reaction, after bleaching, was used for the UV closing reaction. The bleached CDCl₃ solution with some white precipitate, containing the open form 72', (which showed almost no peak in the region expected for internal methyl DHP protons, -1.3 to -1.7 ppm), was irradiated for 3 min at 350 nm, and then the NMR spectrum was repeated. Three peaks in the internal
methyl region were present at $\delta$ -1.359, -1.373 and -1.624, with the -1.624 ppm becoming two peaks at -1.616 and -1.624 ppm as time increased (see Figure 8 for NMR spectra). The peaks at $\delta$ -1.359 and -1.616 belonged to the thermally stable isomer 72 and grew as the irradiation proceeded. The peaks at $\delta$ -1.373 and -1.624 thus belong to the half closed isomer 72''. They grew in very fast initially, but the ratio became smaller with continued irradiation as 72'' closed to 72. At the same time, the white precipitate dissolved as the UV irradiation progressed.

The changes in both the UV-Vis spectra and the NMR spectra during the photo opening and closing processes between 72 and 72' suggest strongly that the intermediate 72'' is involved. This is unlike the case of 50, in which the intermediate can be seen in the closing reaction, but not in the opening.

3.1.2 The Phenyl Substituted Tris-pyrene System 120

From the photochromic studies of the tris-pyrene system 72 above, we have ascertained that a two photon process is involved in both the photo opening and closing. We thus thought it might be possible to separately open and close the two DHP ends if their UV-Vis absorption spectra were sufficiently different. However, as discussed in the synthesis section above, we had considerable difficulty in functionalising one of the DHP ends of 72. The only substituted compound which we could make was 120. The photo opening and closing of this phenyl substituted tris-pyrene system 120 were thus followed by both UV-Vis spectroscopy and $^1$H NMR spectroscopy.
A deaerated cyclohexane solution of 120, about 0.02 mg/mL, in a quartz UV cell was irradiated through a monochromator at 550 nm. The UV-Vis spectra at various time intervals are shown in Figure 9.

The UV-Vis absorption spectrum of 120 was not very different from that of 72. The 409 nm band for 72 shifted to 415 nm and was broader in 120, and the shoulder at 388 nm disappeared.

The solution of 120, upon irradiation with 550 nm light, the 415 nm band decreased and the 284 nm band increased. The same as in the parent 72', the chromophore in the CPD-120' is composed of only benzene rings, and thus its UV absorption should be
around 280 nm. The increased intensity of the band at 284 nm indicates the formation of the isomer $120'$. However, the band at 415 nm also shifted gradually to 407 nm and a shoulder started to appear at 387 nm and shifted to 386 nm with prolonged irradiation. More importantly, there was not an isosbestic point. From this information, we believe a third species is generated in the photo opening of $120$ to $120'$, one in which one of the DHP ends has opened, e.g., $120''$. Because $120$ is not symmetric, the question arises, which DHP ring opens first, the one with the phenyl attached or the unsubstituted one?

In fact, when $72$ was irradiated with 550 nm light, the band at 409 nm also shifted a little to 407 nm, and the shoulder shifted too, from 389 nm to 386 nm. Comparison of the intermediates $72'''$ and the one from the photo opening of $120$ to $120'$, suggests that the absorption bands belonging to the DHP at 386 nm and 407 nm were the same. Thus we believe that the intermediate was $120'''$ in which the open DHP ring was the phenyl substituted one.
Further experimental evidence which supported the structure of 120 was the relative photo opening rate of benzopyrene 21 and phenylbenzopyrene 105. The details of the experiment will be discussed later. The result is that the photo opening rate of 105 is about three times faster than that of 21, and thus because it appears from above that both ends open independently, we might thus expect the phenyl substituted end to open faster.

A NMR study was conducted in order to find more evidence of the intermediate. Thus about 2 mg of dark red 120 was dissolved in 1 mL d8-toluene, and then the solution was filtered through alumina in to an NMR tube. This was then bubbled with argon for 30 min, and then the NMR tube was sealed with parafilm. The sample was cooled with cold water. A 500 W tungsten lamp was used for irradiation through a 590 nm cut-off filter. NMR spectra were taken at various time intervals using a 300 MHz NMR spectrometer.

There are four peaks in the internal methyl region. As we discussed in the synthesis section, two of them, at δ -1.030 and -1.228, belong to the phenyl substituted DHP ring, and the other two, at δ -1.161 and -1.354 belong to the unsubstituted DHP ring. After 15 min irradiation, the two peaks, -1.030 and -1.228, significantly decreased, thus, confirming that the phenyl substituted DHP ring opened first; at the same time two new peaks grew next to the other two peaks, at -1.175 and -1.367, which suggested the intermediate species had a closed unsubstituted DHP ring. With prolonged irradiation, the ratio of the new generated peaks to the original ones became greater. After 55 min irradiation, the peaks at -1.030 and -1.228 had completely disappeared. A further 30 min
irradiation almost fully opened all isomers to form \textbf{120'} (see Figure 10 for the NMR spectra).

\textbf{Figure 10. Sequential $^1$H NMR spectra of the visible light opening of 120 to 120'}

\textbf{using visible light at wavelength > 590 nm.}

The NMR evidence thus confirms that the intermediate species 120'' was present during the photo opening of 120 to 120'.

As with the study of the parent 72', the UV closing of 120' was carried out by sequential irradiation with 350 nm UV light. The spectra are shown in Figure 11.

The spectra obtained during UV closing were not identical to those from the visible opening. In Figure 9, it is easy to see that there is not an isosbestic point. However, in Figure 11, it is not so obvious wherever there is an isosbestic point or not. Careful examination suggests there is not. The shoulder peak at 386 nm in Figure 11 is not so obvious as in Figure 9, though it still can be seen. The shift of the major absorption band
from 407 nm to 415 nm with extended irradiation of UV light still was seen. This evidence suggests that there may be some intermediate species in the UV closing of 120' to 120, although it might not be the same as that in the visible opening of 120 to 120'.

Figure 11. The sequential UV-Vis absorption spectra in the UV closing of 120' via a 350 nm UV light source.

In the study of the UV closing rates of benzopyrene 21 and phenylbenzopyrene 105, it was found that the UV closing rate of 105' to 105 was only 1.1 times that of the closing of 21' to 21. This suggests that the preference to open the phenyl substituted DHP ring is very small, and that the intermediates in the UV closing process of 120' to 120 was probably a mixture of 120'' and 120'''.
The NMR study was done in d$_5$-THF. The sample was prepared in the same way as in the photo opening study, but in a quartz NMR tube. The fully closed NMR spectrum in d$_5$-THF was taken for comparison and the internal methyl region is shown in Figure 12.

**Figure 12.** The internal methyl region $^1$H NMR spectrum of phenyltris-pyrene (120) in d$_5$-THF

The sample was bleached using visible light and then was irradiated by a 254 nm UV light source with a cold water jacket as cooling system. The sequential UV closing spectra are shown in Figure 13.
Figure 13. Sequential NMR spectra of the UV closing of 120' to 120 using UV light at 254 nm.

The peak patterns in Figure 12 and 13 are similar, but not identical. In the process of UV closing, all four groups of peaks which belong to the substituted and unsubstituted DHPs grow together. Mono-closed intermediates are probably present but there appears to be little preference in closing the substituted and unsubstituted DHP rings.

3.2 A Photo Opening and Closing Study of the Dimethyldihydro-pyrenes Using Excess Light

It is important for photochromic materials to have a short photo response time. For this purpose, a pico- or femtosecond laser photolysis experiment is needed. However, instruments are not always available to perform such experiments.
As we stated previously, benzopyrene 21 is one of the best photochromic compounds amongst simple arene annelated DHPs. Thus, we use 21 as a reference to compare photo openings and closings of the photo switch molecules in this thesis.

3.2.1 General Conditions

The photo openings and closings were followed by means of a UV-Vis spectrometer. The solution of benzopyrene 21 and the compound to be compared were prepared in equal molarity in quartz UV cells using cyclohexane as solvent (unless otherwise stated). The prepared solutions were bubbled with argon for 30 min and the UV cells were sealed with parafilm.

For photo-openings, a 500 W tungsten lamp served as a visible light source. Two cells, one containing the reference 21 and the other containing the compound to be compared, were placed side by side and irradiated with visible light using a 590 nm cut-off filter. An electrical fan was used to cool the samples. UV-Vis spectra were taken at various time intervals.

For photo-closings, a mercury pen light which emitted at 254 nm was used as the UV light source. The cells were put side by side in front of the UV light. An electrical fan was used as the cooling system. UV-Vis spectra were taken at various time intervals.

Both photo opening and closing processes were analyzed according to 0th order and 1st order kinetics, and it was found the experimental data fitted 1st order kinetics best. Thus the results reported here were analyzed using 1st order kinetics. Linear curve fitting was done in an MS Excel spreadsheet.
3.2.2 Molecules Containing a Single Pyrene Unit

The relative visible light opening rates of several simple substituted benzopyrenes and the annelated triphenyleno-DHP 119, and the UV closing of their photoisomers were studied first. Compound 119 had to be studied in THF because of low solubility in hydrocarbon solvents. The results are shown in Table 5 (the original plots are shown in the experimental section).

Table 5. Ratios of relative photo opening rates (Vis-open) of some simple DHP systems relative to benzopyrene 21 at room temperature and relative photo closing rates (UV-close) of their photoisomers relative to 21'.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vis-open</th>
<th>Compound</th>
<th>UV-close</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>1.0</td>
<td>21'</td>
<td>1.0</td>
</tr>
<tr>
<td>84</td>
<td>22.0</td>
<td>84'</td>
<td>1.1</td>
</tr>
<tr>
<td>103</td>
<td>6.4</td>
<td>103'</td>
<td>1.3</td>
</tr>
<tr>
<td>105</td>
<td>4.2</td>
<td>105'</td>
<td>1.1</td>
</tr>
<tr>
<td>119</td>
<td>2.8</td>
<td>119'</td>
<td>1.7</td>
</tr>
</tbody>
</table>

All the substituted benzopyrenes and the triphenylene annelated DHP 119 open faster than benzopyrene 21 itself. The acetyl substituted 84 opens the fastest. However, the UV closing rates of all compounds are not much different from that of 21'. Photophysical studies\textsuperscript{47,77,83} show that the quantum yields for the UV closing of all the DHP systems studied are high, e.g., 21' to 21 is about 0.4. Thus, it appears that the UV closing rates for all DHP systems are close and relatively fast. Although the photo opening rate determined here and the quantum yield can not be directly compared, a fast
photo opening rate certainly indicates usefulness as a switch even in the absence of a detailed quantum yield study.

3.2.3 The Tris-pyrene System 72

The photo opening of the tris-pyrene 72 and photo closing of 72' were studied in THF. The results are shown in Figure 14 and Figure 15. As we discussed before, the photo opening process goes through the half opened intermediate state 72'' before becoming the fully opened 72', unfortunately, the UV-Vis spectra of 72 and 72'' overlap each other. In section 3.1.1, we concluded that in our tris-pyrene system, two photons open the molecule, and the two benzopyrene moieties of 72 behave independently.

Figure 14. Plots for visible light opening of 72 (trisdhp) and 21 (bdhp)

![Graph showing photo opening rates](image)

Figure 14 shows the photo opening results. The linear curve fits the experimental data points well, thus, we infer that the photo opening rates of 72 → 72'' and 72'' → 72' were very close. We can imagine the closed form 72 as two substituted benzopyrene molecules and 72''' as one substituted benzopyrene molecule. The photo opening rate
we measured here could be translated to the reaction of the opening of a substituted benzopyrene structure 122.

![Diagram showing the transformation of 122 to 122']

The experiment showed that the photo opening rate of 72 was 2.1 times as that of 21, which is fairly close to the result for triphenylene-DHP 119. This is not surprising because both 119 and 72 can be viewed as a benzopyrene with ortho substituted phenyl rings on the benzene side.

**Figure 15. Plots for UV closing of 72'(triscpd) and 21'(bcpd)**

![Graph showing the UV closing of 72 and 21]

The same as in the photo opening reaction, the UV closing of 72' \( \rightarrow \) 72 that we measure by UV-Vis method is essentially that of the open form structure 122' to its closed form 122. Here, we assume that the two benzopyrene moieties close independently and with a similar closing rate (see Figure 15).
The UV closing rate of \( 72' \rightarrow 72 \) is 0.9 times as that of \( 21' \rightarrow 21 \). Like all other simple systems studied earlier, the UV closing rate does not vary much from that of \( 21' \).

3.2.4 The Phenyl Substituted Tris-pyrene System 120

The study of the photo opening process of the symmetrical compound 72 indicates that the opening rates of the stepwise reactions are almost the same. It would be interesting to see if a system could be obtained where the stepwise reactions have different opening rates. Thus, the phenyl substituted tris-pyrene 120 was studied and the results are presented here.

Figure 16. Plots for visible light opening of 120 (ptrisdhp) and 21(bdhp)

Figure 16 shows the photo opening results of compound 120 and 21 under the same conditions. The photo opening data of 120 can not be fitted into a linear curve. This is expected since the photochromic study showed that the photo opening of 120 went through the intermediate 120''', and then formed the fully opened 120'. The photo
opening process of 120 can be separated into three stages which are expressed by the following equations:

Stage 1: \[120 \rightarrow 120'''\]

Stage 2: \[120 \rightarrow 120''' \quad \& \quad 120''' \rightarrow 120'\]

Stage 3: \[120'''' \rightarrow 120'\]

The initial stage of the photo opening process was almost exclusively the opening of the phenyl substituted DHP ring. The opening rate should be relatively large and early data points should show to a relatively straight line fit. This is shown in Figure 17.

**Figure 17. Plot for visible light opening of 120 (ptrisdhp) in stage 1**

![Plot for visible light opening of 120 (ptrisdhp) in stage 1](image)

In this manner, the initial photo opening rate of 120 is determined to be 6.7 times that of 21. Compared to the model compound phenylbenzopyrene 105, which opens 4.2 times as fast as 21, the substituents at the benzo side further increase the opening rate about two times. This is consistent with the data from the parent 72, which opens 2.1 times as fast as benzopyrene 21. After the initial opening of 120, the fully opened 120' is produced slowly. Thus, the second stage consists of two processes and the average opening rate should decrease. Figure 18 gives the experimental results.
The linear curve fitting gives a qualitative idea on the overall opening rate, which is about 3.4 times as fast as benzopyrene 21. Although the apparent opening rate is slowed down, it is still larger than that of the parent 72, which is as it should be.

The final stage of the opening process of 120 is the opening of the benzopyrene structure 122. Theoretically, we would predict that opening rate of the final stage should be very similar to that of the parent 72. The experiment results are shown in Figure 19.

