Synthesis and Properties of Benzannulenes and Their Metal Complexes

by

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ABSTRACT

A series of bis [e] and [a] fused dibenzannulenes/cyclophanes have been synthesized for the first time using benzyne-like intermediates (annulynes). These include the dibenzannulene *trans*-2,9-di-*t*-butyl-14c,14d-dihydro-14c-14d-dimethyldibenzo[*fg,op*]naphthacene **82b**, and the metacyclophanedienes *anti*-[1,2; 9,10]-dibenzo-5,13-di-*t*-butyl-8,16-dimethyl[2.2]metacyclophane **82a**, and *anti*-[1,2-b; 9,10-b]-dinaphtho-5,13-di-*t*-butyl-8,16-dimethyl[2.2]metacyclophane **85a**.

From these compounds several metal complexes including *trans*-{μ-[(1,2,3,4,4a,14b-η:8a,9,10,11,12,12a-η)-12c,12d-dihydro-12c-12d-dimethylbenzo[rst]pentaphene]]hexacarbonyldichromium **100**, have been synthesized.

Among the bis [e] fused compounds, pairs **82a/82b** and **95a/95b** show reversible and repeatable photo-switching properties both in solution and in the solid state. The pyrene forms **82b** and **95b** are characterized at low temperature and they thermally return to their cyclophane forms **82a** and **95a** at room temperature. A polystyrene based film of **82** shows a much better bistability required for photo-switching units. These properties make them potential candidates for optical memory units. For the similar naphtho[e] fused compound **95a**, no pyrene isomer **95b** was detected upon irradiation with UV light.

Based on the NMR data, relative bond fixing abilities (RBFA) of several species are measured. The order is:

Benzene-Ru^{+2}(HMB) > Benzene-$Cr(CO)_3$ > Benzene > Oxanorbornadiene >

Norbornadiene

The reduced species, oxanorbornene and norbornene, do not induce any significant bond localization on the [14] annulene ring.

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Ar	Aromatic ring
BFA	bond fixing ability
n-BuLi	*n*-butyllithium
t-Bu	*t*-Butyl
^{13}C NMR	carbon-13 nuclear magnetic resonance
$CDCl_3$	chloroform-d
CD_2Cl_2	dichloromethane-d_2
decomp.	decomposition
DMDHP	dimethyldihydropyrene
DMF	dimethylformamide
DMSO	dimethylsulfoxide
d_6-DMSO	dimethylsulfoxide-d_6
EtOH	ethanol
HMB	hexamethylbenzene
^1H NMR	proton magnetic resonance
IR	infrared spectrum
LDA	lithium diisopropylamide
Me	methyl
mp	melting point
CI MS	chemical ionization mass spectrum

EI MS	electron impact mass spectrum
bs	broad singlet
s	singlet
d	doublet
t	triplet
dd	doublet of doublets
m	multiplet
ppm	parts of per million
RBFA	relative bond fixing ability
THF	tetrahydrofuran
d_8-THF	tetrahydrofuran-d_8
UV	ultraviolet spectrum
VT	variable temperature

Acknowledgement

I would like to express my sincere gratitude to Dr. R. H. Mitchell for his guidance and encouragement throughout this work.

The support from members of the group and the department is also gratefully appreciated.

Finally I would like to thank the University of Victoria and the Department of Chemistry for financial support which made this work possible.

To my mom, my wife and my daughter

Chapter One

Introduction

1.1 From Aromaticity to Advanced Materials

Although more than one hundred and fifty years have passed since Michael Faraday[1] discovered benzene in 1825, the core compound of aromatic chemistry, this old but growing discipline is still stimulating many chemists and probably will continue to do so. For example, even recently chemists are still debating what is "aromaticity"[2a,2b] and what are the causes of aromaticity.[2c,2d]

In these 150 years, we have witnessed many historic events in this area of chemistry which have made significant contributions to the whole field of chemistry. The first synthesis of benzene was accomplished by Eilhardt Mitscherlich in 1833 by heating benzoic acid with calcium oxide.[3a] In 1865, August Kekulé proposed an intuitive but creative structure for benzene and later on presented his "mechanical motion" for the equivalence of the six carbons in a benzene molecule.[3b] In the beginning of the twentieth century, Armit and Robinson[4], based on the atomic theory developed by Kossel and Lewis, proposed the idea of the "aromatic sextet" for the electrons of benzene and its aromaticity. Although this was an important factor for aromatic compounds, it was not until the development of modern quantum mechanics in the 1920s, that the unusual behaviour and stability of benzene began to be understood in terms of resonance theory and molecular orbital theory. In 1931 Erich

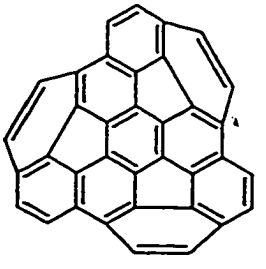
Hückel carried out a series of mathematical calculations with the well-known *Hückel approximation* for monocyclic rings.[5] The stability of benzene was then apparent from Hückel's calculation since the six *p*-electrons from the six carbons of the ring perfectly fill the three π bonding orbitals (the magic sextet!). Furthermore, he pointed out that a "planar monocyclic ring with 2, 6, 10, 14, ..., delocalized electrons should be aromatic",[5] and should have similar closed shells of delocalized electrons like benzene. Those having 4n π electrons would have open shell electron configurations, and therefore be antiaromatic and less stable.

In contrast to this traditional understanding that the source of the stability of a benzene ring and its symmetric structure is due to π delocalization, a recent series of papers by Hiberty and Shaik, and several other groups, argued that the σ system, rather than π system, is entirely responsible for the stability and symmetric structure based on their analysis of the σ and π energy components of the SCF-MO wave functions.[2c,6] Their main argument is that the π component is stabilized by distorting a D_{6h} benzene to a bond alternating "cyclohexatriene" D_{3h} geometry and therefore concluded that "the delocalized π-electrons of benzene possess a propensity to distort to a localized structure, but this propensity is overcome by the σ-frame which restores a hexagonal D_{6h} geometry".[2c] Others have pointed out that the calculation method for this argument is questionable.[7] Another paper stated that "such a result was dubious, since none of the serious workers considered the role of the third term of the molecular virial theorem."[2d]

Another area of theoretical interest is the so-called Mills-Nixon effect.[8] In 1930, Mills and Nixon suggested that the two principal Kekulé structures of benzene could be trapped by small ring annelation based on the existence of the equilibrium of the two Kekulé

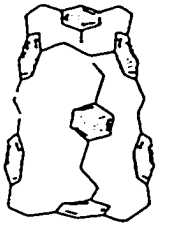
structures.[8a] Although we now know that no such equilibrium exists, much effort both theoretical[8b,8d] and experimental[8g] has been given to the modern structural consequence of the Mills-Nixon postulate, namely bond alternation in annelated benzenes. It is now believed that simple annelation would not cause significant bond alternation[8b-g] due to compensation of strain by "banana" bonds.[8d] High-level calculations, however, as well as experimental data (including X-ray data) do point out that bicyclic annelations or antiaromatic annelations are strong inducers of π-bond localization in aromatic systems.[8c-8f]

Probably, one important reason that aromatic chemistry is seeing a revival is due to the use of aromatic structures in advanced materials for practical applications.[9-20] Several

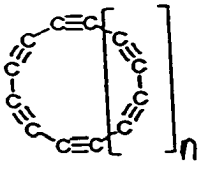


$C_{36}H_{12}$

1, PAH

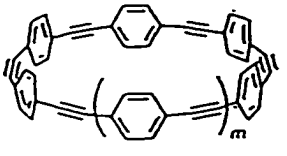


2, cage compound



cyclo-C_{12} (n=1)
cyclo-C_{16} (n=2)
cyclo-C_{20} (n=3)

3, cyclo[n]carbon



m = 1,2,3

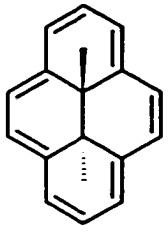
4, dehydroannulene

examples of novel interesting structures include Vollhardt's [n]phenylenes,[9] Diederich's[10]

precursors to C_{60} and Scott's bowl shaped polycyclic aromatic hydrocarbons (PAHs, **1**) to mimic the surface of C_{60}[11], Vogtle's cyclophane-based cage compounds **2** to mimic the fullerene's cavity,[12] Tobe's cyclo[n]carbons **3** as novel carbon allotropes[13] and Oda's phenylacetylene systems (dehydroannulenes, **4**).[14]

The direct pursuit of advanced materials based on novel aromatic compounds attracts even more interest. At least part of the driving force has come from the discovery of C_{60} and now the young but growing "fullerene chemistry". Some important examples of advanced materials are organic electronic materials,[15] organic magnets,[16] organic optical materials-including nonlinear optical (NLO),[17,18] light emitting diode (LED) materials[19] and photo-switchable molecules.[20] Amazingly, there are very few organic advanced materials which are not based on aromatic systems. Probably, this is quite understandable, since all the required physical properties need some kind of π electron flow/interaction. For that, aromatic rings have many advantages over other systems.

Our group has been investigating highly fused annulenes, particularly the derivatives of the bridged [14]annulene (DMDHP), **5**, for about three decades. These compounds have



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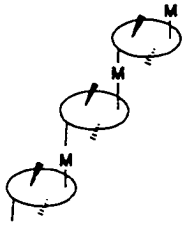

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several very interesting features. First, we have already established that compound **5** is an

excellent probe molecule for ring current and bond localization effects.[21] Thus we could use this molecule to study matters of theoretical interest such as aromaticity, bond-fixation and Mills-Nixon effects.[22] Second, some DMDHP derivatives show very interesting photochromic properties,[20e] and thus have potential as switchable molecules for optical memory units and the controlling gate for functional molecules. Thus one major goal in this thesis is to investigate the synthesis of bis [*a*] and [*e*] fused DMDHP systems and if possible study their photoswitchable properties. Our recent calculations (see below) show that the bis [*e*] fused compounds should be excellent candidates for switchable molecules. Also, the internal methyls in fused derivatives of **5** could act as the orientational group for metal complexing, so that eventually we might be able to make ladder metal complexes such as **6** from the bis fused DMDHPs. As suggested, these complexes with unbroken conjugation might have interesting optical/conducting properties.[23]

1.2 Aromaticity, Ring Currents and the Measurement of Aromaticity

1.2.1 Aromaticity

Various criteria for aromaticity have been discussed.[2a,2b,24,25] The main modern criteria of aromaticity are based on chemical, energetic, structural, or magnetic properties. But none can be exclusively counted on to classify a compound as aromatic, and none when violated is good enough to discount the property. Chemically, aromatic compounds generally favour electrophilic substitution reactions over addition reactions. However some aromatic

compounds, such as phenanthrene, also undergo addition reactions. The energetic criterion is related to "resonance energy" (RE),[26] and says that "cyclic systems having a large resonance energy" are defined as aromatic compounds. However, there are different methods to obtain RE. These include calculational and experimental methods. Under this criterion, some compounds can be either aromatic or non-aromatic based on results using different methods, and furthermore a hypothetical reference structure is needed. The structural criterion refers to the C-C bond lengths in the compound. Applied to annulenes, aromatic systems should have equal bond lengths, whereas nonaromatic or antiaromatic ones should have significant bond alternation. Obviously, this method can not be easily applied to heterocyclic or polycyclic systems because of their lower symmetry. X-ray data are needed for this method, and for many compounds this is not often easy to obtain. Even after the data are acquired, packing forces in the crystals are another factor that might lead to bond alternation . When X-ray data are not available, an alternative method is to estimate bond orders using coupling constants from the proton NMR spectrum.[21,27]

The three most popular and important techniques used in magnetic criteria for aromaticity are ^{1}H NMR diatropism,[25,28a] diamagnetic anisotropy,[28b] and diamagnetic susceptibility exaltation.[28c] Among all of these methods, perhaps the most popular and the easiest method for chemists to determine the aromaticity of a compound is by using ^{1}H NMR spectroscopy (assuming the molecule contains protons inside or outside the ring).