The relative photo opening rate of 120 in the final stage is 1.9 times that of 21, which is very close to that for the parent 72. The fact that the absorption wavelength
during the final stage stays unchanged at 404 nm supports the idea that there is a single final species with a closed DHP ring.

### 3.3 The Thermal Closing Reactions

So far all photochromic dimethylidihydropyrenes also show a thermochromic reaction as well.\textsuperscript{31,46,50} The ultimate goal of shutting off the thermal reaction between the photoisomers has not yet been achieved. However, there are some systems where the thermal reaction rate is sufficiently slow ($\tau_{1/2}$ is about 1 week at room temperature), for example 21, which could thus potentially be put to practical applications.

Thus, knowledge of the thermal closing data is also important to the photochromic properties of dimethylidihydropyrenes.

The thermal reaction was studied using UV-Vis spectroscopy. The photo bleached sample in toluene was held at a fixed temperature and its absorption monitored at the maximum absorption in the wavelength range of 380 nm to 420 nm at various time intervals. Nine compounds were studied and their thermal closing rates were determined at various temperatures.
For easy tracking of the compounds studied, their DHP structures are shown below.

Each thermal reaction was followed at least at three temperatures, 46°C, 60°C and 70°C. The plots and all other thermal data are given in experimental section. The kinetic data at 46°C are presented in Table 6.

Triphenyleno-DHP, which has a medium thermal return reaction rate, was chosen to estimate standard deviation. Three runs were done for each temperature 46°C, 60°C, 70°C. The standard deviation was calculated for each temperature, the largest value (3.8%) was chosen to apply to all kinetic data. Similarly, $E_{act}$, $\Delta H^\circ$ and $\Delta S^\circ$ were
calculated for each run, standard deviations were thus calculated as 2.8%, 2.9% and 44%, respectively to apply to dynamic data.

Table 6. Thermal return rates and half lives $\tau_{1/2}$ at 46°C.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>rate (min$^{-1}$)</th>
<th>$\tau_{1/2}$ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21' to 21$^{50}$</td>
<td>0.00200 ± 0.00008</td>
<td>5.75 ± 0.23</td>
</tr>
<tr>
<td>84' to 84</td>
<td>0.00141 ± 0.00006</td>
<td>8.19 ± 0.33</td>
</tr>
<tr>
<td>86' to 86</td>
<td>0.00123 ± 0.00005</td>
<td>9.39 ± 0.38</td>
</tr>
<tr>
<td>87' to 87</td>
<td>0.00216 ± 0.00009</td>
<td>5.35 ± 0.21</td>
</tr>
<tr>
<td>103' to 103</td>
<td>0.00820 ± 0.00033</td>
<td>1.41 ± 0.06</td>
</tr>
<tr>
<td>105' to 105</td>
<td>0.00214 ± 0.00009</td>
<td>5.40 ± 0.22</td>
</tr>
<tr>
<td>119' to 119</td>
<td>0.00307 ± 0.00012</td>
<td>3.76 ± 0.15</td>
</tr>
<tr>
<td>82' to 82</td>
<td>0.00242 ± 0.00010</td>
<td>4.77 ± 0.19</td>
</tr>
<tr>
<td>72' to 72</td>
<td>0.00204 ± 0.00008</td>
<td>5.66 ± 0.23</td>
</tr>
<tr>
<td>120' to 120</td>
<td>0.00197 ± 0.00008</td>
<td>5.86 ± 0.23</td>
</tr>
</tbody>
</table>

After obtaining the kinetic data, the Arrhenius and Eyring equations were used to determine the activation energies, enthalpies and entropies.
Table 7. Thermal dynamic data derived from the kinetic results.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{act}}$ (kcal mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kcal mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (cal deg$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21$'$ to 21$^{50}$</td>
<td>24.5 ± 0.7</td>
<td>23.9 ± 0.7</td>
<td>3.8 ± 1.7</td>
</tr>
<tr>
<td>84$'$ to 84</td>
<td>24.4 ± 0.7</td>
<td>23.6 ± 0.7</td>
<td>2.2 ± 1.0</td>
</tr>
<tr>
<td>86$'$ to 86</td>
<td>23.6 ± 0.6</td>
<td>22.9 ± 0.6</td>
<td>-0.2 ± 0.1</td>
</tr>
<tr>
<td>87$'$ to 87</td>
<td>23.2 ± 0.6</td>
<td>22.5 ± 0.6</td>
<td>-0.3 ± 0.1</td>
</tr>
<tr>
<td>103$'$ to 103</td>
<td>22.7 ± 0.6</td>
<td>22.0 ± 0.6</td>
<td>0.9 ± 0.4</td>
</tr>
<tr>
<td>105$'$ to 105</td>
<td>23.9 ± 0.6</td>
<td>23.2 ± 0.6</td>
<td>1.9 ± 0.9</td>
</tr>
<tr>
<td>119$'$ to 119</td>
<td>23.9 ± 0.6</td>
<td>23.3 ± 0.7</td>
<td>2.7 ± 1.2</td>
</tr>
<tr>
<td>82$'$ to 82</td>
<td>24.0 ± 0.6</td>
<td>23.4 ± 0.7</td>
<td>2.6 ± 1.2</td>
</tr>
<tr>
<td>72$'$ to 72</td>
<td>24.1 ± 0.7</td>
<td>23.5 ± 0.7</td>
<td>2.6 ± 1.2</td>
</tr>
<tr>
<td>120$'$ to 120</td>
<td>24.2 ± 0.7</td>
<td>23.6 ± 0.7</td>
<td>2.8 ± 1.3</td>
</tr>
</tbody>
</table>

3.3.1 Substituted Benzo-CPD Systems

Although activation energies and enthalpies do not change dramatically on substitution, their effect on the thermal return rate is significant. The presence of the electron withdrawing, nitro and acetyl groups in 84$'$ and 86$'$ reduce the thermal return rates. At 46°C, the thermal decay half lives ($\tau_{1/2}$) of 84$'$ and 86$'$ were 8.19 h and 9.39 h, which are considerably slower than for the parent 21$'$ (5.75 h). We expected that two nitro groups on the DHP ring would slow down the thermal return reaction further. However, in the ortho-dinitro compound 87, the thermal return rate increased from that in 86 such that, $\tau_{1/2}$ was 5.35 h, much the same as the unsubstituted parent 21.
This is different from the dibromo derivative 123'. Ward found that 123' had a slower thermal return rate (τ_{1/2} = 9.50 h) than the parent 21'. He proposed that the two large bromine atoms would sterically hinder each other in the more planar DHP form.

In our case, the second nitro group did not slow down the thermal return rate. A nitrogen atom is not as large as a bromine atom, and so steric hinderence may not have such large an effect as in the case of 123'. However, the nitro group has a much greater electronic effect than bromine, but how this affects the thermal return rate is not clear. Dr. R. V. Williams (University of Idaho) has now been able to locate a calculated transition state for the closing reaction. He finds that it has considerable (50%) radical character. Different electronic groups would thus be expected to affect this transition state, and work is needed to determine just how.

3.3.2 The Triphenyleno-CPD System 119

Triphenylene behaves more like isolated benzene rings than a polycyclic hydrocarbon. Thus the structure of 119 can be drawn as two independent benzene rings connected to a benzopyrene through a six membered ring. Thus, the thermal return reaction of 119' to 119 should theoretically be similar to that of 21' to 21.

Experimentally, the E_{act} of the reaction of 119' to 119 is 23.9 kcal mol^{-1}, which although not significantly different from that of the reaction 21' to 21, does show up in a
rate difference: the half life of its thermal return reaction $\tau_{1/2}$ is 3.76 h, which is slightly faster than that of the reaction 21' to 21, 5.75 h.

Certainly triphenylene annelation would not change strain or bond lengths much from that of benzene annelation, but would stabilize an intermediate radical more and increase the thermal reaction rate.

3.3.3 The Furano System 82'

The thermal return reaction of the furano system 82' to 82 is similar to that of 21' to 21. The furanocyclophane does not affect the thermal return reaction much, except the thermal return rate is slightly faster. The results found here also are consistent with the analogous system 51' to 51, in which the furan is replaced by a benzene.\(^{50}\)

In the visible opening process, the benzopyrene 21 opens either in the presence or absence of oxygen, however, the furano-system 82 only opens when no oxygen is
present. In the presence of oxygen, the UV-Vis absorption spectrum did not change under visible irradiation.

3.3.4 The Tris-CPD System 72'

The thermal return reaction of 72' to 72 was first followed by $^1$H NMR spectroscopy. The sample was prepared as that for the photochromic studies. The NMR tube containing 72 in a solution of CDCl$_3$, cooled with cold water, was irradiated under visible light using a 590 nm cut-off filter to bleach the solution. After ca. 1 h, the solution was almost colorless with some white precipitate, which was believed to be the open form 72'. The bleached sample was stored at 40°C in a water bath in the dark and the thermal return reaction was followed by NMR spectroscopy.

Figure 20. Sequential NMR spectra of thermally closing 72' to 72.
After 30 min, very small peaks at δ -1.359, -1.373 and -1.624 appeared. After 5 h, the peak at -1.359 was significantly larger than that at -1.373, and the peak at -1.624 became two peaks at -1.624 and -1.616. As we discussed previously, the peaks at -1.359 and -1.616 belong to the closed form 72, the peaks at -1.373 and -1.624 belong to the intermediate 72''. The sequential $^1$H NMR spectra are shown in Figure 20.

The NMR spectra clearly show that the thermal return reaction, just like the UV induced closing reaction, goes through intermediate 72'' to form the closed form 72.

\[
72' \xrightarrow{k_1} 72'' \xrightarrow{k_2} 72
\]

The rates of the two consecutive reactions, $k_1$ and $k_2$, should be very similar since each step contains the closing of one benzo-CPD ring. However, the concentration of the intermediate 72'' can not be measured by either NMR or UV-Vis spectroscopy, thus, it is not possible to measure $k_1$ and $k_2$ separately. The kinetics that can be determined thus use one or the other of the following two equations.

\[
72' \rightarrow 72 \quad (1)
\]

\[
72' \rightarrow 72''' + 72 \quad (2)
\]

In the first, a distinct signal for fully closed 72 is needed. This is not easily achieved, due to the partial overlap of the NMR signals of 72 and 72'''.

In this thesis, the kinetic studies of thermal return reactions were followed using UV-Vis spectroscopy. In this specific study, the chromophores of 72 and 72''' are both benzene and benzopyrene, and thus their UV-Vis absorption spectra should be very similar. In fact, in the studies we have done on both the photo opening and closing processes, the intermediate species 72''' was present and the major absorption peak shifted only from 409 nm to 407 nm in cyclohexane or the other way around.
The thermal return reaction was carried out in toluene, and it was found the major absorption peak which was used for kinetic study shifted from 409 nm to 413 nm. As for the UV closing, we assumed that the absorption band measured was the overlap of absorption of 72 and 72\". Thus, the kinetic study performed in this thesis is derived from the second equation.

From the photochromic and thermochromic studies we have made, the conclusion can be drawn that the two benzopyrene ends in 72 act independently. In fact, the absorption coefficient (ε) of 72 is about double the value of benzopyrene 21. Thus, the kinetics of 72 that we measured in the second way should be very similar to 21. Our experimental results prove this point. The activation energy and enthalpy were very close to those determined for benzopyrene 21' to 21. The thermal return half lives for 72' and 21' were 5.66 h and 5.75 h respectively.

3.3.5 The Phenyl Tris-CPD System 120'

Sequential ¹H NMR spectra were taken in d₈-toluene to study the thermal return process. Sample was prepared the same as in the photochromic study and the reaction was performed in 65°C. The dark red solution was irradiated with visible light to form the open isomer 120' such that there was no ¹H NMR signal in the internal methyl DHP region (δ -1 to -2). The bleached sample was then put in a water bath at 65°C and the appearance of internal methyl signals in this region were observed. As we discussed in the synthesis chapter, there are four isomers of the closed form 120. Unlike the symmetric parent 72, all the DHP internal methyls in 120 are different due to the substituent. There could thus be up to 16 signals around the δ -1 region. Fortunately,
not every methyl proton is different enough to generate a distinct signal, as we only observe 4 broad peaks. We assign the two peaks at $\delta$ -1.030 and -1.228 to the phenyl substituted DHP ring, and the two at $\delta$ -1.161 and -1.354 to the unsubstituted DHP ring.

Figure 21. Sequential NMR spectra of thermally closing 120' to 120.

The sample was placed in the water bath, and after 10 min the NMR spectrum was measured. The signals that belonged to the closed isomer 120 were already present. There were also additional peaks: $\delta$ -1.024, -1.041 beside the signal at $\delta$ -1.030, and peaks at $\delta$ -1.175, -1.244 and -1.367 beside the signals at $\delta$ -1.161, -1.228 and -1.354 respectively. With prolonged irradiation, all peaks grow, and the ratio of the signals belonging to the closed form 120 become relatively greater. After about 65 min, the other peaks disappeared and only those peaks that belonged to isomer 120 remain.
The NMR study thus clearly shows that intermediates are formed during the thermal return process. By comparison with the photochromic studies, we believe that these intermediates are the two species $120''$ and $120'''$.

Kinetic studies of $120'$ were carried out as for the parent compound $72'$ in toluene using a UV-Vis spectrometer. As for $72' \rightarrow 72$, the kinetics of $120' \rightarrow 120$ that we measure here are for the overall reaction $120' \rightarrow 120'' + 120''' + 120$. The NMR study implies that the two DHP rings close stepwise independently, and thus we convert the thermal closing of $120' \rightarrow 120$ as the combined results of closing structures of $122' \rightarrow 122$ and $124' \rightarrow 124$.

Since in 105, the phenyl substitution does not alter the thermal return reaction much, we assume the closing reaction rates of $122'$ and $124'$ are the same. Thus, the thermal reaction $120' \rightarrow 120$ is finally converted to the reaction $122' \rightarrow 122$. 

![Diagram of the reactions](image-url)
Our experimental results for the thermal return reaction half life \( \tau_{1/2} \) at 46°C of 120' is 5.86 h, and 5.66 h for the parent 72'. Activation energies and enthalpies are almost identical.

3.4 Electrochemical Readout of the Photoisomers of 72

We recently have shown\textsuperscript{50} that electrochemical readout of the state of the benzo switch 21\( \textit{2}/21' \) is possible. The closed form 21 is essentially an 18\( \pi \) planar system, while the open form 21' contains only isolated 6\( \pi \) systems. Electrochemically, 6\( \pi \) benzenoid systems are rather inert, while an 18\( \pi \) system should be easy to oxidize. Indeed, 21 in dry degassed CH\(_2\)Cl\(_2\) containing TBAPF\(_6\) does show oxidation at \( E_{p,a} = 0.75 \) V (peak anodic current, relative to Ag\(^{0}\) reference electrode). When the electrochemical cell was irradiated, 21' formed and then across the same potential window (0 to 1 V), the open state was redox silent.