1.2.2 Ring Currents and NMR Spectroscopy

The "ring current theory" was first proposed by Pauling in 1936,[29] and later the theory

was applied by Pople in 1956 to account for the position of aromatic protons in the ^{1}H NMR spectrum.[28a] Subsequently, considerable work has been done on the calculation of nuclear magnetic resonance spectra of aromatic hydrocarbons.[30]

In this model for benzene, the applied field, H^0, causes the π electrons to circulate

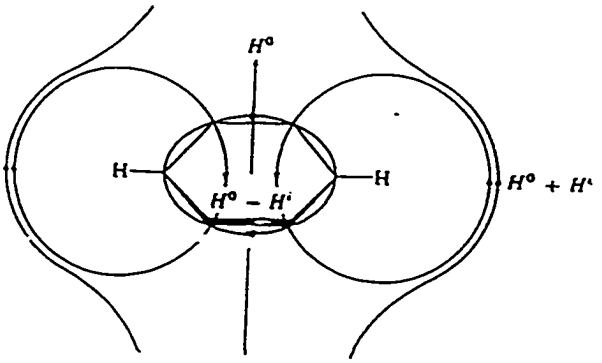
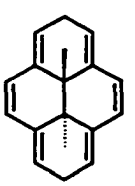


Figure 1. Ring current and the induced magnetic field for aromatic ring[25]

around the six carbon atoms, and thus an extra magnetic field, H^i, is induced. This induced field opposes the external field inside the ring, but reinforces the external field outside the ring. Thus protons outside the ring resonate at a lower external field than protons uninfluenced by the induced field, whereas protons inside the ring resonate at a higher field. For an antiaromatic ring, the reverse will be true.

This model has been supported by a tremendous amount of ^{1}H NMR data of annulenes. For example, the internal methyl protons of annulene **5**, which is almost a "perfect" aromatic compound (even according to other aromatic criteria),[34] appear at δ -4.25 some 5.2 ppm shielded from those of the non - delocalized model **7**.[31]



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Haddon,[30a] and others[30b,30c] have shown that ring current of an annulene relates linearly to its resonance energy (Eq 1.1).

Haddon's equation: $\mathbf{RE} = \pi^2\mathbf{RC/3S}$ (1.1)

RE = resonance energy, RC = ring current, S = the area of the ring (in *cgs* unit)

Then based on the ring current model of annulenes,[29] we should see a linear relationship between the chemical shift *shielding caused by the ring current* with the resonance energies (RE). Indeed, recent experimental ^{1}H NMR data shows the existence of such a relationship.[21] A similar relationship is observed between the chemical shift changes due to ring current and the bond order deviations of annulenes, another criterion of aromaticity.[21,27]

In summary, if one can estimate the chemical shifts *caused by ring current* in annulenes, we can then estimate the aromaticity of the annulenes.

1.2.3 Measurement of Aromaticity - Mitchell's Method

The reason that aromaticity appears to be one of the most controversial concepts in modern chemistry results from the inability to measure these effects *directly* by any physical or chemical experiment. As we discussed earlier, most methods for estimating the aromaticity of annulenes rely on either a hypothetical reference structure (such as energetic and diamagnetic magnetic exaltation criteria) and/or theoretical calculation with many approximations or assumptions (such as the bond order criterion, and the recent "principle component analysis" proposal from Katrizky[32]).

Probably, the only method without these drawbacks is the ^{1}H NMR method. Another

advantage is that only little sample is needed. Furthermore no single crystals are required as in diamagnetic anisotropy and X-ray measurement. However, if ^{1}H NMR chemical shifts are to be used to measure aromaticity quantitatively, then the chemical shift change caused by *just* the ring current must be known.

Several factors affect chemical shift. These are given in equation (1.2).[33]

$$\sigma = \sigma^{RC} + \sigma^{LA} + \sigma_\mu^{\ 0} + \sigma_v^{\ q} \qquad (1.2)$$

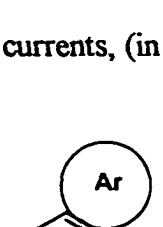
σ: the total chemical shift

σ^{RC}: shift due to ring current; $\sigma_\mu^{\ 0}$: the zero of the chemical shift scale;

σ^{LA}: shift due to local anisotropy; $\sigma_v^{\ q}$: shift due to excess π-electron density

So an ideal probe molecule to measure aromaticity should have all the other factors except σ^{RC} constant or negligible. Extensive work from this group has proven that the bridged annulene, **5**, is one such suitable molecule.[21] In addition to its near *rigid* planarity, its methyl protons show 5.2 (!) ppm of ring current shielding and this shielding is affected only to a small extent by substituents, but greatly by any ring current change.[21,34]

In a fused system, such as **8**, the competition between the two ring currents, (in the macrocyclic 14π ring and the fused ring (Ar)) decreases the ring current in the 14π ring and therefore decreases the shielding effect from this ring current on the internal methyl protons. The more aromatic the fused ring (Ar), the larger is the decrease. Experimentally, a linear relationship is found between the aromaticity of the fused ring and the chemical shift



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change.[21] This makes it possible to measure the aromaticity of the fused ring easily by measuring the chemical shift change of the internal methyl on the [14]annulene ring.[21]

1.2.4 Aromaticity, Bond Alternation and Mills-Nixon Effects

Although all aromatic compounds except benzene have some bond alternation, both calculation and experimental data suggest that when aromaticity decreases, bond alternation will increase. Mills and Nixon's original proposal[8a] was based on the equilibrium of the two Kekulé forms of benzene. This is not acceptable by modern theory, but according to modern VB theory, the real structure of benzene has a 50-50 contribution from these two Kekulé structures. This means that if for some reason (such as fusion of a ring, complexing, etc.), the real molecular structure has more contribution from one structure than from the other one, the structure we would see then is that the benzene will show bond alternation. Similarly, for other annulenes, such as the [14]annulene **5** after fusion, we should see the same effect. Even though it may not be called[8b] "Mills-Nixon" effects, this "Bond-Fixation"/"Bond-alternation" effect due to fusion does exist.

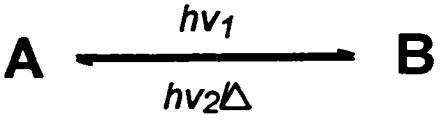
As we mentioned earlier, the chemical shift of the internal methyl protons of compound **5** is very sensitive to a ring current change. So if fusion of a ring onto the [14]annulene causes any change of bond localization and hence ring current, then the chemical shift change of the internal methyl protons should be easily seen. In other words, we can use compound **5** as a molecular probe to measure the "Bond-Fixing" ability of any fragment provided it can be fused onto the [14]annulene to form compound **8** or similar.

1.3 Photochromism, Switchable Molecules and Molecular Devices

1.3.1 Photochromism

Photochromism[35] is defined as a reversible photochemical transformation of a chemical species between two forms having different absorption spectra. The starting material **A** undergoes formation of the product **B**, induced by electromagnetic radiation (Scheme 1). The back reaction **B** →**A** can occur thermally (T-type) or photochemically (P-type). Photochromic systems can be classified into several groups according to the nature of the photochemically induced primary step. These groups include:

Scheme 1



1) photoreversible systems, in which the coloured form **B** undergoes a light-induced reaction back to the form **A**;

2) thermoreversible systems, in which the colour variant **B** reverts thermally to **A**.

Photochromic materials are potentially useful for various opto-electronic devices, such as optical memory, photo-optical switching , sensors, light filters and displays.[35]

1.3.2 Photo Switchable Molecules and Their Possible Applications for Optical Memory

The continuously increasing amount of data to be stored and manipulated has

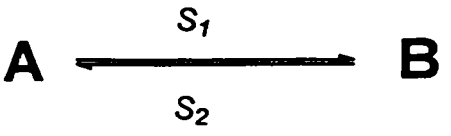
generated the need for high speed computers and large storage capacities. One of the most important challenges in this field is the development of materials and techniques to place as much data as possible on the least amount of material and use photons, which are the fastest vehicle we have, to commute the information. Obviously, the ultimate in this miniaturisation would be to achieve information storage at the molecular or even the atomic level,[36] whereas processing of data should occur at close to the speed of light by the use of all optical switching devices.[37]

Hirshberg's creative conception of a photochemical binary element based on photochromic materials for a computer memory and the possibility of getting a variable density optical shutter initiated an intense research activity in this field in industrial and academic laboratories world-wide.[35b] Optical memory using organic photochromic media could offer advantages over the current magneto-optical recording with regard to speed of writing, multiplex recording capability, and low fabrication cost.[20d,38,39]

Another driving force for these studies is the need for truly *reversible optical* recording media with the opportunity to read, write, erase and rewrite again. This is probably due to the enormous commercial success of the compact disk (CD), which are unfortunately only available in *read-only* and *write-once* forms.

The two states of a switchable molecule can be read/writen optically as a data bit 0 or 1 depending on whether they are colourless or coloured (or any other pair of distinguishable colours). The basic requirement for such a switch is the bistability,[20a] i.e. the occurrence of two different forms of a molecule, which can be interconverted by means of external stimuli (Scheme 2). These stimuli could be photons, electrons, current, or chemicals.

Scheme 2



Forms **A** & **B** must show:

1) Reversibility with different stimuli;

2) **A** and **B** must both be stable (bistability);

3) Distinguishable colours for a photo switch.

The stimuli could be:

1) Photonic;

2) Electronic;

3) Protonic;

4) Other, e.g., ionic.

Photoreversible compounds, where the reversible switching process is based on photochemically induced interconversions, play a major role in this interdisciplinary field. For photo molecular switches, the most important features required are:[20d]

1) Photo-switchable between the two forms;

2) No thermal interconversion of the isomers;

3) High fatigue resistance, which allows highly repeatable

write/erase;

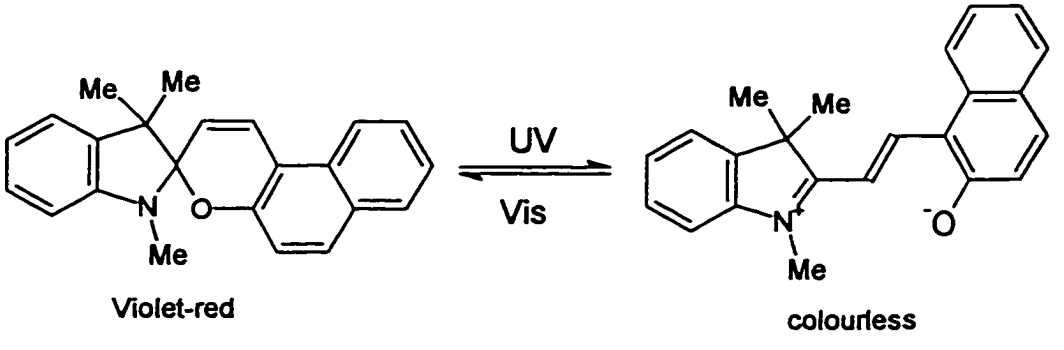
4) Both forms should be readily detectable;

5) Fast response in the switching.

Although various photochromic compounds have been synthesized and studied for optical data storage[20d] or as a molecular device,[40] the photochromic process involved in most of these compounds can be classified as a cis-trans isomerization or a photocyclization reaction. The following gives several examples for three recently studied systems.

Spiropyran systems (Scheme 3)[41]

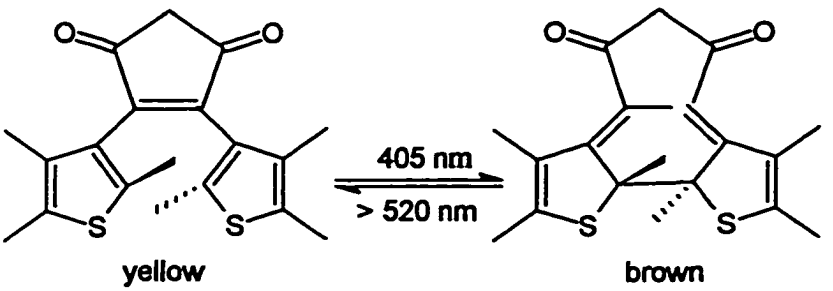
Scheme 3

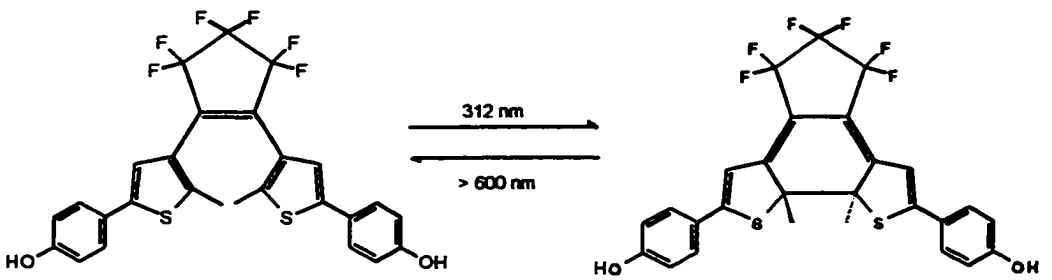


Violet-red colourless

Diarylalkenes (Scheme 4)[42]

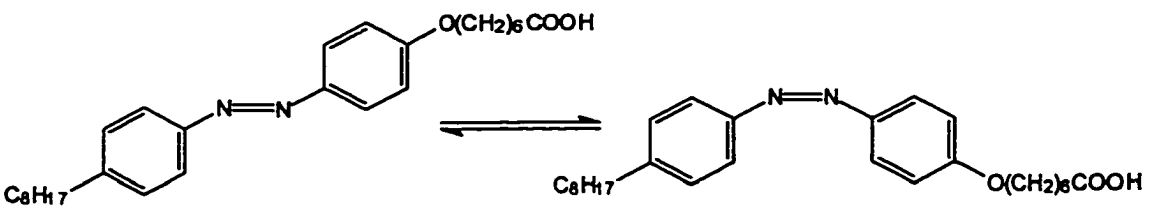
Scheme 4





Azobenzenes (Scheme 5)[43]

Scheme 5

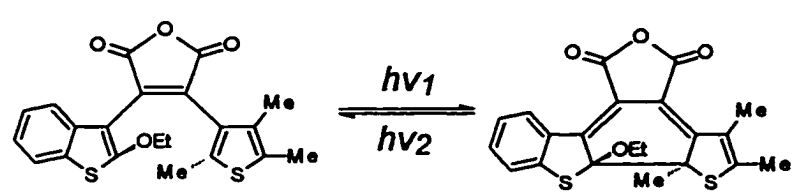


In addition to the systems mentioned above, many others have been studied. These

include fulgides, azulenes, keto-enol systems,[20d,35a] dimethyldihydropyrene systems,[20c] racemic photoresponsive material.[44]

To be suitable for optical memory devices, these molecules have to meet other requirements besides the switching properties. The most important ones are the thermal stability of both isomers and a repeatable switching cycle without loss of activity (high resistance to fatigue). From the many photochromic compounds proposed as being applicable for an optical data storage system or a molecular device, only a few come close to meet all these requirements.[42,44] To improve the properties of the proposed switchable molecules, in addition to developing new molecules, many techniques such as crystal engineering, Langmuir-Blodgett techniques, and polymeric matrices (physically and chemically) have been applied to these materials.[35a] Many other issues also need to be addressed in these molecules. These include the response time (how fast), the properties in the solid or crystal state and the quantum yield of reading/erasing. Recently, two systems have been demonstrated to be very close to practical application,[42h,42c,44] with both fatigue resistance and thermal irreversibility.

Scheme 6



One example from Irie's bistable photochromic systems

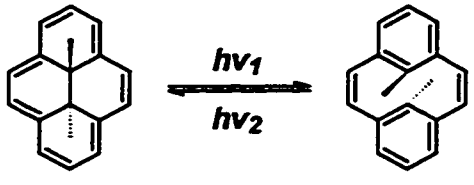
The systems reported by Irie (Scheme 6) have been tested over 10^4 cycles of read/erase without loss of performance.[42h] The response time for reading and writing is fast (less than

10 ps).

Many test models of optical units based on these organic photochromic molecules have been developed and patented recently.[45]

Previous studies show that dimethyldihydropyrene 5 (Scheme 7), and many of its substituted dervatives[46] and [e] mono-fused systems[47] show reversible photochromism between the pyrene and cyclophane forms. In all these cases, the thermodynamically stable isomers are the dihydropyrenes. However, calculation[48] shows that in the case of bis [e] fused systems (Scheme 8), such as **9**, the stable form would be the cyclophane (e.g. **9b**) and that

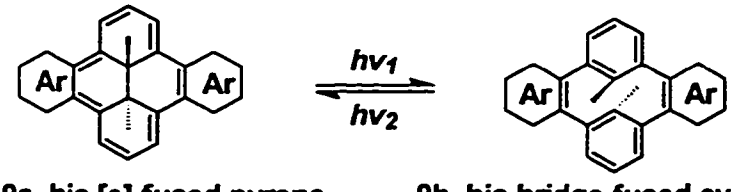
Scheme 7



5a, pyrene **5b, cyclophane**

they should show the desired reversible photo switchable process between the pyrene and the cyclophane.[47] Thus to synthesize these compounds and study their photochromic properties

Scheme 8



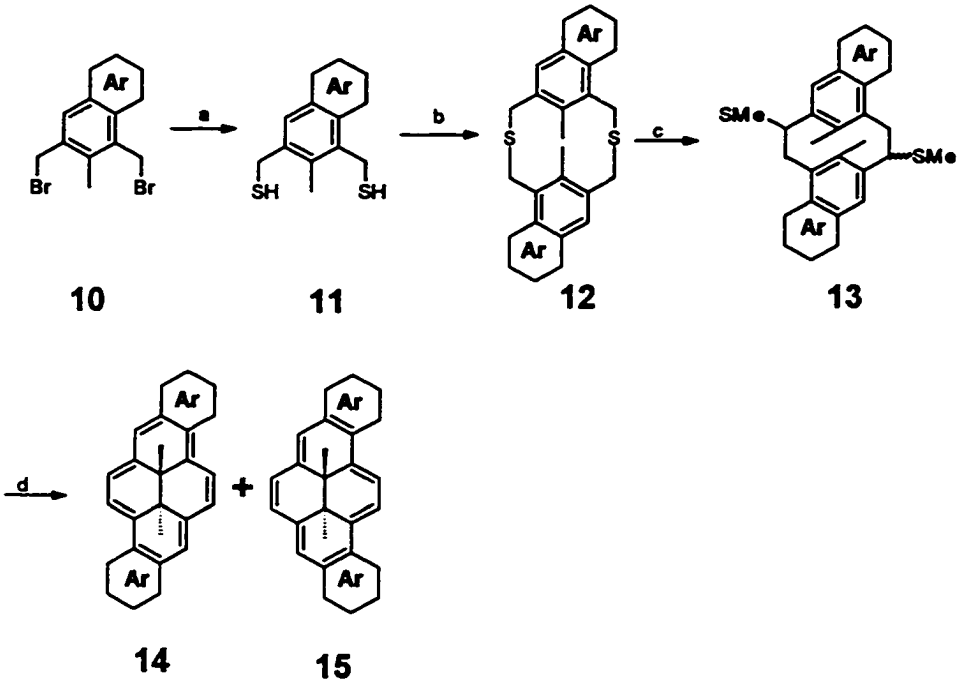
9a, bis [e] fused pyrene **9b, bis bridge-fused cyclophane**

is defined as a major goal of this thesis.

1.4 Synthetic Strategies to Bis Fused DMDHP

There are currently two strategies to synthesize the fused DMDHPs. The first starts with fused 2,6-bis(bromomethyl)toluenes **10** (Scheme 9a). This route has proved very

Scheme 9a



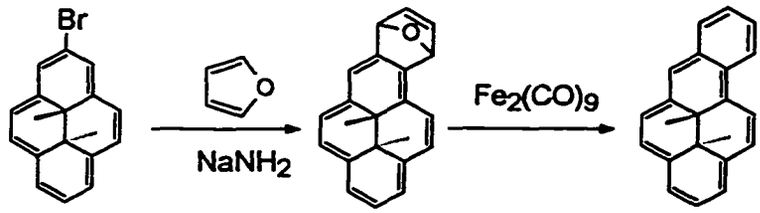
10 **11** **12** **13**

14 **15**

(Typical reagents and conditions: (a) i) $SC(NH_2)_2$, ii) KOH; iii) H^+ (b) KOH, Ethanol/Benzene, only transoid isomer product shown; (c) BuLi/MeI, many isomers produced; (d) i) $(MeO)_2CHBF_4$, ii) t-BuOK/THF.)

successful for many [*a*] fused systems.[21] One major disadvantage of this strategy is that it involves the synthesis of a different substituted bis(bromomethyl)arene for each target

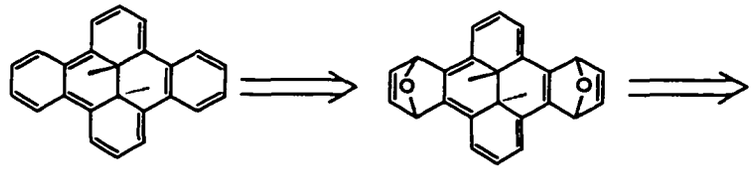
Scheme 9b



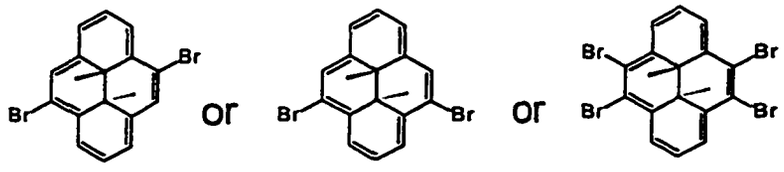
41 **15a** **15b**

molecule. The second strategy uses a reactive aryne intermediate and forms the target molecules using a Diels-Alder reaction (Scheme 9b).[21] This route is shorter and more efficient