Similarly, the open isomer 72' has essentially isolated benzene rings, whereas, the closed form 72, consists of two benzopyrenes connected via a benzenoid cyclophane spacer. The large \( \pi \) system of 72 should be considerably easier to oxidize electrochemically than the isolated 6\( \pi \) systems of 72'.

A solution of tris-pyrene 72 in dry degassed CH\(_2\)Cl\(_2\) (0.1 mol L\(^{-1}\)) containing TBAPF\(_6\) was placed in a quartz cell using Pt button electrodes and Ag\(^{0}\) reference electrode, using a scan rate of 100 mV/sec over a potential window from 0 to 1.00 V (ferrocene \( E_{p,a} = 0.55 \) V). Two peak anodic current were found centered at 0.45 V and 0.69 V. The cell was then irradiated with a 500 W household tungsten lamp affixed with a 400 nm cut-off filter for a few seconds, which opened 72 to 72', and then across the
same potential window, the opened form was relatively redox silent. The voltammogram is shown in Figure 22.

**Figure 22. Voltammogram of tris-pyrene 72 (red line) and photoisomer 72’ (blue line)**

The voltammogram clearly demonstrates that 72 is electrochemically very different from 72’. It would appear that there are two oxidation peaks for 72, one of which is at a similar potential to that of 21, and one which is at a lower potential. Further work is required to determine exactly why this is.
Chapter Four  Conclusions

Two useful intermediates, the furan 77 and 79 were synthesized from the bis-furan adduct 74. These two furans ultimately led to the successful syntheses of tris-pyrene system 72, the furanocyclophanedhp 82, and the phenyl substituted tris-pyrene 120. These are the most highly condensed DHP containing systems so far known.

A number of new benzopyrene systems have also been synthesized for comparison to the above condensed systems. The acetyl and nitro benzopyrene 84 and 86 were obtained by direct substitution. The phenyl derivative 105 and the phenylethynyl benzopyrene 103 were obtained by Suzuki and Sonogashiracouplings.

The naphtho fused tetracene analogue, 116 was obtained from isofuran 47 and adduct 70.

The photochromism of all these systems was studied. The multistate systems appear to open each DHP end separately rather than synchronously. Photo opening and closing rates were obtained relative to the benzopyrene 21. We have found that the substituents, phenyl, phenylethynyl, acetyl increase the relative photo opening rate by 4, 5 and 21 times, respectively. This is important for generation of faster switches.

The phenyl substituted DHP end of 120 was also found to open faster than the unsubstituted end. UV closing rates are not much affected in these systems.

Thermal closing rates were also studied. Although activation energies do not change dramatically from that of 21 (unlike non-benzo[e]pyrene system), reaction rates do change with substitution. A nitro group slows the thermal return rate the most, with an acetyl group close behind. Since the acetyl group speeds the photo opening the most,
the combination of increased photo opening rate and decreased thermal closing rate makes the acetyl derivative 84 now the best switch so far. This may be very important if the switch is to be incorporated into a functional unit, eg, a conducting circuit.

In multistate switches, we have shown that the ends can act independently, even with the relative poor differentiation, such as phenyl group. If an acetyl group shows the same properties to a multiswitch that it does to the benzopyrene system 21, then a true three way switch operating in the visible region may be possible.
5.1 General Experimental Conditions and Instrumentation

Melting points were determined on a Reichert 7905 melting point apparatus integrated to an Omega Engineering Model 199 Chromel-alumel thermocouple. Infrared spectra were recorded on a Bruker IFS25 FT-IR spectrometer as KBr discs, calibrated with polystyrene and only the major peaks are reported. UV-Vis spectra were recorded on a Cary 5 UV-VIS-NIR spectrometer in the stated solvents. Proton NMR spectra were recorded at 360 MHz on a Bruker AMX 360 spectrometer, or at 300 MHz on a Bruker AC 300 spectrometer in CDCl₃ using the solvent residual peak (7.240 ppm for CHCl₃) for calibration. Carbon NMR spectra were recorded on a Bruker AMX 360 (90.6 MHz), using the solvent peak at 77.0 ppm for calibration. Where peaks within the same sample are very close in chemical shift, a third decimal place is given. Mass spectra were recorded on a Finnigan 3300 gas chromatography-mass spectroscopy system using methane as a carrier gas for chemical ionization or electron impact (EI) at 70 eV. FAB or LSI mass spectra and exact mass measurements were done on a Kratos Concept-H instrument using perfluorokerosene as the standard. Elemental analyses were performed by Canadian Microanalytical services Ltd., Vancouver, B.C. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous MgSO₄ or K₂CO₃ as appropriate. Silica gel (SiGel) refers to Merck silica gel, 60-200 mesh. Alumina refers to Aldrich aluminum oxide, activated, neutral, Brockmann I, standard grade, ~150 mesh. All alumina and deactivated silica gel were deactivated with 4% (by weight) aqueous
ammonia solution (28-30% by weight). Where NMR assignments are made, these were
on the basis of 2D COSY/NOESY experiments for 1H and HETCORR/HMQCB
experiments for $^{13}$C.

5.2 Syntheses

9,18-Epoxy-2,7,11,16-tetra-tert-butyl-trans-17b,17c,18c,18d-tetramethyl-
17b,17c,18c,18d-tetrahydrotetrabenzo[de,uv,jk,op]pentacene (68)

The isofuran $47^{31}$ (80.0 mg, 0.208 mmol) and the bromide $69^{31}$ (132.0 mg, 0.312
mmol) were added to an oven dried two neck round bottom flask. Dry THF (20 mL) was
added via syringe and then NaNH$_2$ (400 mg, 10 mmol) and KO$^+$Bu (~ 5 mg). The mixture
was then stirred over night under argon. The solvent was evaporated and the residue was
dissolved in benzene (40 mL) and was filtered through alumina with a thin layer of celite
on top, using benzene as eluant. The green filtrate was collected and evaporated. The
residue was carefully washed with hexanes (about 1 mL each time) until hexane was
almost colorless. The solid was then air dried to give 118 mg (78%) of the adduct 68 as a
mixture of two isomers in an approximate 1:1 ratio, (in later cases, when more than one
isomers were obtained, no preference was observed with any particular isomer, unless
otherwise stated). After the next step, the deoxygenation, some of these isomers were
returned, but now in unequal amounts (approximate 2:1 ratio of isomer I and II below),
the NMR spectra of this sample enabled us to identify the signals from both isomers, mp (dec) 207-213 °C;  
\(^1\)H NMR, Isomer I, (360 MHz) \(\delta\) 8.77 (d, \(J = 1.2\) Hz, 2H, H-1,8 or 10,17), 8.61 (d, \(J = 1.3\) Hz, 2H, H-1,8 or 10,17), 8.28 (unresolved doublets, 2H, H-3,6, or 12,15), 8.22 (d, \(J = 0.9\) Hz, 2H, H-3,6, or 12,15), 8.21 & 8.166 (AB, \(J = 8.3\) Hz, 4H, H-4,5,13,14), 7.92 (s, 2H, H-9,18), 1.73 (s, 18H, C(CH\(_3\))\(_3\)), 1.66 (s, 18H, C(CH\(_3\))\(_3\)), -3.40 (s, 6H, CH\(_3\)), -4.37 (s, 6H, CH\(_3\)). Isomer II, \(\delta\) 8.80 (d, \(J = 1.3\) Hz, 2H, H-1,8 or 10,17), 8.66 (d, \(J = 1.2\) Hz, 2H, H-1,8 or 10,17), 8.26-8.25 (overlapping unresolved doublets, 4H, H-3,6,12,15), 8.18 (s, 4H, H-4,5,13,14), 7.98 (d, \(J = 0.63\) Hz, 1H, H-9 or 18), 7.92 (d, \(J = 0.64\) Hz, 1H, H-9 or 18), 1.71 (s, 18H, C(CH\(_3\))\(_3\)), 1.70 (s, 18H, C(CH\(_3\))\(_3\)), -3.44 (s, 6H, CH\(_3\)), -4.38 (s, 6H, CH\(_3\)).  
\(^{13}\)C NMR (90.6 MHz) (isomer assigned referred only to peak labeled) \(\delta\) 145.44, 145.36, 145.20, 137.39, 137.35, 137.09, 137.00, 136.93, 136.86, 136.78, 127.20, 127.09, 126.74, 126.54, 124.17 (I), 124.09 (II), 124.02 (I), 121.24 (I), 121.05 (I), 120.93 (II), 116.19 (II), 115.74 (I), 115.39 (I), 115.23 (II), 81.53 (II), 81.09 (I), 80.82 (II), 35.90, 35.81, 32.76, (I), 32.55 (II), 31.79, 31.72, 30.60 (I), 30.38 (II), 30.32 (II), 16.00 (II), 15.91 (I), 14.13 (I), 13.97 (II); IR (KBr) 1616, 1456, 1360, 1346, 1262, 1212, 1045, 886, 869, 649 cm\(^{-1}\); LSIMS \(m/z\) 727.5 (MH\(^+\)); Anal. Calc’d for C\(_{54}\)H\(_{62}\)O: C, 89.66; H, 7.34. Found: C, 89.96; H, 7.19.
Tris-pyrene (72)

TrisDHP precursor 75 (crude 21 mg, 0.019 mmol) and Fe$_2$(CO)$_9$ (10 mg, 0.027 mmol) were refluxed in benzene under argon for 1 hr and the mixture was slowly cooled to room temperature. The solvent was evaporated and the residual was chromatographed on deactivated SiGel using hexanes/benzene (6:1) as eluant and gave 9 mg (44%) of the product 72 as a mixture of three isomers. Further purification of 72 was carried out by recrystalization from toluene, mp (dec) 176-181°C. These peaks of the NMR spectrum then appeared in two groups in unequal amount due to the different solubilities of the various isomers.

$^1$H NMR (360 MHz), group I:  δ 9.00 (s, 4H total, H-9,13,22,26), 8.37 (br. s, 4H, H-1,8,14,21), 7.40 (d, J = 0.9 Hz, 4H, H-3,6,16,19), 7.17 (s, 8H, H-4,5,17,18,10,12,23,25), 1.53 (s, 36H, C(CH$_3$)$_3$ from DHPs), 1.365, 1.360 (s, 36H total, C(CH$_3$)$_3$ from cyclophane), 1.28 (br. s, 6H, CH$_3$ from cyclophane), -1.37 (br. s, 12H, CH$_3$ from DHPs).

$^1$H NMR (360 MHz), group II:  δ 9.142 & 9.136 (s, 4H, H-9,13,22,26), 8.55 (br. s, 4H, H-1,8,14,21), 7.52 (br. s, 4H, H-3,6,16,19), 7.31 (s, 4H, H-4,5,17,18), 7.17 (s, 4H, H-10,12,23,25), 1.56 (s, 36H, C(CH$_3$)$_3$ from DHPs), 1.365, 1.360 (s, 36H total, C(CH$_3$)$_3$ from cyclophane), 1.28 (br. s, 6H, CH$_3$ from cyclophane), -1.63 (br. s, 12H, CH$_3$ from DHPs).
$^{13}$C NMR (90.6 MHz) $\delta$ 150.28, 144.74, 144.50, 141.93, 141.49, 140.10, 139.95, 138.63, 138.48, 137.93, 134.92, 134.48, 129.46, 129.25, 129.07, 124.38, 123.42, 121.25, 120.99, 119.87, 117.35, 116.77, 35.62, 35.56, 35.49, 34.99, 34.37, 31.53, 30.91, 30.76, 30.46, 29.71, 18.84, 17.96, 17.46; UV (chloroform) $\lambda_{\text{max}}$ ($\epsilon_{\text{max}}$) nm 287 (53,400), 310 (47,700), 394 (43,600), 413 (74,200), 513 (9,600), 628 (1,100); El MS $m/z$, 1078 (MH$_2^+$); HRMS. Calc'd for C$_{82}$H$_{92}$ (MH$^+$): 1077.7277. Found: 1077.7256. Anal. Calc'd for C$_{82}$H$_{92}$: C, 91.39; H, 8.61. Found: C, 90.32; H, 8.79.

Tris-pyrene precursor (75)

NaNH$_2$ (400 mg, 10 mmol) and KOBu (2 mg) were added to a solution of the furanodihydropyrene adduct 79 (20 mg, 0.026 mmol) and the bromide 69 (18 mg, 0.043 mmol) in dry THF (15 mL) under N$_2$, and the mixture was stirred for 5 hr and filtered through a short alumina column (2 cm). Usually, the solvent was evaporated and the residual was used directly for the next reaction step. Since the product 75 had poor solubility and was not very stable in solution, purification tried at this step was not very successful. Benzene and hexanes/CH$_2$Cl$_2$ (1:1) were used, but not polar enough to elute 75 effectively. With increasing polarity of the eluant, much brownish material eluted with 75. The crude product which contained 6 isomers was used for $^1$H NMR (300 MHz), The chemical shift regions were as follows: $\delta$ 8.86-8.44, 8.08-7.87 (ring protons), 1.87-1.76
(t-Bu on the middle ring), 1.64-1.55 (t-Bu on the side rings), -3.36, -3.37, -3.39, -3.50, -4.54, -4.57, -4.58, -4.62, -5.25, -5.28, -5.30 (internal methyls).