Scheme 10



16 **17**

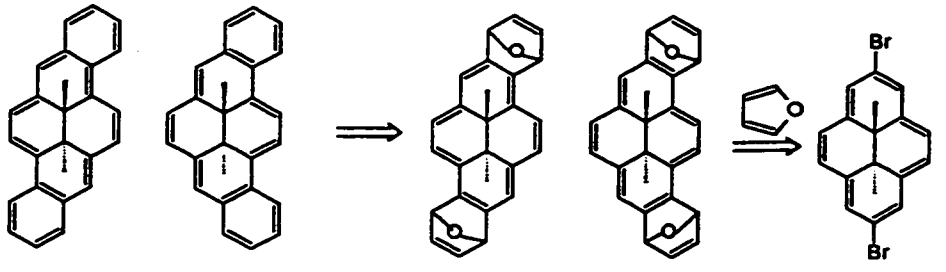


18a **18b** **18c**

and has been proved successful for several mono [*a*] fused systems.[21] We hope that this strategy would apply to bis fused systems and especially to the bis [e] fused systems

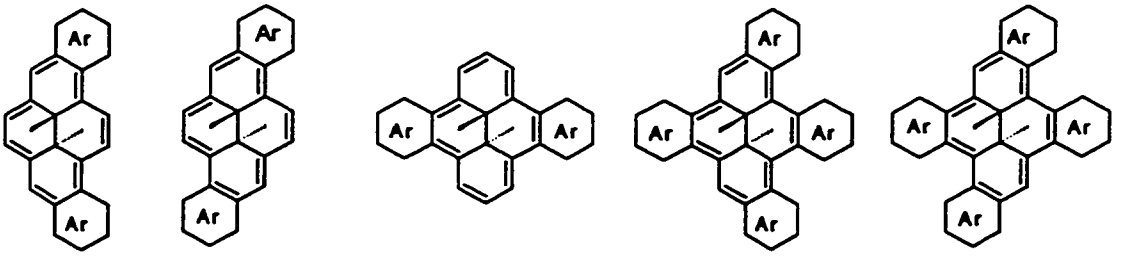
(Schemes 10 and 11). The annulyne intermediate may be generated from the related bromides with strong base. For the bis [*a*] fused systems (such as **22a** and **22b**), the 2,7-dibromide **21** is required. This was reported first by Boekelheide in 1967 in 20% yield.[49] For use to generate

Scheme 11



19a 19b 20a 20b 21

an aryne intermediate, this yield must be improved and further substitution needs study. To generate the bis-aryne for a bis [*e*] fused DMDHP such as **23**, the 4,5/9,10-substituted



22a 22b 23 24a 24b

bromides (such as, **18a-18c**) of DMDHP are required. These bromides have not been reported.

1.5 Goals and Objectives

In summary, we will pursue the following goals and objectives in this thesis.

1.5.1 Synthesis

The first objective will be to test the aryne route on the dibromide **21a** to obtain the bis [a] fused adducts, e.g., *cisoid* and *transoid* adducts **20a/20b**. This will also determine whether the Diels-Alder reaction strategy might be used for other bis [a] and [e] fused systems, since this route is shorter and more efficient than the traditional method and has the flexibility for different targets with the same synthon (aryne).The Diels-Alder adducts also are interesting because the mono adduct **15a** showed extensive bond fixation, so it will be interesting to compare the bond localization of **20a** and **20b**.

As a second synthetic objective, these adducts will then be converted to the bis benzannulenes **19a** and **19b**. Since no metal complexes of these dibenzannulenes are known and the internal methyls in fused derivatives of **5** could act as the orientational group for metal complexing, we will investigate the bis Cr, Fe and Ru complex formation for **19a/19b**. Such a complexation is necessary if ladder polymers such as **6** containing dihydropyrene units are going to be prepared. As suggested, these complexes with unbroken conjugation might have interesting optical/conducting properties.[23]

Since the chemical shifts of the internal methyl protons are very sensitive to the bond location of the [14] annulene in **8** or the relative metal complexes, which are induced by these fusion or metal complexation, should these metal complexes are synthesized, the relative bond

fixing abilities of these organometallic moieties will be calculated and discussed.

The third synthetic objective will be to investigate the synthesis of bis [e] fused systems by first finding a suitable bromide, such as **18**, and then applying the aryne route to obtain the bis [e] fused DMDHPs or their metalcyclophane isomers. Bis [e] fused systems, such as **23**, have been pursued for more than 20 years without success, and are especially interesting because AM1 calculations suggest that the cyclophane will be the thermally stable form. As well the AM1 calculations suggest the heat of formation difference (ΔH_f) of the pyrene and cyclophane forms of the bis [e] fused compounds are much smaller than that for the corresponding bis [a] fused systems. This would make both their cyclophane and dihydropyrene forms accessible, and thus better candidates for photo switchable molecules.

1.5.2 Property Studies

If we are successful in the synthesis of these bis [e] fused compounds and they show the properties as predicted above, we will investigate the photo switchable properties of these compounds both in solution and the solid state.

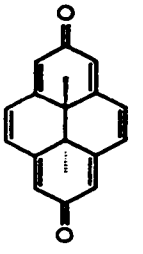
Should these target molecules be synthesized successfully, we will have a series of DMDHPs with different annelating species on the [14] annulene. The resultant NMR data from these compounds will be used to measure the relative bond fixing abilities of the annelating species.

Chapter Two

Synthesis

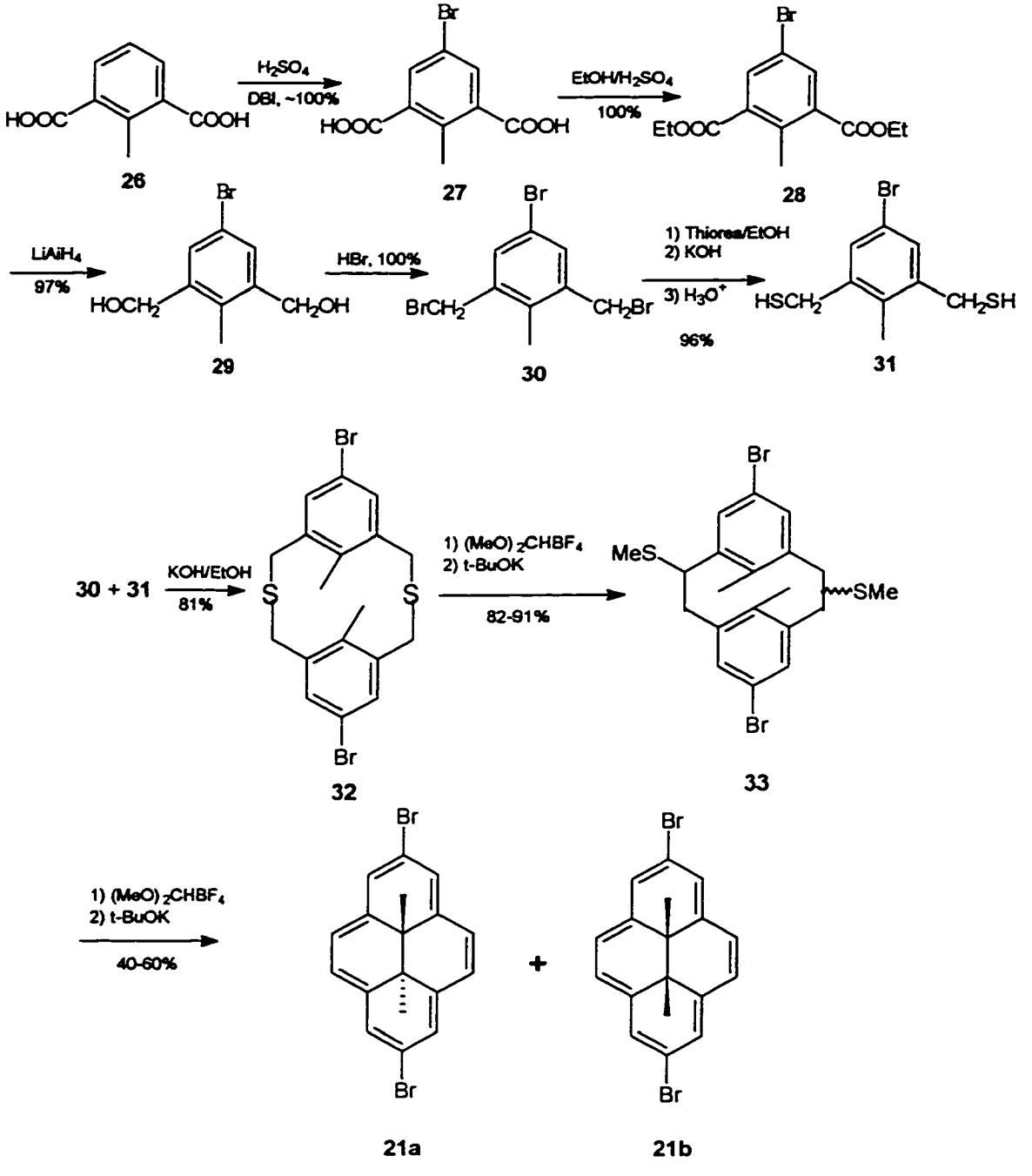
2.1 Synthesis of the Bromide Precursors

As mentioned in the introduction, to synthesize bis fused dimethyldihydropyrenes via the aryne intermediates, the key precursors are the related bromides, such as **18** and **21**. Bromide **21** was first reported by Boekelheide and co-workers in 1967 in only ~20% yield by the reaction of NBS in refluxing CCl_4 on compound **5** directly.[49] Since relatively large amounts of this bromide are needed, a more efficient route is required. Our group has found NBS/DMF works quite well to brominate many active aromatic systems.[50] So dihydropyrene **5** was reacted with 2 equivalents of NBS in dry DMF and indeed, the bromide **21** was isolated in good yield on most attempts. However, this reaction needs care, since traces of water in the DMF produce significant amounts of quinone **25**.[51] As well, the high boiling point of DMF make it difficult to remove it completely in the work-up due to its limited solubility in water. We thus thought that a better strategy would be to use 4-bromo-2,6-bis(bromomethyl)toluene as the starting material for the synthesis of the pyrene, i.e. to functionalize the benzene ring at an early stage. Thus the diacid **26** was prepared from 2,6-dicyanotoluene by hydrolysis (Scheme 12). Although the bromination of **26** should be straightforward, various methods that we tried failed, including $KBrO_3/H_2SO_4$,[52a] $CF_3COBr/CF_3COOH/HgO$,[52b] and



25

Scheme 12



$Br_2/HgO/H_2SO_4$.[52c] Finally, we succeeded in the bromination of this diacid by using dibromoisocyanuric acid (DBI)[53a] in concentrated sulfuric acid, an extremely powerful reagent