Isofuran-furan adduct (77)

Tetrazine\textsuperscript{73} 71 (51.3 mg, 0.217 mmol) was added to a cooled (0°C) solution of the bis adduct\textsuperscript{72} 77 (103.4 mg, 0.217 mmol) in dry THF (50 mL) under N\textsubscript{2} and was stirred for 3 hr. The solvent was evaporated and the residual was chromatographed on alumina using hexanes/benzene (1:1) as eluant and gave 28.3 mg (29%) of the product 77 as a red-orange solid, mp (dec) 182-183°C; \textsuperscript{1}H NMR (360 MHz) δ 8.017 & 8.012 (d each, J = 1.7 Hz, 2H, H-11,12), 6.836 & 6.830 (d each, J = 1.4 Hz, 2H, H-1,10), 6.675 & 6.570 (dd each, J = 5.6, 1.8 Hz, 2H, H-5,6), 6.409 & 6.381 (d each, J = 1.4 Hz, 2H, H-3,8), 5.737 & 5.701 (dd each, J = 1.8, 1.4 Hz, 2H, H-4,7), 1.241 (s, 9H, C(CH\textsubscript{3})\textsubscript{3}), 1.239 (s, 9H, C(CH\textsubscript{3})\textsubscript{3}), 0.373 (s, 3H, CH\textsubscript{3}), 0.137 (2, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (90.6 MHz) δ 144.56, 144.28, 137.01 & 136.99 (C-11,12), 136.69 & 135.45 (C-5,6), 132.12, 131.67, 131.10, 131.04, 128.75, 128.60, 120.72, 120.61, 116.79 & 116.74 (C-1,10), 113.76 & 113.71 (C-3,8), 78.83 & 78.81 (C-4,7), 42.37, 41.64, 34.67, 34.65, 29.56 (C(CH\textsubscript{3})\textsubscript{3}), 22.04, 19.76; IR (KBr) 1617, 1366, 1251, 1163, 1050, 1030, 874, 854, 822, 771, 643 cm\textsuperscript{-1}; CI MS m/z, 451 (MH\textsuperscript{+}); HRMS. Calc’d for C\textsubscript{32}H\textsubscript{34}O\textsubscript{2}: 450.2559. Found: 450.2559.
Isofuran adduct (78)

NaNH₂ (400 mg, 10 mmol) and KO'Bu (2 mg) were added to a solution of the iso-furan-furan adduct 77 (45.9 mg, 0.102 mmol) and the bromide 69 (56.1 mg, 0.133 mmol) in dry THF (40 mL) under N₂, and the mixture was stirred for 5 hr. The solvent was evaporated and the residual was filtered through alumina and hexanes/benzene (1:1) as eluant and gave 58 mg (72%) of the product 78 as a green solid as a mixture of four isomers, LSIMS m/z 793.6 (MH⁺); HRMS. Calc'd for C₅₈H₆₄O₂ (MH⁺): 793.4985. Found: 793.4987. These four isomers on further chromatography over aluminum oxide using hexanes/benzene (1:1) as eluant, were separated into two portions which were oxygen bridge syn- and anti- isomers, each containing two methyl isomers.

anti-Isomers (ud), mp (dec) 183-188°C; ¹H NMR (360 MHz) isomer I: δ 8.85 (d, J = 1.3 Hz, 1H), 8.67 (d, J = 1.3 Hz, 1H), 8.66 (d, J = 1.2 Hz, 1H), 8.57 (d, J = 1.3 Hz, 1H), 8.22 (m, 2H), 8.161-8.152 (m, 2H), 8.084 (s, 2H), 7.97 (d, J = 0.72 Hz, 1H), 7.88 (d, J = 0.72 Hz, 1H), 7.23-7.20 (m, 1H), 7.10 (dd, J = 5.47, 1.80 Hz, 1H), 6.57-6.52 (m, 2H), 1.75, 1.72, 1.71, 1.69, 1.68, 1.67, 1.63 (s(I +II), 72H, C(CH₃)₃), -3.28, -3.77, -4.23, -4.41 (s, 3H each, CH₃). Isomer II: δ 8.79 (d, J = 1.2 Hz, 1H), 8.70 (d, J = 1.2 Hz, 1H), 8.65 (d, J = 1.2 Hz, 1H), 8.53 (d, J = 1.4 Hz, 1H), 8.25 (d, J = 1.0 Hz, 1H), 8.20 (d, J = 1.3 Hz, 1H), 8.17 (d, J = 1.2 Hz, 1H), 8.13 (d, J = 1.2 Hz, 1H), 8.080 (2H), 7.93 (d, J = 0.70 Hz, 1H), 7.90 (d, J = 0.72 Hz, 1H), 7.23-7.20 (m, 1H), 7.10 (dd, J = 5.47, 1.80 Hz, 1H), 6.57-6.52 (m, 2H), 1.75, 1.72, 1.71, 1.69, 1.68, 1.67, 1.63 (s(I +II), 72H, C(CH₃)₃),
\[ \text{NMR (90.6 MHz)} \delta 145.50, 145.41, 145.21, 144.98, 141.04, 140.95, 140.68, 140.41, 140.27, 137.92, 137.76, 137.35, 137.23, 137.08, 136.98, 136.91, 136.67, 128.56, 128.24, 128.10, 127.88, 127.59, 127.46, 127.20, 126.88, 124.29, 124.26, 121.34, 121.20, 121.08, 117.63, 117.31, 116.53, 116.40, 115.72, 115.30, 115.15, 115.02, 114.83 \text{ (aromatic & alkene carbons)}, \ 81.90, 81.70, 81.62, 81.52, 81.38, 81.19 \text{ (carbons attached to oxygen bridge)}, \ 35.98, 35.89, 35.83, 35.77, 33.06, 32.91, 32.81, 32.71, 32.28, 32.15, 31.25, 31.07, 30.32 \text{ (aliphatic carbons)}, 31.94, 31.91, 31.65, 31.62 (C(CH\textsubscript{3})\textsubscript{3}), 16.39, 16.29, 15.07, 15.00, 14.44, 14.28, 14.14 (CH\textsubscript{3}).

\text{syn-Isomers (uu), mp (dec) 179-182°C}; \text{IR (KBr):} \ 1614, 1463, 1392, 1362, 1260, 1035, 871, 646 \text{ cm}\textsuperscript{-1}; \text{H NMR (360 MHz) isomer III:} \ \delta 8.84 \text{ (d, } J = 1.2 \text{ Hz, } 1\text{H}), 8.687-8.684 \text{ (m, } 1\text{H}), 8.66-8.65 \text{ (m, } 1\text{H}), 8.55 \text{ (d, } J = 1.3 \text{ Hz, } 1\text{H}), 8.16 \text{ (d, } J = 1.1 \text{ Hz, } 1\text{H}), 8.14 \text{ (d, } J = 1.3 \text{ Hz, } 1\text{H}), 8.13 \text{ (d, } J = 1.3 \text{ Hz, } 1\text{H}), 8.11 \text{ (d, } J = 1.2 \text{ Hz, } 1\text{H}), 8.068 \text{ (s, } 2\text{H}), 7.97 \text{ (d, } J = 0.6 \text{ Hz, } 1\text{H}), 7.89 \text{ (d, } J = 0.54 \text{ Hz, } 1\text{H}), 7.07 \text{ (dd, } J = 5.5, 1.9 \text{ Hz, } 1\text{H}), 6.93 \text{ (dd, } J = 5.5, 1.8 \text{ Hz, } 1\text{H}), 6.58 \text{ (dd, } J = 1.8, 0.7 \text{ Hz, } 1\text{H}), 6.56 \text{ (dd, } J = 1.8, 0.8 \text{ Hz, } 1\text{H}), 1.76, 1.722, 1.719, 1.685, 1.677, 1.65, 1.61 \text{ (s (III +IV), } 72\text{H, C(CH}_3\text{)_3)}, -3.29, -3.47, -4.32, -4.70 \text{ (s, } 3\text{H each, } CH_3). \text{Isomer IV:} \ \delta 8.82 \text{ (d, } J = 1.1 \text{ Hz, } 1\text{H}), 8.687-8.684 \text{ (m, } 1\text{H}), 8.66-8.65 \text{ (m, } 1\text{H}), 8.51 \text{ (d, } J = 1.2 \text{ Hz, } 1\text{H}), 8.27 \text{ (d, } J = 1.1 \text{ Hz, } 1\text{H}), 8.21 \text{ (d, } J = 1.2 \text{ Hz, } 2\text{H}), 8.20 \text{ (d, } J = 1.1 \text{ Hz, } 1\text{H}), 8.063 \text{ (s, } 2\text{H}), 7.93 \text{ (d, } J = 0.5 \text{ Hz, } 1\text{H}), 7.90 \text{ (d, } J = 0.6 \text{ Hz, } 1\text{H}), 7.09 \text{ (dd, } J = 5.5, 1.8 \text{ Hz, } 1\text{H}), 6.94 \text{ (dd, } J = 5.5, 1.8 \text{ Hz, } 1\text{H}), 6.53 \text{ (dd, } J = 1.9, 0.8 \text{ Hz, } 1\text{H}), 1.76, 1.722, 1.719, 1.685, 1.677, 1.65, 1.61 \text{ (s (III +IV), } 72\text{H, C(CH}_3\text{)_3)}, -3.26, -3.48, -4.31, -4.73 \text{ (s, } 3\text{H each, } CH_3). \text{13C NMR (90.6 MHz)} \delta 145.47, 145.44, 145.39, 145.32, 145.23, 145.00, 144.82, 141.05, 140.92, 140.84, 140.74, 140.52, 140.45, 140.27, 137.72, 137.62, 137.59, 137.46,
137.13, 137.08, 136.95, 136.88, 136.79, 128.75, 128.16, 127.99, 127.87, 127.83, 127.71,
127.63, 127.43, 127.21, 127.07, 126.76, 124.25, 124.21, 121.32, 121.28, 121.16, 121.07,
117.66, 117.31, 116.57, 116.46, 115.77, 115.32, 115.08, 114.82, 114.77, 114.65
(aromatic & alkene carbons), 81.92, 81.69, 81.62, 81.50, 81.39, 81.24 (carbons attached
to oxygen bridge), 35.98, 35.91, 35.82, 35.79, 35.74, 34.66, 33.84, 33.77, 33.03, 32.89,
31.41, 31.26, 31.21, 31.01 (aliphatic carbons), 31.96, 31.91, 31.65, 31.60 (C(CH₃)₃),

Furanodihydropyreneadduct (79)

Tetrazine⁷³ 71 (18.3 mg, 0.078 mmol) was added to a solution of the isofuran
adduct 78 (56 mg, 0.071 mmol) in dry THF (20 mL) under N₂ and was stirred for 1 hr.
The solvent was evaporated and the residual was filtered through alumina using
hexanes/benzene (1:1) as eluant and gave 51 mg (93%) of the product 79 as a reddish-
brown solid as a mixture of unequal amounts of two isomers, mp (dec) 190°C; ¹H
NMR (300 MHz), Isomer I, δ 8.54 (s, 1H), 8.43 (s, 1H), 8.40 (s, 1H), 8.36 (s, 1H), 8.324
(s, 1H), 8.316 (s, 1H), 7.98 (s, 1H), 7.97 (s, 1H), 7.07 (s, 1H), 7.05 (s, 1H), 7.00 (d, J =
1.6Hz, 1H), 6.84 (d, J = 1.6Hz, 1H), 6.81 (d, J = 1.6Hz, 1H), 6.76 (d, J = 1.6Hz, 1H),
1.694, 1.66, 1.35, 1.28 (s, 9H each, C(CH₃)₃), 0.45, -0.54, -3.68, -4.02 (s, 3H each, CH₃).
Isomer II, δ 8.58 (s, 1H), 8.48 (s, 1H), 8.40 (2H), 8.33 (2H), 7.96-7.99 (2H), 7.09 (s,
The unequal amount of a mixture of isomers of furan 79 (31 mg, 0.040 mmol) and Fe₂(CO)₉ (17.6 mg, 0.048 mmol) were refluxed in benzene (20 mL) for 1 hr. The solvent was evaporated and the residual was chromatographed on alumina using hexanes/benzene (6:1) as eluant and gave 24.3 mg (80%) of cyclophane 82 as a mixture of unequal amount of two isomers, red crystals, mp (dec) 172°C. ¹H NMR (360 MHz), isomer I: δ 9.10 (s, 2H, H-4,13), 8.51 (d, J = 1.2 Hz, 2H, H-3,14), 7.79 (s, 2H, H-8,9), 7.50 (d, J = 1.1 Hz, 2H, H-1,16), 7.30 (s, 2H, H-17,18), 7.12 (d, J = 2.2 Hz, 2H, H-5,12), 7.06 (d, J = 2.2 Hz, 2H, H-7,10), 1.53 (s, 18H, C(CH₃)₃ from DHP), 1.32 (s, 18H, C(CH₃)₃ from cyclophane), 1.03 (s, 6H, CH₃ on cyclophane), -1.66 (s, 6H, CH₃ on DHP). ¹³C NMR (90.6 MHz) δ 137.97 (C-8,9), 129.20 (C-5,12), 127.67 (C-7,10), 123.62 (C-4,13), 121.23 (C-17,18), 119.86 (C-1,16), 116.74 (C-3,14), 35.52, 34.88, 34.20, 31.44 (C(CH₃)₃ from DHP), 30.84 (C(CH₃)₃ from cyclophane), 18.21 (CH₃ on cyclophane), 17.36 (CH₃ on DHP), + see below.

¹H NMR (360 MHz), isomer II: δ 8.95 (s, 2H, H-4,13), 8.31 (d, J = 1.2 Hz, 2H, H-3,14), 7.78 (s, 2H, H-8,9), 7.37 (d, J = 1.1 Hz, 2H, H-1,16), 7.15 (s, 2H, H-17,18), 7.12 (d, J =
2.2 Hz, 2H, H-5,12), 7.05 (d, J = 2.2 Hz, 2H, H-7,10), 1.49 (s, 18H, C(CH₃)₃ from DHP),
1.31 (s, 18H, C(CH₃)₃ from cyclophane), 1.03 (s, 6H, CH₃ on cyclophane), -1.37 (s, 6H,
CH₃ on DHP). ¹³C NMR (90.6 MHz) δ137.97 (C-8,9), 128.99 (C-5,12), 127.67 (C-7,10),
124.68 (C-4,13), 120.96 (C-17,18), 119.86 (C-1,16), 117.40 (C-3,14), 35.59, 35.44,
34.30, 30.67 (C(CH₃)₃ from DHP), 30.29 (C(CH₃)₃ from cyclophane), 18.21 (CH₃ on
cyclophane), 17.96 (CH₃ on DHP), + see below. The following 18 quaternary ¹³C NMR
peaks could not be assigned to a particular isomer: 150.09, 144.72, 144.43, 141.12,
140.65, 140.48, 140.36, 138.56, 138.42, 137.63, 137.49, 135.73, 134.83, 134.33, 131.73,
130.07, 129.38, 128.97; UV (cyclohexane) λ_max (ε_max) nm 280 (25,700), 303 (21,300),
354 (17,200), 385 (24,200), 405 (35,100), 455 (4,000), 481 (4,000), 509 (4,200), 627
(500); IR (KBr) 1593, 1465, 1361, 1264, 1225, 1043, 872, 790, 748, 669 cm⁻¹; LSIMS
m/z, 750.5 (M⁺); HRMS Calc’d for C₅₆H₆₂O (M⁺): 751.4879. Found: 751.4869.

4-Acetyl-2,7-di-t-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene (84)

Ac₂O (1 mL) was added to a solution of the benzo[e]pyrene 21³¹ (25.0 mg, 0.0635
mmol) in CH₂Cl₂ (20 mL) under argon. After stirring for 10 min, ten drops of BF₃Et₂O
were added and the mixture was stirred for another 30 min. Saturated NaHCO₃ solution
was then added to quench excess Ac₂O and BF₃Et₂O. The organic phase was then
washed, dried and evaporated. The residual was chromatographed over SiGel, using
hexanes/CH₂Cl₂ (1:1) to give 21 mg (77%) of the product 84 as purple crystals, mp 173-
$^{1}$H NMR (360 MHz) $\delta$ 9.76-8.72 (m, 2H, H-9,12), 8.65 (d, $J = 1.2$ Hz, 1H, H-3), 8.33 (d, $J = 1.3$ Hz, 1H, H-1), 8.27 (d, $J = 1.3$ Hz, 1H, H-8), 7.67-7.60 (m, 2H, H-10,11), 7.48 (d, $J = 0.71$ Hz, 1H, H-5), 7.377-7.375 (m, 1H, H-6), 2.73 (s, 3H, COCH$_3$), 1.51 (s, 9H, C(CH$_3$)$_3$), 1.49 (s, 9H, C(CH$_3$)$_3$), -1.48 (s, 3H, CH$_3$), -1.55 (s, 3H, CH$_3$); $^{13}$C NMR (90.6 MHz) $\delta$ 201.16, 151.32, 145.27, 141.95, 137.97, 137.01, 134.63, 129.61, 129.11, 127.99, 126.59, 126.12, 124.79, 124.39, 120.56, 120.21, 117.81, 117.59, 116.95, 36.92, 36.25, 35.38, 34.74, 30.78, 30.54, 18.03, 17.40; UV (cyclohexane) $\lambda_{\text{max}}$ ($\epsilon_{\text{max}}$) nm 228 (23,600), 256 (13,200), 311 (16,200), 328 (17,900), 342 (20,200), 385 (24,000), 518 (5,000), 636 (1,000); IR (KBr) 1670, 1475, 1360, 1252, 1222, 1203, 878, 753, 641 cm$^{-1}$; CI MS m/z, 437(MH$^+$); HRMS. Calc'd for C$_{32}$H$_{36}$O: 436.2766. Found: 436.2768. Anal. Calc'd for C$_{32}$H$_{36}$O: C, 88.02; H, 8.31. Found: C, 87.66; H, 8.60.

2,7-Di-$t$-butyl-4-nitro-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene (86), and 2,7-Di-$t$-butyl-4,5-di-nitro-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene (87)

A solution of the benzopyrene 21 (50 mg, 0.127 mmol) in CH$_2$Cl$_2$ (4 mL) was added to a previously stirred mixture of Ac$_2$O (0.5 mL) and Cu(NO$_3$)$_2$·2.5H$_2$O (44.2 mg, 0.190 mmol) under argon. The mixture was stirred at room temperature and was monitored by TLC until the starting material had disappeared in about 20 min. The
reaction mixture was washed with saturated NaHCO₃ solution and then H₂O and dried and evaporated. The residual was chromatographed over SiGel using first hexanes/CH₂Cl₂ (2:1) to elute the mononitrobenzopyrene to give 16 mg (28%) of 86, mp (sublimes) 161-162°C; second hexanes/CH₂Cl₂ (3:2) to elute the dinitrobenzopyrene to give 7 mg (11%) of 87, mp (dec) 195°C;

Mononitro 86 : ¹H NMR (360 MHz) δ 8.73-8.69 (m, 2H, H-9,12), 8.63 (d, J = 1.3 Hz, 1H, H-3), 8.34 (d, J = 1.3 Hz, 1H, H-1), 8.25 (d, J = 1.3 Hz, 1H, H-8), 7.74 (d, J = 0.92 Hz, 1H, H-5), 7.64-7.71 (m, 2H, H-10,11), 7.380-7.386 (m, 1H, H-6), 1.53 (s, 9H, C(CH₃)₃), 1.47 (s, 9H, C(CH₃)₃), -1.28 (s, 3H, CH₃), -1.35 (s, 3H, CH₃); ¹³C NMR (90.6 MHz) δ 155.13, 146.89, 139.46, 139.05, 137.82, 137.51, 134.97, 129.98, 128.82, 127.54, 126.69, 125.07, 124.49, 120.42, 118.47, 116.98, 115.58, 115.05, 38.81, 36.72, 35.48, 35.43, 30.44, 30.39, 18.18, 17.91; IR (KBr) 1490, 1310, 1287, 1259, 874, 753, 639 cm⁻¹; CI MS m/z, 440 (MH+); HRMS. Calc’d for C₃₀H₃₃NO₂: 439.2511. Found: 439.2508.

Dinitro 87 : ¹H NMR (360 MHz) δ 8.53-8.55 (m, 2H, H-9,12), 8.10 (d, J = 1.2 Hz, 2H, H-1,8), 7.98 (d, J = 1.3 Hz, 1H, H-3,6), 7.68-7.71 (m, 2H, H-10,11), 1.46 (s, 18H, C(CH₃)₃), -0.70 (s, 6H, CH₃); ¹³C NMR (90.6 MHz) δ 156.23, 139.11, 136.02, 129.43, 128.46, 125.01, 118.34, 113.00, 39.80, 36.57, 30.37, 29.90, 19.14;
UV (cyclohexane) λ_max (ε_max) nm 221 (31,100), 234 (29,700), 251 (21,200), 401 (13,300), 417 (11,500), 503 (2,200), 619 (300); CI MS m/z, 485 (MH+); HRMS. Calc’d for C₃₀H₃₂N₂O₄: 484.2362. Found: 484.2360.
4-Bromo-2,7-di-t-butyl-9-nitro-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (96) & 4-Bromo-2,7-di-t-butyl-5-nitro-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (97)

A solution of the bromide 69 (145 mg, 0.342 mmol) in CH₂Cl₂ (10 mL) was added to a homogenized mixture of Ac₂O (10 ml) and Cu(NO₃)₂·2.5H₂O (120 mg, 0.516 mmol) under argon. The mixture was stirred under room temperature for 1 hr and washed with saturated NaHCO₃ solution and then H₂O and dried and evaporated. The residual was chromatographed over SiGel using hexanes/CH₂Cl₂ (1:1) as eluant. The first green band was collected to give 14 mg (9%) of the first product 97, mp (sublimes) 151°C; The second brownish band was a mixture of the 2nd product 96 and the 4,10-cis-bromonitro-DHP 98. The total brownish mixture weighed 105 mg. These two compounds could not be separated by chromatography, however, their solubilities are slightly different. By carefully washing a few times with small amount of pentane, the residual, 96 turned out to be pure enough for characterization, mp 224-226°C;

4-bromo-5-nitro-dihydropyrene 97: ¹H NMR (360 MHz) δ 8.91 (d, J = 1.3 Hz, 1H, H-6), 8.57 (d, J = 1.2 Hz, 1H, H-8), 8.56 (d, J = 1.1 Hz, 1H, H-1), 8.529 (AB, J = 8.3 Hz, 1H, H-9 or 10), 8.517 (AB, 1H, H-9 or 10), 8.41 (d, J = 1.2 Hz, 1H, H-3), 1.69 (s, 9H, C(CH₃)₃), 1.63 (s, 9H, C(CH₃)₃), -3.68 (s, 3H, CH₃), -3.70 (s, 3H, CH₃); ¹³C NMR (90.6 MHz) δ 150.82, 149.68, 143.07, 138.21, 137.92, 135.79, 131.78, 126.82, 125.93,
125.17, 123.83, 123.09, 122.59, 114.99, 36.53, 36.45, 32.34, 31.68, 31.60, 30.02, 14.49, 14.47; IR (KBr) 1540, 1358, 1347, 1263, 1234, 668 cm⁻¹

4-bromo-9-nitro-dihydropyrene 96: ¹H NMR (360 MHz) δ 9.669-9.667 (m, 1H, H-10), 9.171-9.169 (m, 1H, H-8), 8.922-8.918 (m, 1H, H-1), 8.744-8.743 (m, 1H, H-3), 8.703-8.697 (m, 1H, H-6), 8.539-8.546 (m, 1H, H-5), 1.68 (s, 18H, C(CH₃)₃), -3.65 (s, 3H, CH₃), -3.68 (s, 3H, CH₃); ¹³C NMR (90.6 MHz) δ 154.25, 148.58, 140.02, 138.76, 134.67, 132.63, 130.45, 128.03, 125.84, 125.65, 121.90, 120.32, 119.12, 118.77, 36.98, 36.29, 32.03, 31.83, 31.72, 31.67, 15.37, 14.57; IR (KBr) 1592, 1527, 1304, 1243, 1143, 949, 857, 769, 673 cm⁻¹; CI MS m/z, 467 (MH⁺, ⁷⁹Br); HRMS. Calc'd for C₂₆H₃₀BrNO₂: 467.1460 (⁷⁹Br). Found: 467.1464.

4-Bromo-2,7-di-t-butyl-9-iodo-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (100)

I₂ (150 mg, 0.591 mmol) was added to a solution of Ag(collidine)₂PF₆ ⁷⁸ (292 mg, 0.590 mmol) in CH₂Cl₂ (50 mL). The mixture was stirred for 5 min to dissolve as much I₂ as possible and then the bromide 69 (100 mg, 0.236 mmol) was added to the turbid mixture, which was then stirred under argon at room temperature overnight. Aqueous NaHSO₃ (~10%, 20 mL) was added and the reaction mixture was stirred vigorously for 5 min and hexanes (50 mL) was then added. The whole mixture was filtered through celite to a separatory funnel. More Aqueous NaHSO₃ (~10%) was used to wash the organic...
phase and then followed by water. The organic phase was dried over MgSO₄ and solvent was evaporated. The green residual was chromatographed over SiGel using hexanes/CH₂Cl₂ (6:1) as eluent to give 118 mg crystalline solid, which contained 4-bromo-9-iodo-dihydropyrene 100 (67%), 4-bromo-10-iodo-dihydropyrene 104 (33%) by NMR spectral integration. The mixture was used directly in the next reaction. Some of the product was carefully washed with a small amount of pentane a few times. The solid which remained mainly 4-bromo-9-iodo-dihydropyrene 100 (over 92% by NMR), mp (sublimes) 162°C; ¹H NMR (360 MHz) δ 8.90 (s, 1H, H-5), 8.82 (d, J = 1.2 Hz, 1H, H-8), 8.65 (d, J = 1.2 Hz, 1H, H-3), 8.64 (s, 1H, H-10), 8.48 (br. s, 1H, H-1), 8.45 (br. s, 1H, H-6), 1.68 (s, 9H, C(CH₃)₃), 1.67 (s, 9H, C(CH₃)₃), -3.86 (s, 6H, CH₃); ¹³C NMR (90.6 MHz) δ 148.89, 147.97, 138.04, 137.70, 136.00, 133.50, 132.30, 126.97, 126.72, 122.15, 121.65, 121.38, 116.72, 93.13, 36.32, 36.27, 32.42, 32.23, 31.86, 14.37, 14.18; IR (KBr) 1586, 1478, 1461, 1378, 1362, 1351, 1231, 1178, 1118, 1087, 949, 891, 769, 673 cm⁻¹; Cl MS m/z, 549 (MH+, ⁷⁹Br); HRMS. Calc'd for C₂₆H₃₀BrI (⁷⁹Br): 548.0576. Found: 548.0580.

4-Bromo-2,7-di-tert-butyl-9-phenylethynyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (101)

Phenylacetylene (61 mg, 0.598 mmol) was added to a solution of a mixture of the bromoiodopyrenes (100 + 104) (300 mg, 0.547 mmol) in THF (30 mL) and HNEt₂ (10
mL). Then catalyst Pd(PPh$_3$)$_2$Cl$_2$ (38 mg, 0.0542 mmol) and CuI (15 mg, 0.0789 mmol) were added. The reaction mixture was stirred overnight under argon in room temperature. The mixture was filtered through celite and the solvent was evaporated. The brownish residual was chromatographed over SiGel using firstly hexanes to elute starting materials, and secondly hexanes/CH$_2$Cl$_2$ (10:1) to elute the product, which was a mixture (241 mg, yield 84%) of bromophenylethynylpyrene (4,9- and 4,10-isomers). This mixture was used directly in the next step. A small portion of relatively pure 4-bromo-9-iodopyrene 100 (91%) was used to make pure 4-bromo-9-phenylethynylpyrene 101 for characterization, mp 158-161°C; $^1$H NMR (360 MHz) δ 9.11 (d, J = 1.3 Hz, 1H, H-3), 8.79 (d, J = 1.2 Hz, 1H, H-1), 8.64 (s, 1H, H-5 or 10), 8.64 (s, 1H, H-5 or 10), 8.52 (d, J = 0.8 Hz, 1H, H-6), 8.48 (d, J = 0.9 Hz, 1H, H-8), 7.77-7.73 (m, 2H, H-2',6'), 7.47-7.38 (m, 3H, H-3',4',5'), 1.71 (s, 9H, C(CH$_3$)$_3$), 1.69 (s, 9H, C(CH$_3$)$_3$), -3.75 (s, 3H, CH$_3$), -3.77 (s, 3H, CH$_3$); $^{13}$C NMR (90.6 MHz) δ 148.38, 147.48, 147.48, 138.40, 137.86, 136.22, 132.50, 132.21, 131.55, 128.54, 128.43, 128.13, 126.71, 126.35, 124.03, 122.47, 122.19, 121.16, 120.37, 116.95, 115.12, 95.25, 89.89, 86.31, 36.25, 32.04, 31.87, 30.51, 14.95, 14.56; IR (KBr) 2196, 1594, 1485, 1441, 1378, 1361, 1238, 1118, 892, 754, 687, 670 cm$^{-1}$; Cl MS m/z 523 (MH+, $^{79}$Br); HRMS. Calc'd for C$_{34}$H$_{35}$Br (M+, $^{79}$Br): 522.1922. Found: 522.1920.
2,7-Di-\(t\)-butyl-9,12-epoxy-4-phenylethynyl-trans-12c,12d-dimethyl-9,12,12c,12d-
tetrahydrobenzo[e]pyrene (102)