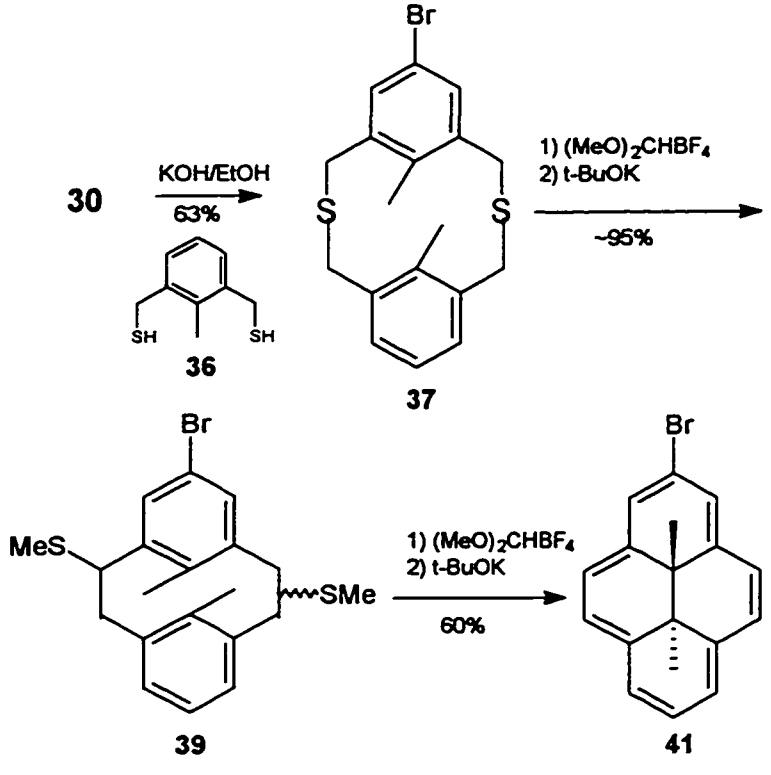
for difficult brominations.[53b,53c] This method normally gave a quantitative yield and has a convenient work-up, simply pouring the reaction mixture onto crushed ice, followed by filtration and washing, yielded the product **24**, mp 255-257°C with satisfactory CH analysis. The brominated diacid **27** was then esterified to **28** and reduced to the dialcohol **29** using standard procedures. The latter was then converted in quantitative yield to the desired tribromide **30** and dimercaptan **31** as shown in Scheme **12**. Coupling of **30** and **31** in benzene/ethanol with KOH gave 81% of the thiacyclophane **32** as a mixture of *syn* and *anti* isomers (ratio ~ 1:4). The *anti* and *syn* isomers could be separated by chromatography or fractional recrystallization since the *anti*-isomer is the least soluble. The structures of these two isomers were evident from their mass spectra and the chemical shifts of the internal methyl protons; the *anti* isomer, mp 290-292 °C, showed the shielded internal methyl protons at δ 1.37. In contrast, the *syn* isomer, mp 268-270 °C, showed the methyl protons at δ 2.43. Full spectral data can be found in the Experimental Section.

Methylation of the *anti* isomer **32a** with Borch reagent, $(MeO)_2CHBF_4$,[54] yielded the product salt **33a** with quantitative yield. The sulfonium salt **33a** was then subjected directly to a Stevens reaction with KOBu^t in THF at room temperature for 3 hours to give 92% yield of the rearranged products **34a** as a mixture of stereo isomers where the internal methyl protons were at δ 0.6 - 1.1 and the thiomethyl protons at δ 2.0-2.2. This mixture, **34a**, was directly remethylated with Borch reagent, to give 83% of the *anti* sulfonium salts, **35a**, which were subjected to KOBu^t in THF again for a Hofmann elimination at room temperature for 3 hours to yield the *trans* dibromopyrene **21a** in 40 - 60% total yield of this two steps. Chromatography or recrystallization from $CHCl_3$ was applied if necessary to yield deep green

crystals, mp 212-214 °C (lit[49]: 213-214 °C). Applying a similar procedure to the *syn* isomer of the thiacyclophane, **32b,** yielded a mixture of the *anti* and *syn* dibromide **21a** and **21b** in ratio of 6:4 in 77% yield. The *cis* isomer, **21b,** shows its internal methyls at δ - 1.95, consistent with other *cis* DMDHPs.[21] Recrystallization or chromatography can separate these two isomers and isolation of this *cis* dibromopyrene provides an opportunity to examine the *cis* fused dihydropyrenes.

Similarly, unsymmetrical coupling of the tribromide **30** with 2,6-bis(thiomethyl)-toluene,[51c] **36**, proceeded smoothly to give a mixture of the *anti* and *syn* (6:1) isomers **37** in

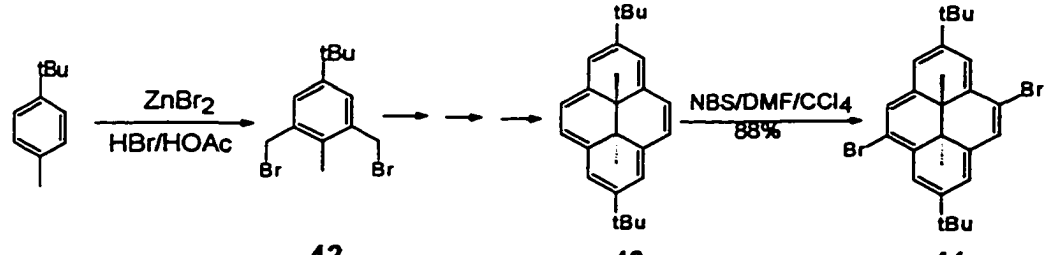
Scheme 13



63% yield (Scheme 13). Fractional recrystallization of the mixture yielded pure colourless crystals of *anti* isomer **37a**, mp 199-200 °C with internal methyl protons at δ 1.25 and 1.40 in the ^{1}H NMR spectrum. The mother liquor was then chromatographied over silica gel to separate the two isomers, the *syn* isomer has mp 154-155 °C and its two internal methyl protons δ 2.46 and 2.51 in its ^{1}H NMR. Similarly, the *anti* isomer was subjected to the standard procedure of methylation with Borch reagent, Stevens rearrangement, remethylation and finally Hofmann elimination with KOBu^t/THF and gave the *trans* isomer of the monobromopyrene **41**, mp 110-111 °C (lit.[50]: 111-112 °C) in overall yield ~35-40% from 2,6-dichlorotoluene.

To synthesize the [*e,l*] fused dihydropyrenes via aryne intermediates, the key precursor is the dibromide **18** or similar bromide. Electrophilic substitution of **5** occurs at the 2 and 7

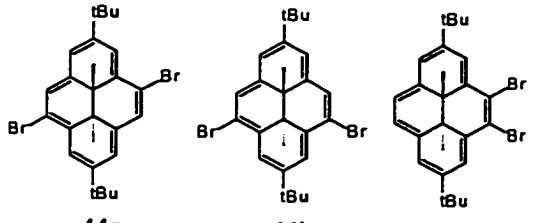
Scheme 14



42 **43** **44a**

positions,[49,50] and so to brominate at the 4 and 9 positions, the 2, 7 positions must be blocked. 2,7-Di-*t*-butyl-dimethyldihydropyrene **43** seems a good starting material, since the bulky *t*-butyl groups should inhibit substitution at the 1 position and it is readily accessible.[55a] Thus this pyrene was made from 2,6-bis(bromomethyl)-4-*t*-butyltoluene using the literature procedure,[55a] but starting with the direct bromomethylation of 4-*t*-butyltoluene in HOAc/HBr

with anhydrous $ZnBr_2$ as the catalyst.[55b] Then the NBS/DMF method[50] to brominate was modified slightly using NBS in DMF/CCl_4 (7:1) and gave the dibromide **44a** in 88% isolated yield, mp 220-222 °C. The utilization of some CCl_4 improved the solubility of the starting pyrene **43** (Scheme 14). Interestingly, although there are three possible isomers of the



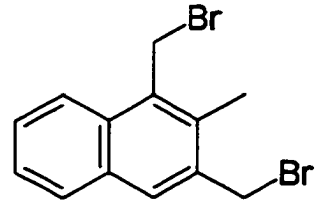
44a **44b** **44c**

dibromides (**44a** , **44 b**, and **44c**) only **44a** was isolated under these conditions. The structure of this isomer **44a** is clearly supported by its proton NMR spectrum which has only one singlet peak for its internal methyl protons at δ -3.83. The isomer **44b** should have two singlet peaks for its internal methyl protons. Isomers **44a** and **44c** should have the same pattern of peaks in their NMR spectra, but the following Diels-Alder reaction (see below) on this bromide proved that the two bromine atoms must be on different sides. This bromination reaction proceeded very well on both the mg or gram scale.

When NBS/$CHCl_3$ was used, a mixture of the two isomers **44a** and **44b** was isolated in a ratio of ~4:6 with a total yield of ~ 100%. As expected the second isomer **44b** has two signals for its internal methyl protons at δ -3.68 and -3.70 respectively. Combining this result with that from the NBS/DMF system, indictaes that the bromination is probably kinetically controlled in these solvents.

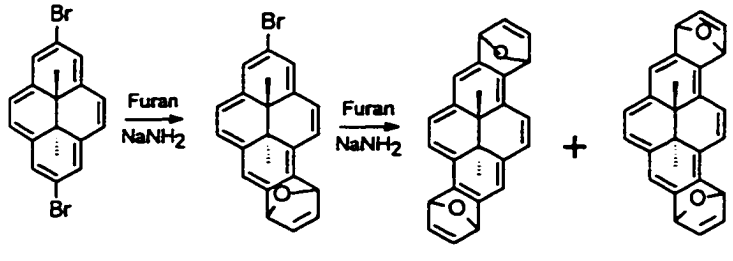
2.2 Synthesis of [*a*] fused dihydropyrenes

The first method used to obtain highly annelated systems in our group involved the synthesis of suitably substituted bis(bromomethyl)arenes, followed by cyclization to the dithiacyclophane, ring contraction, and elimination of Me_2S (Scheme 9). However, the sequence involved is long, and for each new system, a new starting bromide **10** is required. Moveover, the synthesis of the required dibromide often is very time consuming. For example, the dibromide **45**, the starting materials for [*a*] fused benzannelated dihydropyrenes required seven steps and was obtained in a overall yield of 18%.[56] This strategy however is not applicable to [e,l] fused systems. Use of the aryne intermediate discovered by Mitchell and Zhou[21] seemed attractive

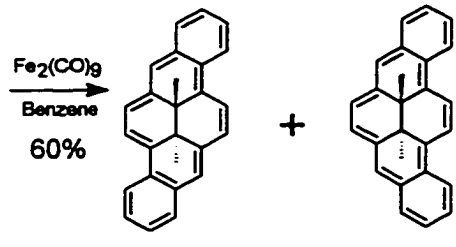


45

Scheme 15



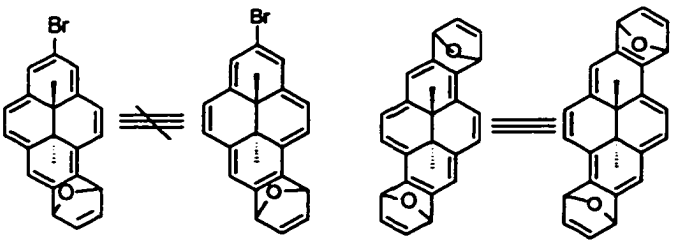
21a **46** **47** **48**



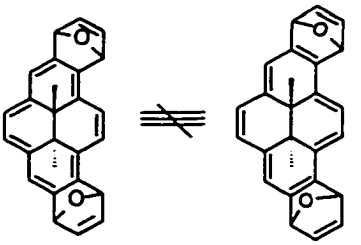
49a **49b**

for the synthesis of the bis fused systems. With useful amounts of dibromides **18** and **21** on hand, we decided to try this strategy for various bis fused dihydropyrenes **22** and **23**.

Reaction of the dibromide **21a** with sodium amide and a catalytic amount of KOBu^t in THF with an excess of furan trapped the aryne intermediate to give the bis adducts **47** and **48** in 62% yield (Scheme 15). The bis adducts are probably formed in a step-wise process, since some of the mono adducts **46** (two pairs of enantiomers) were also isolated. By NMR



46A ⟷ **46B** **47A** ⟷ **47B**

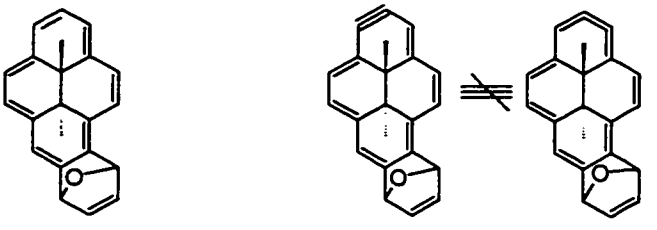


48A ⟷ **48B**

the ratio of **47** to **48** was ~ 3:1, and both **47** and **48** consist of three diastereoisomers each. The isomers of **47** showed their methyl protons centered around δ -4.0, while those of **48** were around δ -2.3 (See below for a discussion of their shifts). Fractional recrystallization and careful chromatography gave a sample of the three isomers of **47** and an enriched sample of the three isomers of **48**. The gross structures of the isomeric mixture of **47** and **48** were easily proved by deoxygenation of the respective isomeric mixture using $Fe_2(CO)_9$ in benzene to the known dibenzannulenes **49a** and **49b**. The *transoid*[66b] isomers **47** could not be separated from

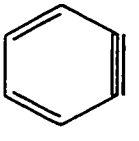
each other, but the mixture gave a mass spectrum M^+ at 364.1485 (HRMS, EI), consistent with that calculated for $C_{26}H_{20}O_2$ (364.1463). Most convincingly, this mixture **47** with internal methyl protons around δ -3.80 to -4.15 gave only the *transoid*-dibenzannulene **49a** after deoxygenation, while the enriched sample of isomeric **48** gave an enriched product of **49b** with less of **49a**, thus proving the relative orientations of the annelation in the bis adducts **47** and **48**.

The related monoadduct **46c** shows substantial bond localization based on both ^1H coupling constants and X-ray data[22] and thus we might expect that resonance structure **46A** to be preferred over **46B** energically. Thus if the bis adducts are formed via a stepwise mechanism as described above, the reaction via intermediate aryne **50A** should be faster than



46c **50A** **50B**

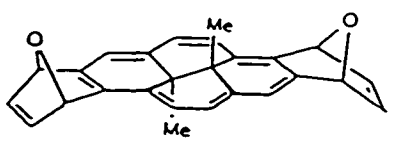
that via **50B**. This is consistent with the fact that we obtained more **47** than **48**. Since the two paths via the two intermediates **50A** and **50B** should be very similar (if not the same), we would then expect that **50A** is more stable than **50B**. Thus the structure of the species, generated from the dehydrobromination of the bromide **46**, is more likely aryne-like as in **50A** rather than cumulene-like as in **50B**. This result is consistent with the benzyne structure **50C**, which has been observed



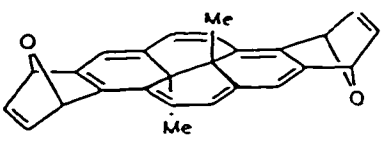
50C

directly at 8 K.[56c]

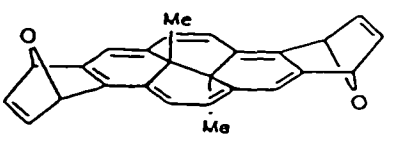
Due to C_1 symmetry of the **udud**[56d] and the **uudd** isomers of **47**, each would be expected to display a single ^{1}H NMR methyl resonance for the internal methyl protons; while the unsymmetrical **uduu** isomer has two different internal methyl groups and therefore two signals are expected for this isomer. Indeed, four methyl signals were observed, with the two signals of **47uduu** (δ -3.80 and δ -4.15) being of equal intensity, the other signals (δ -3.96 and -4.01) were not specifically assigned but must be from **47uudd** and **47udud**. The relative integrations of the three sets of signals for these three isomers in the crude sample was ~5:1:2. After several recrystallization, the same ratio changed to ~14:5:1. So not only is the **47uduu** isomer formed preferentially it also has the least solubility (in CH_3OH/CH_2Cl_2). In its ^{13}C NMR, each type of carbon has three resonances. This confirms the three isomers. Similarly, the three isomers of **48** also give four methyl signals. Analogously, **48uduu** gave signals at δ -2.17 and -2.48 for its internal methyl; the other two isomers gave signals at δ -2.29 and -2.34. The relative integration of these being ~ 2:3:1, in this case the **uduu** isomer is not formed preferentially. Detailed spectra are given in the Experimental Section.



47uduu



47udud



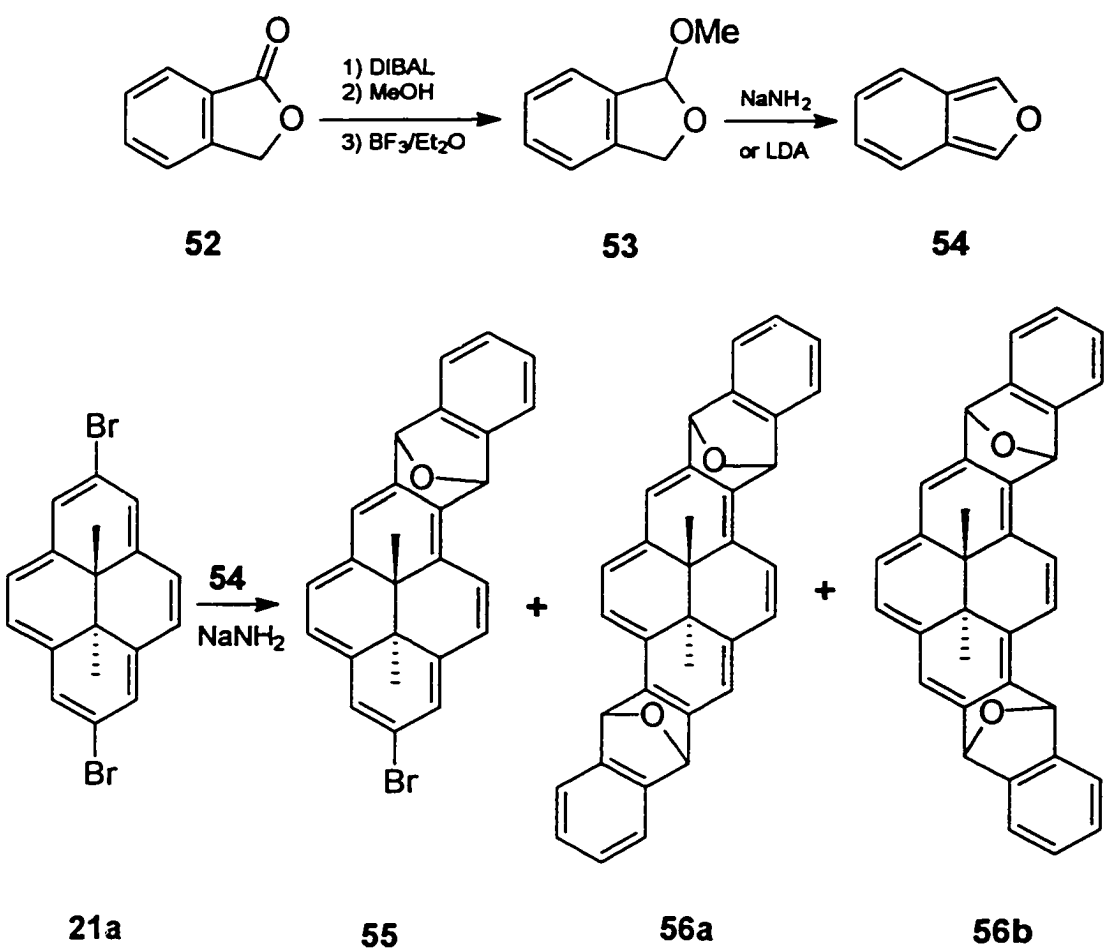
47uudd

The deoxygenation products **49** are not very stable, especially the *transoid* isomer, which decomposes during work-up and in $CDCl_3$ solution for NMR.

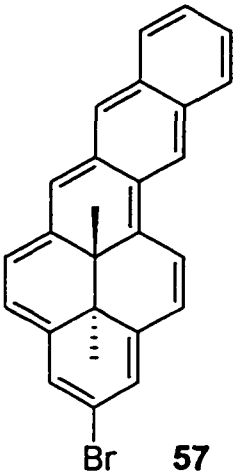
Both the *cisoid* and *transoid* adducts and the deoxygenated products have very different NMR spectra. This will be discussed in next chapter.

This route to the bis fused dihydropyrenes **49** is much shorter than the original one[56] and proceeds in higher yield, and more importantly it opens up an efficient strategy to other bis-fused systems. Our next target was the bis-fused naphtho[*a,h/i*]dihydropyrenes **51**.

Scheme 16

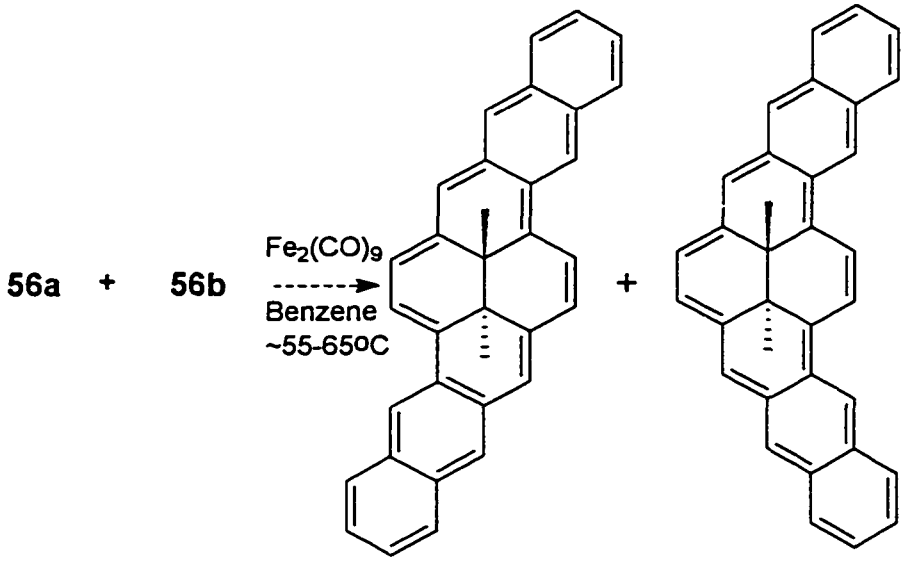


(Schemes 16 and 17. Note in the schemes, dotted arrows mean that the reactions have been tried, but did not succeed.) Starting from phthalide, **52**, the 1-methoxyphthalan **53** was obtained in almost quantitative yield using a one-pot reaction modified from the literature.[57] Then a reasonably stable solution of the isobenzofuran, **54**, was prepared on treatment of **53** with either LDA or $NaNH_2$ in THF (Scheme 16). The subsequent addition of dibromide **21a**, and $NaNH_2$ gave a mixture of the expected bis adducts **56** (23%) as well as some mono adducts **55** (10%) and some deoxygenated products **57** (17%) derived from these mono adducts. In some trials, only mono adducts **55** and their deoxygenated products **57** were isolated. (Scheme 16).