Distilled furan (8 mL) was added to a solution of the bromophenylethynylpyrene
101 (100 mg, 0.192 mmol) in dry THF (10 mL) under argon, and then NaN\(\text{H}_2\) (600 mg,
15 mmol) and KO\(^{\text{t\-Bu}}\) (5 mg) were added. The mixture was stirred overnight under argon.
Methanol was added dropwise to quench excess base. The reaction mixture was extracted
with water, was dried and evaporated. The brownish residual was chromatographed over
deactivated SiGel using first hexane/benzene (6:1) to elute the reduced starting material
phenylethynylpyrene and secondly hexane/EtOAc (6:1) to elute 71 mg (73%) of the
product 102 as a mixture of two isomers, mp 214-215°C; \(^1\)H NMR (360 MHz) \(\delta\) 8.79-
8.78 (m, 2H, H-3), 8.46 (s, 2H, H-5), 8.22-8.21 (m, 2H, H-6), 8.14-8.11 (m, 4H, H-1, 8),
7.73-7.70 (m, 4H, H-2',6'), 7.46-7.35 (m, 6H, H-3', 4',5'), 7.19-7.16 (m, 2H, H-10 or
11), 7.08-7.04 (m, 2H, H-10 or11), 6.56-6.51 (m, 4H, H-9,12), 1.656 & 1.653 (s, 9H
each, C(CH\(_3\))\(_3\)), 1.608 & 1.604 (s, 9H each, C(CH\(_3\))\(_3\)), -3.158 & -3.162 (s, 3H
each, CH\(_3\)), -3.416 & -3.424 (s, 3H each, CH\(_3\)); \(^13\)C NMR (90.6 MHz) \(\delta\) 146.33, 146.02,
145.73, 140.41, 140.30, 140.15, 140.03, 136.89, 136.57, 136.46, 136.35, 136.30, 136.27,
136.10, 135.86, 131.57, 128.94, 128.57, 128.51, 128.40, 128.36, 128.07, 127.94, 127.64,
124.05, 122.60, 122.55, 120.88, 120.80, 115.99, 115.89, 115.58, 115.31, 114.98, 94.52,
94.49, 89.85, 89.79, 81.22, 80.87, 80.82, 36.04, 35.78, 33.18, 32.65, 32.30, 31.75, 31.63,
31.52, 17.04, 16.54, 14.59, 14.11; IR (KBr) 2191, 1618, 1598, 1488, 1362, 1347, 1258,
Distilled furan (3 mL) was added to a solution of the bromophenylethynylpyrene 101 (101 mg, 0.193 mmol) in dry THF (10 mL) under argon, and then NaN₃ (800 mg, 20 mmol) and KO'Bu (5 mg) were added. The mixture was stirred under argon for two hours. The solution was settled, carefully decanted, and filtered through celite. More THF was used to rinse off all the product. The filtrate was dried and column chromatographed over deactivated SiGel using hexanes to elute first the yellowish green band, then the following pink band was collected and dried and gave the product 103 (47.2 mg) in 50% yield. The column was further washed with hexanes/ EtOAc (6:1) to elute 9% of the adduct 102 (9.2 mg); The dark pink solid of 103 has a mp 152-154°C; 

$^1$H NMR (360 MHz) δ 8.74-8.70 (m, 2H, H-9,12), 8.28 (d, J = 1.3 Hz, 1H, H-1), 8.23 (d, J = 1.2 Hz, 1H, H-8), 8.03 (d, J = 1.3 Hz, 1H, H-3), 7.63-7.60 (m, 4H, H-10,11,2’,6’), 7.40-7.36 (m, 2H, H-3’,5’), 7.34-7.31 (m, 2H, H-6,4’), 7.25 (d, J = 0.9 Hz, 1H, H-5), 1.54 & 1.48 (s, 9H each, C(CH₃)₃), -1.40 & -1.42 (s, 3H each, CH₃); $^{13}$C NMR (90.6 MHz) δ 147.30, 145.49, 141.89, 138.01, 136.89, 135.22, 131.59, 129.69, 129.47, 128.64,
125

128.00, 126.40, 126.24, 124.83, 124.41, 122.95, 119.58, 118.50, 117.56, 117.41, 113.25, 94.61, 89.94, 36.78, 36.06, 35.63, 35.50, 30.80, 30.77, 18.17, 18.08; UV (cyclohexane) \( \lambda_{\text{max}} \) nm 236 (18,300), 264 (14,600), 312 (18,300), 325 (19,600), 342 (21,500), 377 (23,400), 395 (31,300), 509 (5,000), 624 (300); IR (KBr) 2189, 1593, 1473, 1367, 1255, 1117, 872, 753, 688 cm\(^{-1}\); CI MS \( m/z \), 495 (MH\(^+\)); HRMS. Calc’d for C\(_{38}\)H\(_{38}\): 494.2974. Found: 494.2980.

2,7-Di-\( t \)-butyl-4-phenyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene (105)

Fe\(_2\)(CO)\(_9\) (52.9 mg, 0.145 mmol) was added to a solution of the phenylbenzopyrene adduct 109 (47.1 mg, 0.0969 mmol) in benzene (20 mL). The mixture was refluxed for 1 h in the dark and allowed cool to room temperature. The mixture was then filtered through SiGel in benzene and the solvent was evaporated. The residual was chromatographed over SiGel using hexanes/benzene (6:1) as eluant to give 37 mg (81%) of the product 105 as a bright reddish solid, mp 180-181°C; \(^1\)H NMR (360 MHz) \( \delta \) 8.80-8.74 (m, 2H, H-9,12), 8.31-8.29 (m, 2H, H-1,8), 7.64-7.59 (m, 2H, H-10,11), 7.58-7.55 (m, 3H, H-3,2',6'), 7.53-7.45 (m, 2H, H-3',5'), 7.39-7.34 (m, 2H, H-6,4'), 7.225 (d, J = 0.8 Hz, 1H, H-5), 1.49 (s, 9H, C(CH\(_3\))\(_3\)), 1.39 (s, 9H, C(CH\(_3\))\(_3\)), -1.453 (s, 3H, CH\(_3\)), -1.456 (s, 3H, CH\(_3\)); \(^1^3\)C NMR (90.6 MHz) \( \delta \) 144.84, 144.71, 141.89, 137.81, 134.90, 134.81, 133.54, 132.93, 129.95, 129.48, 129.17, 128.12, 126.62, 125.76, 125.68, 124.59,
124.44, 124.40, 119.69, 117.62, 117.03, 117.00, 35.77, 35.61, 35.40, 35.24, 30.64, 17.78, 17.60; IR (KBr) 1363, 1256, 891, 877, 871, 762, 752, 704, 694 cm⁻¹; UV (cyclohexane) λ_max (ε_max) nm 236 (18,900), 269 (14,500), 312 (23,100), 325 (24,900), 342 (27,700), 377 (31,400), 395 (42,700), 509 (6,900), 610 (500); CI MS m/z, 471(MH⁺); HRMS. Calc’d for C₃₆H₃₈: 470.2974. Found: 470.2974.

2,7-Di-t-butyl-4-phenyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (106)

An aqueous solution of Na₂CO₃ (2M, 20 mL) was added to a mixture of PhB(OH)₂ (60 mg, 0.492 mmol) and the bromide 69 (104 mg, 0.246 mmol) in THF (30 mL), and then Pd(PPh₃)₂Cl₂ (6 mg) was added. The mixture was refluxed for 2 hr under argon and then cooled to room temperature. Hexanes (30 mL) were added to the mixture, which then was transferred to a separatory funnel. The organic phase was washed with water, dried and evaporated. The residual was chromatographed on SiGel using firstly hexanes as eluant. A very small amount of the green parent 20 eluted first. Secondly, hexanes/benzene (6:1) eluted the second bright green band to give 90 mg (87%) of the product 106, mp 162-163 °C; ¹H NMR (360 MHz) δ 8.65 (d, J = 1.1 Hz, 1H, H-3), 8.52-8.53 (m, 3H, H-1,6,8), 8.48 (s, 1H, H-5), 8.440 & 8.438 (AB, J = 7.9 Hz, 2H, H-9,10), 7.85-7.81 (m, 2H, H-2',6'), 7.61-7.57 (m, 2H, H-3',5'), 7.50-7.46 (m, 1H, H-4'), 1.68 (s, 9H, C(CH₃)₃), 1.59 (s, 9H, C(CH₃)₃), -3.84 (s, 3H, CH₃), -3.86 (s, 3H, CH₃);
$^{13}$C NMR (90.6 MHz) $\delta$ 145.86, 145.59, 142.81, 137.00, 136.72, 136.30, 134.98, 133.29, 131.00, 128.10, 126.74, 124.88, 122.84, 122.51, 120.84, 120.54, 120.07, 36.06, 35.93, 31.93, 31.83, 30.05, 29.73, 14.79, 14.38; IR (KBr) 1597, 1477, 1461, 1446, 1382, 1359, 1344, 1231, 884, 700, 666 cm$^{-1}$; CI MS m/z, 421(MH$^+$); Anal. Calc’d for C$_{32}$H$_{36}$: C, 91.37; H, 8.63. Found: C, 91.63; H, 8.81.

4-Bromo-2,7-di-t-butyl-9-phenyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (107)

NBS (38 mg, 0.215 mmol) in dry DMF (10 mL) was added dropwise to a stirred solution of the phenylpyrene 106 (90 mg, 0.214 mmol) in dry CH$_2$Cl$_2$ (50 mL) cooled in a dry ice/acetone bath under argon with stirring. After the addition was complete, a small amount of CH$_2$Cl$_2$ (2 x 1 mL) was used to rinse the addition funnel into the reaction mixture. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and continued stirring for 1 hr. Hexanes (50 mL) was added to the mixture and the organic phase was extracted with water (6 x 100 mL) and dried. The green residual was chromatographed over SiGel using hexanes/CH$_2$Cl$_2$ (6:1) as eluant. $^1$H NMR spectroscopy showed that product contained 3% starting material and the 4-bromo-10-phenylpyrene 12%. The total residual weighed 98 mg (92%) after chromatography. Some of the mixture was carefully washed with small amount of
pentane a few times. The residual dark green solid, 107, was about 95% pure judging by

\(^1\)H NMR, mp (sublimes) 162°C; \(^1\)H NMR (360 MHz) \(\delta\) 8.77 (br. s, 1H, H-3), 8.62 (br.
s, 1H, H-8), 8.60 (s, 1H, H-5), 8.52 (d, \(J \approx 1.0\) Hz, 1H, H-1), 8.47 (s, 1H, H-10), 8.44 (d, \(J \approx 1.0\) Hz, 1H, H-6), 7.80-7.78 (m, 2H, H-2',6'), 7.61-7.56 (m, 2H, H-3',5'), 7.51-7.46 (m,
1H, H-4'), 1.69 (s, 9H, C(CH\(_3\))\(_3\)), 1.56 (s, 9H, C(CH\(_3\))\(_3\)), -3.72 (s, 3H, CH\(_3\)), -3.75 (s, 3H,
CH\(_3\)); \(^13\)C NMR (90.6 MHz) \(\delta\) 147.31, 147.00, 142.24, 137.38, 136.70, 135.82,
134.12, 131.70, 130.90, 128.20, 127.02, 126.11, 125.69, 121.96, 120.89, 120.86, 120.53,
115.43, 36.24, 36.11, 32.36, 31.88, 31.69, 30.26, 14.76, 14.36; IR (KBr) 1598, 1590,
1478, 1462, 1377, 1362, 1348, 1238, 953, 897, 761, 703, 666 cm\(^{-1}\); CI MS \(m/z\), 499
(MH\(^+\), \(^79\)Br); HRMS. Calc'd for C\(_{32}\)H\(_{35}\)Br \((^{79}\)Br): 498.1922. Found: 498.1919.

2,7-Di-\(t\)-butyl-9,12-epoxy-4-phenyl-\(trans\)-dimethyl-9,12c,12d-tetrahydro-
benzo[e]pyrene (109)

NaNH\(_2\) (400 mg, 10 mmol) and KO\(^1\)Bu (5 mg) were added to a solution of the
bromophenylpyrene 107 (100 mg, 0.201 mmol) in dried furan (7 mL) and THF (15 mL).
The mixture was stirred at room temperature under argon for 5 hr. Methanol was added
dropwise to quench the excess base. Hexanes (15 mL) were added and the mixture was
transferred to a separatory funnel and the organic phase was extracted with water and
dried and solvent was evaporated. The residual was chromatographed over deactivated
SiGel using hexanes/EtOAc (6:1) as eluant. The first portion was small amount of reduced phenylpyrene 106. The second green band was collected to give 78 mg (80%) of the product 109 as equal mixture of two isomers, mp 212-214°C; $^1$H NMR (360 MHz) δ 8.16 & 8.14 (s, 1H each, H-5), 8.10-8.07 (m, 4H, H-3,6), 8.03-8.01 (m, 4H, H-1,8), 7.74-7.71 (m, 4H, H-2',6'), 7.57-7.53 (m, 4H, H-3',5'), 7.48-7.43 (m, 2H, H-4'), 7.18-7.15 (m, 2H, H-10 or 11), 7.05-7.03 (m, 2H, H-10 or 11), 6.55-6.50 (m, 4H, H-9,12), 1.602 & 1.599 (s, 9H each, C(CH$_3$)$_3$), 1.502 & 1.496 (s, 9H each, C(CH$_3$)$_3$), -2.88 & -2.90 (s, 3H each, CH$_3$), -3.13 & -3.17 (s, 3H each, CH$_3$); $^{13}$C NMR (90.6 MHz) δ 145.75, 145.46, 145.38, 145.04, 142.30, 142.24, 139.96, 139.65, 137.01, 136.83, 136.44, 135.28, 135.20, 135.02, 134.87, 134.76, 130.72, 128.16, 128.04, 127.77, 127.63, 127.35, 126.96, 125.97, 121.67, 121.62, 121.44, 121.33, 114.69, 114.50, 114.42, 114.25, 81.08, 81.06, 80.76, 80.65, 35.83, 35.70, 33.61, 33.39, 32.69, 32.50, 31.40, 31.24, 17.21, 16.69, 14.69, 14.27; IR (KBr) 1618, 1600, 1476, 1461, 1443, 1361, 1344, 1258, 1033, 876, 858, 844, 765, 700, 676, 649 cm$^{-1}$; El MS m/z 486 (M+); Anal. Calc’d for C$_{36}$H$_{38}$O: C, 88.84; H, 7.87. Found: C, 88.54; H, 8.20.