57

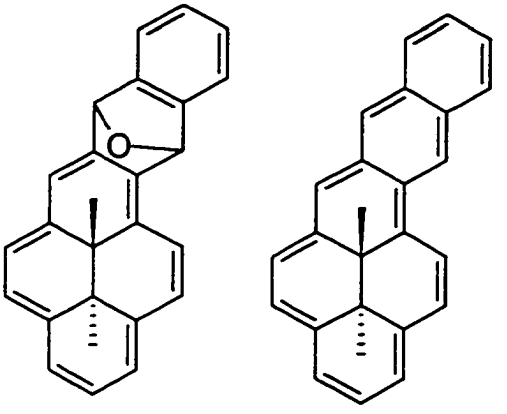
Scheme 17



51a **51b**

Based on the result for **47**, **48** and the mono isobenzofuran adduct **58**,[21] we expected that the bis adducts **56** would have two groups of peaks for their internal methyl protons centred at δ -4.0 for the *transoid* **56a** and -3.0 for the *cisoid* isomers **56b**. Although we could not purify and characterize these compounds completely due to their instability (they decompose both in the solid state and in solution), we observed two sets of signals centred around δ -4.0 and δ -3.1 for these compounds and also obtained CI MS peaks at 433 for MH^+.

Unfortunately in this case the deoxygenation reaction of **56** with $Fe_2(CO)_9$ in benzene at 55-65°C gave only some unidentified decomposed compounds. (Scheme 17)

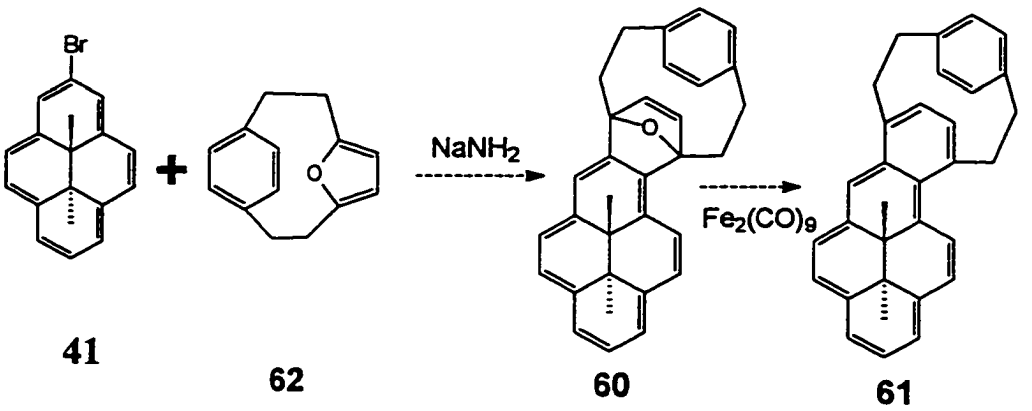


58 **59**

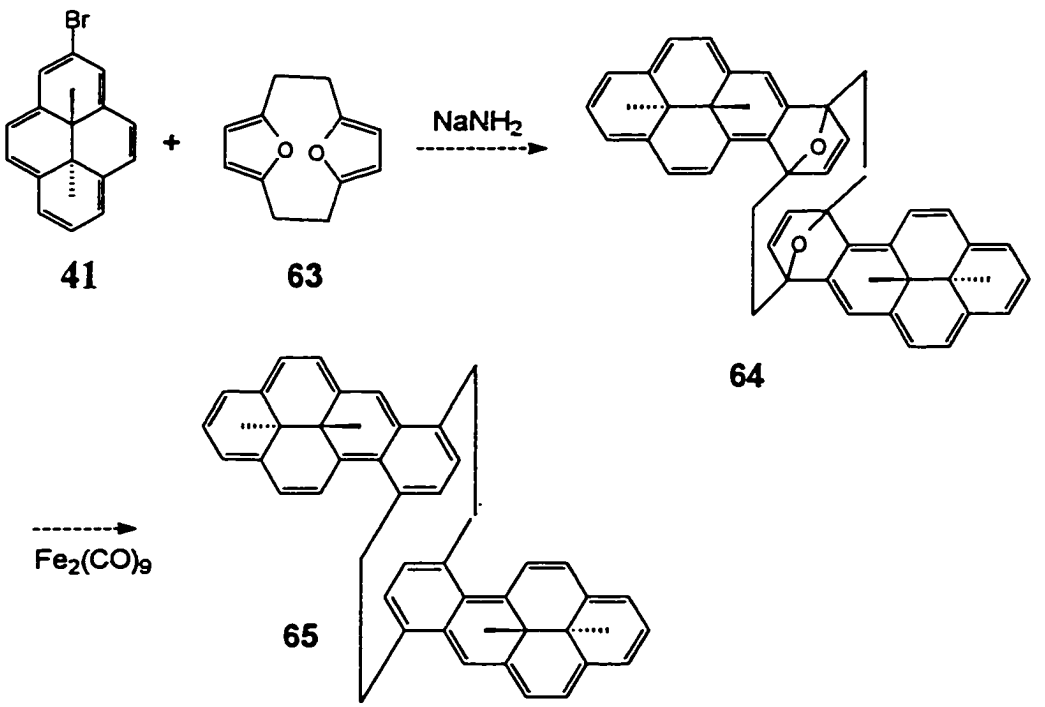
The mono adduct **55** however is relatively stable. Its major isomer showed the internal methyl protons at δ -3.64 and -4.01 and the pyrene **57** showed its internal methyl protons at δ -0.39 and -0.41. These data are consistent with the related compounds **58** (δ -3.66 and -4.01) and **59** (-0.44) without the bromine on the ring.[21]

We thought it would be very interesting to synthesize the layered compounds **61**, **65** and **67** (Schemes 18, 19 and 20). Using the literature methods[58], furans **62** and **63** were synthesized (Scheme 21) and tried in the aryne reactions, but unfortunately, they were

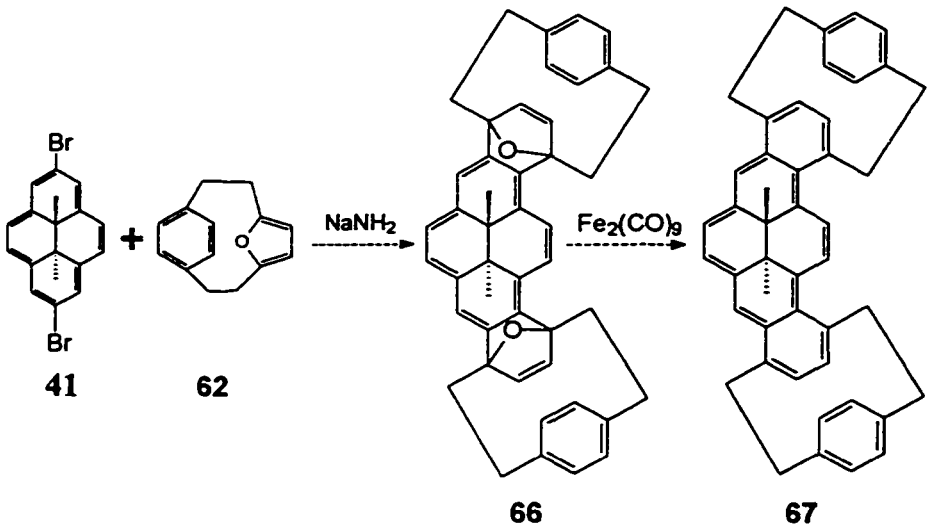
Scheme 18



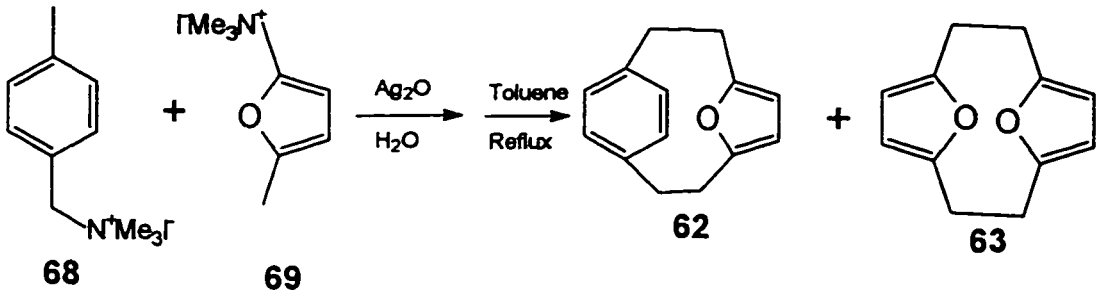
Scheme 19



Scheme 20



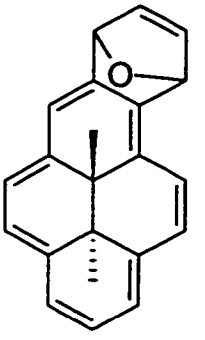
Scheme 21



extremely sluggish to react and no adducts or other identified products were isolated. Most of the starting furans **62/63** were recovered.

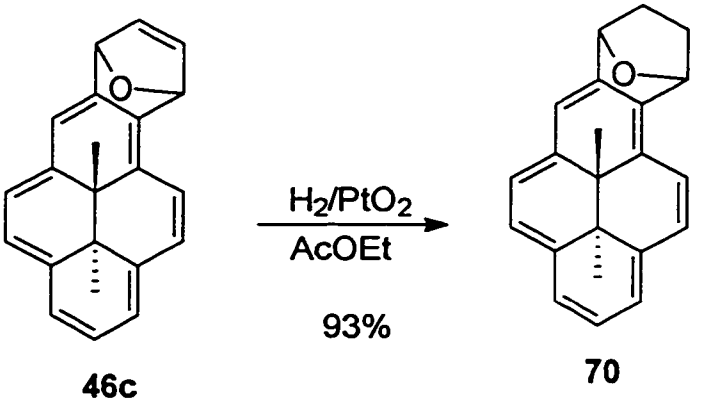
It has been suggested recently that simple small annelation of aromatic systems will not produce bond alternation in the aromatic (the so-called "Mills-Nixon" effects) because of "Banana-Bonding" in the small ring.[8d] Bicyclic annelation on the other hand should be a good

inducer of π-bond localization in aromatic systems.[8f] Since any bond-localization would reduce the ring current on the [14] π ring in dimethyldihydropyrene **5**, and therefore would affect the chemical shift of the internal methyl protons greatly, compound **5** then is an excellent probe molecule to study the bond-fixation caused by small ring fusion.[22] The mono adduct of furan, **46c**, has significant bond alternation in its X-ray structure,[21] which is consistent with the NMR data of **46c**.[22] To study further the interaction causing the bond-alternation or ring current reduction in these macrocyclic annulenes, we decided to synthesize compounds **70** and **71**. Thus compound **70**, mp 112-113 °C, was produced by H_2/PtO_2 hydrogenation of **46c** in ethyl acetate at room temperature. The chemical shifts of the internal methyl protons of compound **70** shifts to δ -4.13 and -4.23 from δ-3.34 and -3.51ppm in **46c** (Scheme 22).