Bis-isopyranofuran adduct (114)

The isofuran 47$^{31}$ (133 mg, 0.346 mmol) and adduct 70$^{31}$ (116 mg, 0.283 mmol) were held under vacuum for 2 hr in an oven baked two neck round bottom flask. Dry toluene (8 mL) was then added to the flask under argon. The mixture was refluxed
overnight and then cooled in an ice bath. The solvent was carefully decanted and the green solid was washed with hexanes (4 X 4 mL) and air dried to give 168 mg (75%) of the product 114. Crystallization from toluene gave fine green needles as a mixture of two isomers, mp (dec) 219-224 °C; ¹H NMR (360 MHz) δ 8.51, 8.48, 8.46, 8.44 (d, J = 1.2 Hz, 2H each, H-1,8,11,18), 8.39-8.37 (m, 8H total, H-3,6,13,16), 8.31-8.30 (m, 8H total, H-4,5,14,15), 6.667, 6.651, 6.640, 6.633 (s, 8H total, H-9,10,19,20), 2.503 (s, 2H, H-20a,20b, isomer I), 2.505, 2.413 (d, J = 6.5 Hz, 1H each, H-20a,20b, isomer II), 1.710, 1.659 (s, 18H each, C(CH₃)₃, isomer I), 1.681, 1.679 (s, 18H each, C(CH₃)₃, isomer II), -3.861, -4.29 (s, 6H each, CH₃, isomer I), -3.866, -4.34 (s, 6H each, CH₃, isomer II); ¹³C NMR (90.6 MHz) δ 145.68, 145.61, 145.54, 138.56, 138.05, 138.01, 136.64, 136.59, 136.49, 136.40, 126.14, 125.95, 125.53, 125.47, 124.00, 123.94, 123.76, 123.71, 121.39, 121.28, 121.09, 121.03, 116.27, 116.22, 115.49, 115.43, 81.53, 81.49, 81.38, 81.34, 54.14, 53.92, 53.87, 36.10, 36.05, 31.95, 31.80, 29.32, 29.24, 15.04, 15.00, 14.19, 13.87; IR (KBr) 1603, 1461, 1345, 1262, 1225, 1007, 922, 886, 867 cm⁻¹; LSIMS m/z 794.4 (M+); HRMS. Calc’d for C₅₈H₆₆O₂ (M+): 794.5063. Found: 794.5100.

2,7,12,17-Tetra-r-butyl-trans-19c,19d,20c,20d-tetramethyl-19c,19d,20c,20d-tetrahydrotetrabenzon[de,yz,lm,qr]hexaphene (116)

P₂S₅ (50.0 mg, 0.225 mmol) was added to the solution of the adduct 114 (50.0 mg, 0.063 mmol) in CS₂ (20 mL) under argon. The mixture was stirred for 2 hr and then was
filtered through celite. The solvent was removed and the solid was chromatographed over SiGel using firstly hexanes to elute the red band, and secondly hexanes/benzene (10:1) to elute the green band which was collected to give 15 mg (31%) of the product 116 as two isomers in equal amount. The product was washed by hexanes (4 x 4 mL) and then the ratio of the two isomers was about 2:3, which allowed assignment of the $^1$HNMR for the two isomers. This sample showed mp (dec) 173-178 °C; $^1$H NMR, isomer I, (360 MHz) $\delta$ 9.196 (s, 4H, H-9,10,19,20), 8.05 (d, J = 1.2 Hz, 4H, H-1,8,11,18), 6.843 (d, J = 1.0 Hz, 4H, H-3,6,13,16), 6.594 (s, 4H, H-4,5,14,15), 1.474 (s, 36H, C(CH$_3$)$_3$), -0.325 (s, 12H, CH$_3$). Isomer II, $\delta$ 9.190 (s, 4H, H-9,10,19,20), 8.03 (d, J = 1.2 Hz, 4H, H-1,8,11,18), 6.835 (d, J = 1.0 Hz, 4H, H-3,6,13,16), 6.587 (s, 4H, H-4,5,14,15), 1.470 (s, 36H, C(CH$_3$)$_3$), -0.310 (s, 12H, CH$_3$). $^{13}$C NMR (90.6 MHz) $\delta$ 144.72, 139.48, 136.11, 129.34, 129.29, 128.79, 122.25, 121.11, 119.92, 117.75, 117.66, 38.17, 35.16, 31.52, 30.32, 30.25, 25.61, 19.69, 19.62; UV (cyclohexane) $\lambda_{\text{max}}$ ($\epsilon_{\text{max}}$) nm 235 (15,100), 260 (14,600), 331 (13,100), 346 (18,300), 417 (27,100), 441 (43,600), 624 (2,100); IR (KBr) 1622, 1474, 1431, 1359, 1228, 1155, 898, 870 cm$^{-1}$; LSIMS $m/z$ 760.6 (M$^+$); HRMS. Calc’d for C$_{58}$H$_{64}$ (MH$^+$): 761.5086. Found: 761.5064.
2,7-Di-\(\tau\)-butyl-9,18-epoxy-18c,18d-dimethyl-9,18,18c,18d-tetrahydrotetrabenzo-[ed,i,k,pq]naphthacene (118)

NaNH\(_2\) (570 mg, 14.6 mmol) and KO\(^{\text{tBu}}\) (2 mg) were added to a stirred solution of the isofuran 47\(^{31}\) (84.3 mg, 0.220 mmol) and 9-bromophenanthrene 117\(^{84}\) (281.8 mg, 1.097 mmol) in dried THF (25 mL) under argon. The mixture was stirred overnight and then methanol (5 mL) and hexanes (25 mL) were added. The organic phase was washed, dried and evaporated. The solid was chromatographed over deactivated SiGel using benzene/hexanes (1:1) as eluant. The green band was collected and gave 104 mg (85\%) of the adduct 118, which on recrystallization from toluene gave dark green crystals, mp 221-222 °C; \(^1\)H NMR (360 MHz) \(\delta\) 8.59 (d, J = 8.3 Hz, 2H, H-13,14), 8.43, 8.40 (d, J \sim 1.2 Hz, 1H each, H-1 or 8), 8.41, 8.27 (dd, J = 8.1 Hz, 1.1 Hz, 1H each, H-10 or 17), 8.13, 8.10 (d, J = 1.2 Hz, 1H each, H-3 or 6), 8.07 (s, 2H, H-4,5), 7.63, 7.61 (s, 1H each, H-9 or 18), 7.72-7.64, 7.59-7.52 (m, 2H each, H-11,16 or 12,15), 1.66, 1.63 (s, 9H each, C(CH\(_3\))\(_3\)), -3.14, -4.12 (s, 3H each, CH\(_3\)); \(^{13}\)C NMR (90.6 MHz) \(\delta\) 145.52, 145.30, 145.01, 144.66, 137.28, 136.22, 136.18, 135.76, 129.61, 129.47, 127.81, 127.22, 126.78, 126.75, 126.67, 126.62, 126.04, 125.97, 124.47, 124.36, 124.23, 124.03, 123.57, 121.23, 115.47, 114.70, 81.72, 81.14, 35.74, 35.69, 34.21, 33.32, 31.54, 31.51, 16.50, 14.25; IR (KBr) 1616, 1448, 1363, 1343, 1260, 883, 865, 777, 755, 745, 721, 716, 671, 632 cm\(^{-1}\); CI MS m/z, 561(MH\(^+\)); Anal. Calc’d for C\(_{42}\)H\(_{40}\)O: C, 89.96; H, 7.19. Found: C, 89.66; H, 7.34.
2,7-Di-t-butyl-trans-18c,18d-dimethyl-18c,18d-dihydrotetrabenzo[cd,i,k,pq]-naphthacene (119)

A mixture of the epoxide 118 (88 mg, 0.157 mmol) and Fe₂(CO)₉ (88 mg, 0.242 mmol) in benzene (30 mL), was refluxed under argon in the dark for 5 hr. After cooling to room temperature, the mixture was filtered through a short column (5 cm) of deactivated SiGel, using benzene as eluant. The solvent was then removed and the dark purple solid product was carefully washed with pentane until the initial brownish color disappeared and gave 73 mg (86%) of the product 119. Slow evaporation from hexanes/CH₂Cl₂ yield dark purple crystals, mp (dec) 188-193 °C; ¹H NMR (360 MHz) δ 9.92 (s, 2H, H-9,18), 8.92 (dd, J = 8.2 Hz, 1.3 Hz, 2H, H-10,17), 8.67 (dd, J = 8.2 Hz, 1.2 Hz, 2H, H-13,14), 8.40 (d, J = 1.3 Hz, 2H, H-1,8), 7.78-7.74 (m, 2H, H-11,16), 7.71-7.67 (m, 2H, H-12,15), 7.23 (d, J = 1.2 Hz, 2H, H-3,6), 6.99 (s, 2H, H-4,5), 1.55 (s, 18H, C(CH₃)₃), -1.07 (s, 6H, CH₃); ¹³C NMR (90.6 MHz) δ 144.51, 138.81, 135.19, 130.15, 130.06, 128.59, 127.54, 127.46, 127.37, 123.53, 123.33, 121.26, 120.15, 118.57, 117.43, 36.47, 35.39, 30.63, 18.31; UV (CHCl₃) λ_max (ε_max) nm 284 (43,200), 337 (38,600), 374 (22,200), 392 (46,200), 412 (72,400), 529 (5,700), 644 (600); IR (KBr) 1627, 1605, 1490, 1434, 1360, 1227, 886, 872, 754, 719, 673 cm⁻¹; CI MS m/z, 545(MH⁺); Anal. Calc’d for C₄₂H₄₀: C, 92.60; H, 7.40. Found: C, 92.58; H, 7.64.
Phenyl-tris-pyrene (120)

The impure phenyltrisDHP precursor 121 (15 mg, 0.013 mmol) and Fe₂(CO)₉ (10 mg, 0.027 mmol) were refluxed in benzene (15 ml) under argon for 1 h. The mixture was slowly cooled to room temperature and the solvent was evaporated. The residual was chromatographed over alumina using hexanes/benzene (6:1) and gave 4 mg (27%) of the product 120 as a red solid, mp (dec) 168-172°C; ¹H NMR (360 MHz), similar groups of peaks were observed as for trisDHP 72. group I: δ 9.01 (br. s, 4H, H-9,13,22,26), 8.40-8.37 (m, 4H, H-1,8,14,21), 7.74-7.61 (m, 2H, H-2',6'), 7.54-7.49 (m, 2H, H-3',5'), 7.43-7.39 (m, 5H, H-3,6,16,19,4'), 7.19-7.18 (m, 7H, H-5,17,18,10,12,23,25), 1.57(s), 1.54(s), 1.47(s), 1.44(s), 1.37-1.36 (108H total, C(CH₃)₃), 1.30 (br. s, 6H, CH₃ from cyclophane), -1.23, -1.36 (br. s, 12H total, CH₃ from DHPs).

¹H NMR (360 MHz), group II: δ 9.16-9.15 (m, 4H, H-9,13,22,26), 8.59-8.57 (m, 4H, H-1,8,14,21), 7.74-7.61 (m, 2H, H-2',6'), 7.54-7.49 (m, 6H, H-3,6,16,19,3',5'), 7.43-7.39 (m, 1H, H-4'), 7.32 (br. s, 3H, H-5,17,18), 7.19-7.18 (m, 4H, H-10,12,23,25), 1.57(s), 1.54(s), 1.47(s), 1.44(s), 1.370-1.363 (108H total, C(CH₃)₃), 1.30 (br. s, 6H, CH₃ from cyclophane), -1.49, -1.62 (br. s, 12H total, CH₃ from DHPs). LSIMS m/z, 1153.6 (MH+); HRMS. Calc’d for C₈₈H₉₆ (MH+): 1153.7590. Found: 1153.7576.
Phenyltris-pyrene precursor (121)

NaNH₂ (400 mg, 10 mmol) and KO'Bu (5 mg) were added to a solution of the furan 79 (50 mg, 0.065 mmol) and the phenylbromide 107 (100 mg, 0.201 mmol) in dry THF (15 mL). The reaction mixture was stirred under argon for 2.5 hr and was filtered through celite. The solvent was evaporated and the residual was chromatographed on alumina over a short column (5 cm) using first hexanes/benzene (1:1) to elute the reduced starting material and second using hexanes/EtOAc (6:1) to elute 18 mg (23%) of the product 121 which was a mixture of isomers and some impurities which could not be separated from the product. The product 121 was not stable in CDCl₃. A crude ¹H NMR (300 MHz) spectrum was quickly taken in C₆D₆. The three groups of internal methyl proton chemical shifts were: -2.67 to -3.00 & -4.14 to -4.32 & -4.97 to -5.03. The material was used directly in the next step.

5.3 Photochromic and Thermochromic Kinetic Studies

For first order reactions: \[ \ln(c_t) = kt + \text{constant} \]

From Beer's law: \[ c = \frac{A}{ed} \]

- \( c \) ----- concentration (mol L⁻¹)
- \( A \) ----- absorbance
- \( d \) ----- path length (cm)
Thus: \( \ln(A_0/8d) = kt + \text{constant} \)

At a particular wavelength, \( \varepsilon \) is constant and \( d \) is 1 cm. The above equation can then be re-written as: \( \ln(A_t) = kt + \text{Constant'} \).

For photo openings, the measured absorption is due to the reactant, and thus the above equation was used directly for the calculation. In the following graphs: \( x = A_t \).

For photo closings and thermal return reactions, the measured absorption is from the product. Thus, the concentration of reactant \( c_r = c_0 - c_t \); \( c_0 \) is the initial reactant concentration, which can be measured in terms of absorbance \( (A_0) \) before the sample is bleached. The above equation becomes:

\( \ln(A_0 - A_t) = kt + \text{constant'} \). In the following graphs: \( x = A_0 - A_t \).

### 5.4 Experimental Error Determination

Triphenyleno-DHP 119 has a medium thermal return rate, and a moderate photo opening rate as well, thus we thought 119 could serve as a model compound for experimental error determination.

#### 5.4.1 Thermal Return Reaction of CPD to DHP

The thermal return reaction of triphenyleno-CPD to DHP in toluene was monitored by UV-Vis spectroscopy. Three independent runs, in which each run included three temperatures, 46°C, 60°C and 70°C, were performed. The experiment results were monitored at two different wavelengths, and the thermal return rates were calculated according to first order kinetics.
Thermal return rates of triphenyleno-CPD to DHP
1st run measured at 411 nm

\[ y = -0.28811 - 0.0033055x \quad R = 0.99996 \]
\[ y = -0.2351 - 0.014406x \quad R = 0.99993 \]
\[ y = -0.21234 - 0.040299x \quad R = 0.99988 \]

Thermal return rates of triphenyleno-CPD to DHP
1st run measured at 391 nm

\[ y = -0.75579 - 0.0032774x \quad R = 0.99996 \]
\[ y = -0.69773 - 0.014268x \quad R = 0.99994 \]
\[ y = -0.67427 - 0.040054x \quad R = 0.99989 \]
Thermal return rates of triphenyleno-CPD to DHP
2nd run measured at 411 nm

\[ y = -0.56041 - 0.0031429x \quad R= 0.99997 \]
\[ y = -0.20835 - 0.014947\% \quad R= 0.99997 \]
\[ y = -0.34683 - 0.042306\% \quad R= 0.99988 \]

Thermal return rates of triphenyleno-CPD to DHP
2nd run measured at 391 nm

\[ y = -1.0267 - 0.0031145x \quad R= 0.99997 \]
\[ y = -0.67424 - 0.015031\% \quad R= 0.99997 \]
\[ y = -0.81251 - 0.041978\% \quad R= 0.99989 \]
Thermal return rates of triphenyleno-CPD to DHP
3rd run measured at 411 nm

\[ y = -0.25912 - 0.0030706x \quad R = 0.99999 \]

\[ y = -0.2372 - 0.014872x \quad R = 0.99999 \]

\[ y = -0.22468 - 0.042505x \quad R = 0.99988 \]

Thermal return rates of triphenyleno-CPD to DHP
3rd run measured at 391 nm

\[ y = -0.70704 - 0.0030688x \quad R = 0.99999 \]

\[ y = -0.67781 - 0.014881x \quad R = 0.99997 \]

\[ y = -0.66049 - 0.042894x \quad R = 0.99991 \]
Rates measured at 411 nm wavelength

<table>
<thead>
<tr>
<th>Temperature</th>
<th>319K</th>
<th>333K</th>
<th>343K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>0.0033055</td>
<td>0.014406</td>
<td>0.040299</td>
</tr>
<tr>
<td>2nd Run</td>
<td>0.0031429</td>
<td>0.014947</td>
<td>0.042306</td>
</tr>
<tr>
<td>3rd Run</td>
<td>0.0030706</td>
<td>0.014872</td>
<td>0.042506</td>
</tr>
<tr>
<td>sd</td>
<td>0.000120308</td>
<td>0.000293105</td>
<td>0.001220252</td>
</tr>
<tr>
<td>sd%</td>
<td>3.6</td>
<td>2.0</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Rates measured at 391 nm wavelength

<table>
<thead>
<tr>
<th>Temperature</th>
<th>319K</th>
<th>333K</th>
<th>343K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>0.0032774</td>
<td>0.014268</td>
<td>0.040054</td>
</tr>
<tr>
<td>2nd Run</td>
<td>0.0031145</td>
<td>0.015031</td>
<td>0.041978</td>
</tr>
<tr>
<td>3rd Run</td>
<td>0.0030688</td>
<td>0.014881</td>
<td>0.042894</td>
</tr>
<tr>
<td>sd</td>
<td>0.00010965</td>
<td>0.000404235</td>
<td>0.001449508</td>
</tr>
<tr>
<td>sd%</td>
<td>3.5</td>
<td>2.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The tables above summarized the rate constants and calculated the relative standard deviations. The maximum value of which is 3.8%, and was used in the calculation of deviations of rate constants in the text.

The $E_{act}$, $H^s$ and $S^s$ were calculated with each run at two wavelengths as follows.

Plots of $E_{act}$ for the thermal return reaction of triphenyleno-CPD to DHP

Calculations of $E_{act}$ and relative standard deviations

<table>
<thead>
<tr>
<th>Temperature</th>
<th>319K</th>
<th>333K</th>
<th>343K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>0.0033055</td>
<td>0.014406</td>
<td>0.040299</td>
</tr>
<tr>
<td>2nd Run</td>
<td>0.0031429</td>
<td>0.014947</td>
<td>0.042306</td>
</tr>
<tr>
<td>3rd Run</td>
<td>0.0030706</td>
<td>0.014872</td>
<td>0.042506</td>
</tr>
<tr>
<td>sd</td>
<td>0.000120308</td>
<td>0.000293105</td>
<td>0.001220252</td>
</tr>
<tr>
<td>sd%</td>
<td>3.6</td>
<td>2.0</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The maximum value, 2.8%, was used to calculate the deviations for $E_{act}$ in the text.
Plots of $H^e$ and $S^e$ for the thermal return reaction of triphenyleno-CPD to DHP

Calculations of $H^e$ and $S^e$, and relative standard deviations

<table>
<thead>
<tr>
<th>Slope</th>
<th>$H^e$</th>
<th>Intercept</th>
<th>$S^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>11052</td>
<td>21.97</td>
<td>23.161</td>
</tr>
<tr>
<td>2nd Run</td>
<td>11521</td>
<td>22.90</td>
<td>24.586</td>
</tr>
<tr>
<td>3rd Run</td>
<td>11649</td>
<td>23.16</td>
<td>24.966</td>
</tr>
</tbody>
</table>

sd 0.6249 0.6652

sd% 2.8 37.7

Measured at 391 nm wavelength

<table>
<thead>
<tr>
<th>Slope</th>
<th>$H^e$</th>
<th>Intercept</th>
<th>$S^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>11062</td>
<td>21.99</td>
<td>23.182</td>
</tr>
<tr>
<td>2nd Run</td>
<td>11535</td>
<td>22.93</td>
<td>24.626</td>
</tr>
<tr>
<td>3rd Run</td>
<td>11690</td>
<td>23.24</td>
<td>25.094</td>
</tr>
</tbody>
</table>

sd 0.6504 0.9967 0.8140

sd% 2.9 4.1 43.7

Thus, 2.9% and 44% were used to calculate the deviations of $H^e$ and $S^e$ in the text, respectively.

5.4.2 Photo Opening Reaction of DHP to CPD

1. Concentration effect

Three samples, C1, C2, C3 of triphenyleno-DHP, 119 in dry THF in quartz UV cells, with initial absorbances at 410 nm as 0.6672, 1.0531 and 1.8721, and one benzo-DHP, 21 in THF with a initial absorbance at 388 nm as 0.8712, were placed side by side.
A 500 W tungsten lamp was used as a light source, and a 590 nm cut-off filter was used. The samples were irradiated at various time intervals, the results were plotted according to first order kinetics.

The above table lists the photo-opening rates of 21 and 119 at different concentrations and the relative photo-opening rate ratios. The relative deviation of 3.3% suggests that the photo-opening rate does not depend on the sample concentration.

2. Distance between lamp and sample

A fresh pair of samples of triphenyleno-DHP and benzo-DHP in dry THF were irradiated with a 500 W tungsten lamp using a 590 nm cut-off filter. Three distances between the samples and the lamp were chosen as 115cm, 70cm and 40cm. The absorbance was monitored at 410 nm and 388 nm for triphenyleno-DHP and benzo-DHP, respectively.
Rate constants were listed below, and rate ratios were calculated accordingly.

<table>
<thead>
<tr>
<th></th>
<th>d=115cm</th>
<th>d=70cm</th>
<th>d=40cm</th>
<th>sd</th>
<th>sd%</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate constant (triphenyleno-DHP)</td>
<td>0.0333</td>
<td>0.0645</td>
<td>0.1252</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate constant (benzo-DHP)</td>
<td>0.0119</td>
<td>0.0220</td>
<td>0.0409</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate ratio</td>
<td>2.80</td>
<td>2.93</td>
<td>3.06</td>
<td>0.13140826</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The rate constants for both triphenyleno-DHP and benzo-DHP increase dramatically with decrease in distance between lamp and sample. However, the rate ratio does not show a significant change, in fact, the relative standard deviation is only 4.5%.
In order to check the change of rate ratio with the change of light source, a 300 nm cut-off filter was used, the distance between the lamp and sample was kept 115 cm.

The rate constants increased for both the samples compared to the same sample lamp distance using a 590 nm cut-off filter. Also, the ratio changes from 2.8 to 2.1.

The change of concentration and distance between the lamp and the sample did not seem to affect the relative rate ratio very much. Within each experiment, the relative standard deviation is within 5%. When the two experiment results calculated together, the overall standard deviation is 7.1%.
Plots for visible light opening of 84 (acetylbdhp) and 21 (bdhp)

\[ y = -0.0154x + 0.4242 \]
\[ R^2 = 0.9971 \]

\[ y = -0.3390x + 0.4115 \]
\[ R^2 = 0.9946 \]

Plots for UV closing of 84' (acetylbcpd) and 21' (bcpd)

\[ y = -0.0392x + 0.6061 \]
\[ R^2 = 0.9915 \]

\[ y = -0.0372x + 0.0902 \]
\[ R^2 = 0.9994 \]
Plots for visible light opening of 103 (padhp) and 21 (bdhp)

$$y = -0.0154x + 0.4242$$
$$R^2 = 0.9971$$

$$y = -0.0983x + 0.4269$$
$$R^2 = 0.9995$$

Plots for UV closing of 103' (pabcpd) and 21' (bcpd)

$$y = -0.0372x + 0.0902$$
$$R^2 = 0.9994$$

$$y = -0.0471x + 0.1858$$
$$R^2 = 0.9984$$
Plots for visible light opening of 105 (phenylbdhp) and 21 (bdhp)

\[ y = -0.0259x + 0.3980 \]
\[ R^2 = 0.9978 \]

\[ y = -0.1079x + 0.4974 \]
\[ R^2 = 0.9999 \]

Plots for UV closing of 105' (phenylbcpd) and 21' (bcpd)

\[ y = -0.0302x + 0.1701 \]
\[ R^2 = 0.9983 \]

\[ y = -0.0281x - 0.0138 \]
\[ R^2 = 0.9998 \]
Plots for visible light opening of 119 (triphenylenodhp) and 21 (bdhp)

- **bdhp**
  - $y = -0.0360x + 0.2119$
  - $R^2 = 0.9992$

- **triphenylenodhp**
  - $y = -0.0999x + 0.5508$
  - $R^2 = 0.9999$

Plots for UV closing of 119' (triphenylenocpd) and 21' (bcpd)

- **bcpd**
  - $y = -0.0202x - 0.0329$
  - $R^2 = 0.9997$

- **triphenylenocpd**
  - $y = -0.0350x + 0.3908$
  - $R^2 = 0.9974$
Thermal decay plots of acetylbenzo-CPD 84°C closing to DHP 84°C

\[
y = -0.086268 - 0.0014144x \quad R = 1
\]

\[
y = -0.34691 - 0.0070378x \quad R = 1
\]

\[
y = -0.19313 - 0.020417x \quad R = 0.99997
\]
Thermal decay of furano-CPD 82' closing to DHP 82

- $y = -0.94455 - 0.0024202x \quad R = 0.99993$
- $y = -1.3828 - 0.0070599x \quad R = 0.99993$
- $y = -0.97009 - 0.011675x \quad R = 0.99993$
- $y = -0.93433 - 0.020672x \quad R = 0.99993$
- $y = -1.0463 - 0.034394x \quad R = 0.99988$

- 319K
- 328K
- 333K
- 338K
- 343K

![Graph showing the decay with temperature and time]
Thermal decay of dinitrobenzo-CPD 87' closing to DHP 87

\[ y = -0.69065 - 0.0021591x \quad R = 0.99997 \]

\[ y = -0.6635 - 0.0059549x \quad R = 0.99998 \]

\[ y = -0.56778 - 0.010043x \quad R = 0.99993 \]

\[ y = -0.61675 - 0.016852x \quad R = 0.99995 \]

\[ y = -0.81498 - 0.027888x \quad R = 0.99990 \]
Thermal decay of nitrobenzo-CPD 86' closing to DHP 86

\[ y = -0.82492 - 0.0012294x \quad R = 0.99999 \]

\[ y = -1.1631 - 0.0059088x \quad R = 0.99989 \]

\[ y = -0.93613 - 0.0098267x \quad R = 0.99996 \]

\[ y = -0.6147 - 0.01591x \quad R = 0.99998 \]
Thermal decay plots of phenylethynylbenzo-CPD 103'

closing to DHP 103

\[ y = -0.20827 - 0.0082026x \quad R = 0.99998 \]

\[ y = 0.062617 - 0.02183x \quad R = 0.99998 \]

\[ y = -0.095884 - 0.036753x \quad R = 0.99989 \]

\[ y = 0.017359 - 0.060436x \quad R = 0.99998 \]

\[ y = 0.17829 - 0.101x \quad R = 0.99994 \]
Thermal decay plots of phenylbenzo-CPD 105' closing to DHP 105

\[ y = -0.83542 - 0.0021413x \quad R = 0.99998 \]
\[ y = -0.92488 - 0.0060439x \quad R = 0.99993 \]
\[ y = -0.70962 - 0.010687x \quad R = 0.99991 \]
\[ y = -0.53736 - 0.029814x \quad R = 0.99994 \]
Thermal decay of phenyltris-CPD 120° closing to DHP 120

\[
\begin{align*}
\text{---} & y = -0.076826 - 0.0019652x \quad R = 0.99926 \\
\text{---} & y = 0.03532 - 0.0097919x \quad R = 0.99965 \\
\text{---} & y = 0.17464 - 0.02852x \quad R = 0.99993
\end{align*}
\]
Thermal decay plots of tris-CPD 72' closing to DHP 72

\[ y = -1.0681 - 0.0020418x \quad R = 0.99997 \]

\[ y = -0.69994 - 0.0098504x \quad R = 0.99997 \]

\[ y = -1.329 - 0.02933x \quad R = 0.99992 \]
Arrhenius plots for the thermal return of CPD to DHP

\[ y = 31.628 - 12183x \quad R = 1 \]

\[ y = 31.861 - 12083x \quad R = 0.99984 \]

\[ y = 30.98 - 11416x \quad R = 0.99997 \]
Arrhenius plots for the thermal return of CPD to DHP

\[
\begin{align*}
\text{1st plot:} & \quad y = 30.396 - 11653x \quad R = 0.99999 \\
\text{2nd plot:} & \quad y = 30.43 - 11844x \quad R = 0.99998
\end{align*}
\]

Arrhenius plots for the thermal return of CPD to DHP

\[
\begin{align*}
\text{1st plot:} & \quad y = 31.489 - 12004x \quad R = 0.99993 \\
\text{2nd plot:} & \quad y = 31.951 - 12180x \quad R = 1
\end{align*}
\]
Eyring plots for the thermal return reactions of CPD to DHP

\[ y = 24.827 - 11853x \quad R = 1 \]

\[ y = 25.06 - 11752x \quad R = 0.99983 \]

\[ y = 24.179 - 11086x \quad R = 0.99997 \]

\[ y = 25.055 - 11810x \quad R = 0.99995 \]
Eyring plots for the thermal return reactions of CPD to DHP

\[ y = 23.595 - 11323x \quad R = 0.99998 \]

\[ y = 23.63 - 11514x \quad R = 0.99998 \]

\[ \ln(\delta T) \]

\[ 1/T \]

Eyring plots for the thermal return reactions of CPD to DHP

\[ y = 24.688 - 11673x \quad R = 0.99992 \]

\[ y = 25.151 - 11850x \quad R = 1 \]

\[ \ln(\delta T) \]

\[ 1/T \]
Chapter Six Thesis References


(79) Aldrich, P2000-9, 97% [98-80-6], mp 217-220°C.


(82) PCMODEL V. 7.0, Serena Software, Bloomington, IN 47402-3076.

(84) Aldrich, B7540-9, 96% [573-17-1], mp 60-64°C