46c

Scheme 22

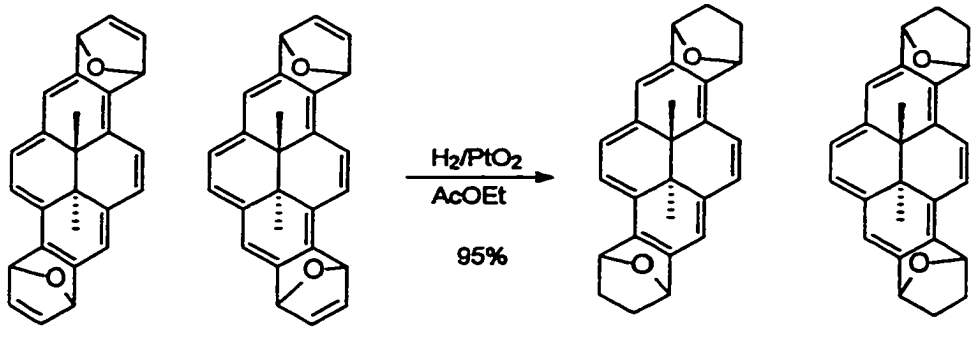


46c **70**

Similarly isomers **71** were obtained in the same way from compounds **47/48** (as a mixture of *cisoid* and *transoid* isomers) (Scheme 23). The ^1H NMR spectrum of the products,

a mixture of isomers, should have in total eight singlets for its internal methyl protons.

Scheme 23



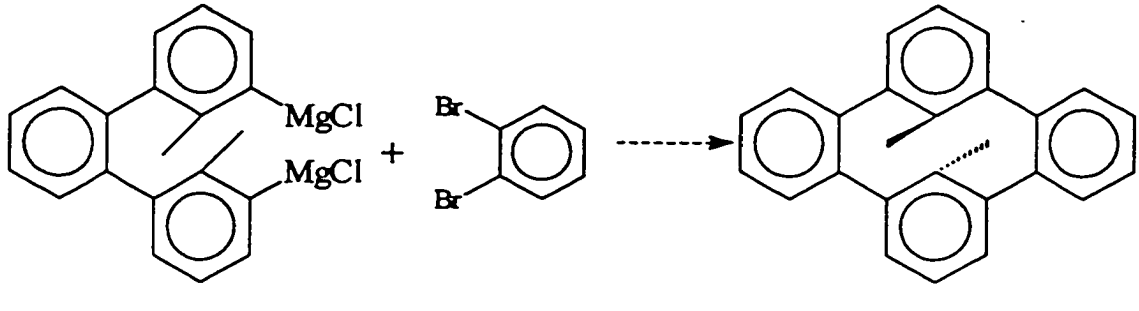
47 48 71a 71b

Experimentally, eight peaks at -3.94, -4.02, -4.18, -4.19, -4.20, -4.26, -4.36, and -4.43 were observed. No peaks were observed at more positive chemical shift than δ -3.94 for the internal methyl protons.

2.3 Synthesis of Bis [*e*] Fused Dihydropyrenes

Previous work from this group[47] and calculations[59] (see the Computation section in

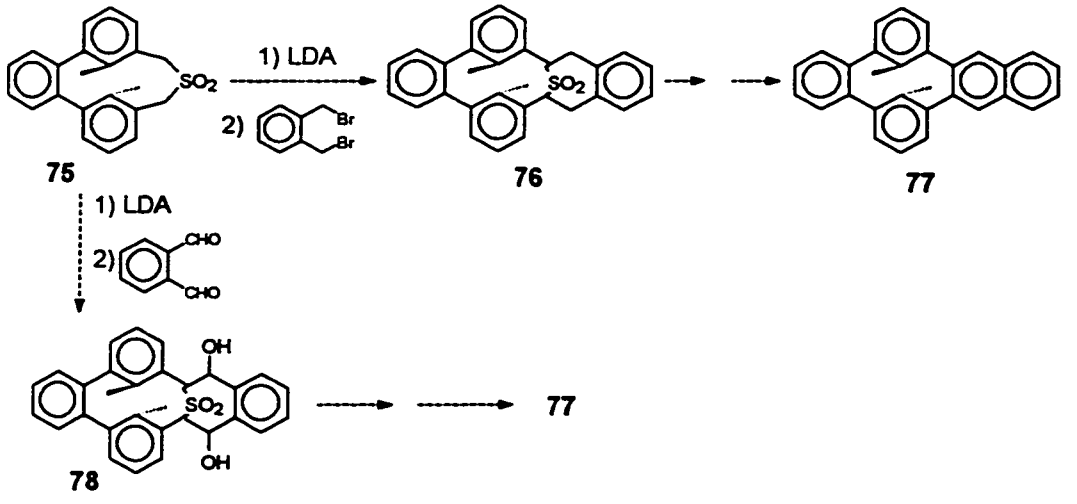
Scheme 24



72 73 74

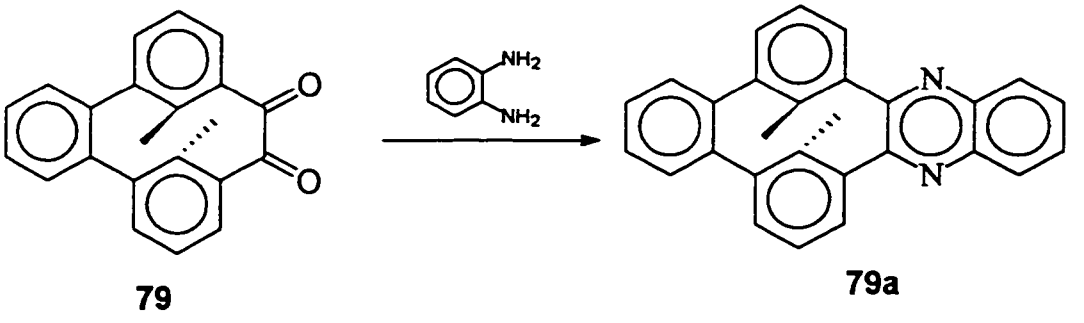
the Expermential for the details) show that [e] fused dihydropyrenes might show photoswitchable and other interesting properties. In the bis [e] fused systems, the cyclophane

Scheme 25



forms actually are calculated to be more stable than the dihydropyrenes. Our group has tried to synthesize the dibenzocyclophane **74** and its pyrene form for over 20 years. Routes tried

Scheme 26

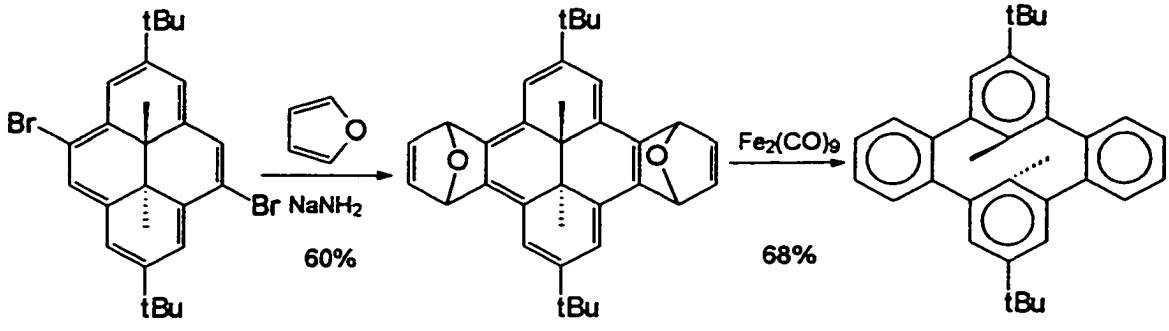


include the bis-Grignard coupling reaction, either under normal addition or inverse addition conditions (Scheme 24),[60] the bis coupling of the 1,3-dianion of sulfone **75** with *ortho*-xylylenedibromide or *ortho*-phthalaldehyde to finally yield **77** (Scheme 25)[60b], but both failed. The only synthetic strategy which was successful was the conversion of **79** to **79a**.[61]

Irradiation of **79a** produced a coloured species, probably the dihydropyrene, but it was not stable enough to characterize.[61](Scheme 26)

A retro-synthetic study of the target molecules shows it might be possible to

Scheme 27

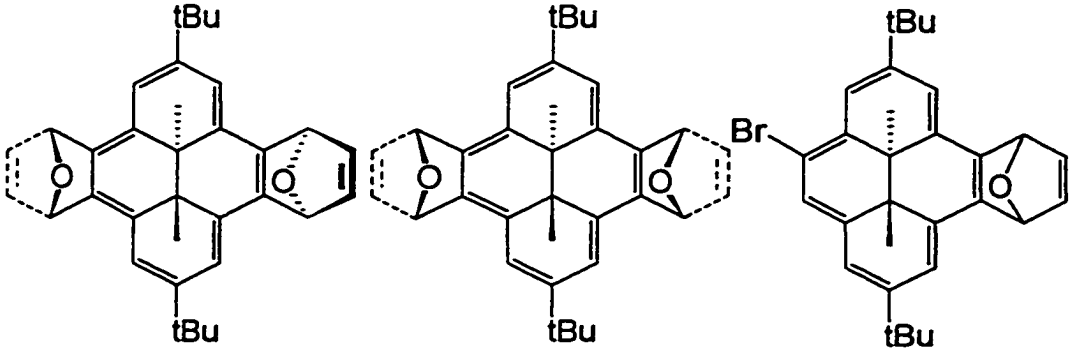


44a **81** **82a**

synthesize the target molecules though double Diels-Alder reactions, if we have the right precursors for the di-aryne intermediates as seen in Scheme **10**.

In fact, the reaction of the dibromide **44a** with $NaNH_2$ as the base to generate the aryne intermediate in THF, and the subsequent Diels-Alder reaction of this with furan at room temperature gave 59% yield of the desired bis-adducts **81** as a 1:1 mixture of two isomers (Scheme 27) along with a minor amount of the mono adduct **81c**. The all *anti* isomer **81a**, mp 236-238 °C, could be separated by fractional recrystallization from cyclohexane. This isomer has C_i symmetry, and thus shows one singlet for its internal methyl protons at δ -3.99. The more soluble isomer **81b**, which has C_s symmetry, shows two singlets at δ -3.70 and -4.30 for its two internal methyl protons. Their structures are also apparent from the CI MS (MH^+ at 477) and satisfactory elemental analyses. The still very negative chemical shifts of the

internal methyl protons and UV properties of **81** show these compounds are dihydropyrenes

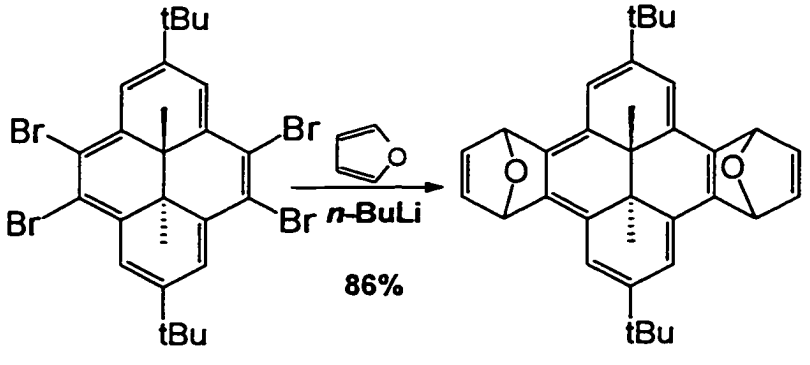


81a **81b** **81c**

and not cyclophanedienes. Note that the chemical shift difference between the two internal methyl protons in the C_s isomer **81b** is large (0.60ppm). This is unusual and probably is caused by the bending of the [14]annulene ring in this isomer.

The similar reaction for the tetrabromide **80** (made from pyrene **43** using Br_2/CCl_4)[55], but with BuLi as the base, gave a better yield (86%) of **81** and the reaction was complete in 2-3 hours (Scheme 28).

Scheme 28

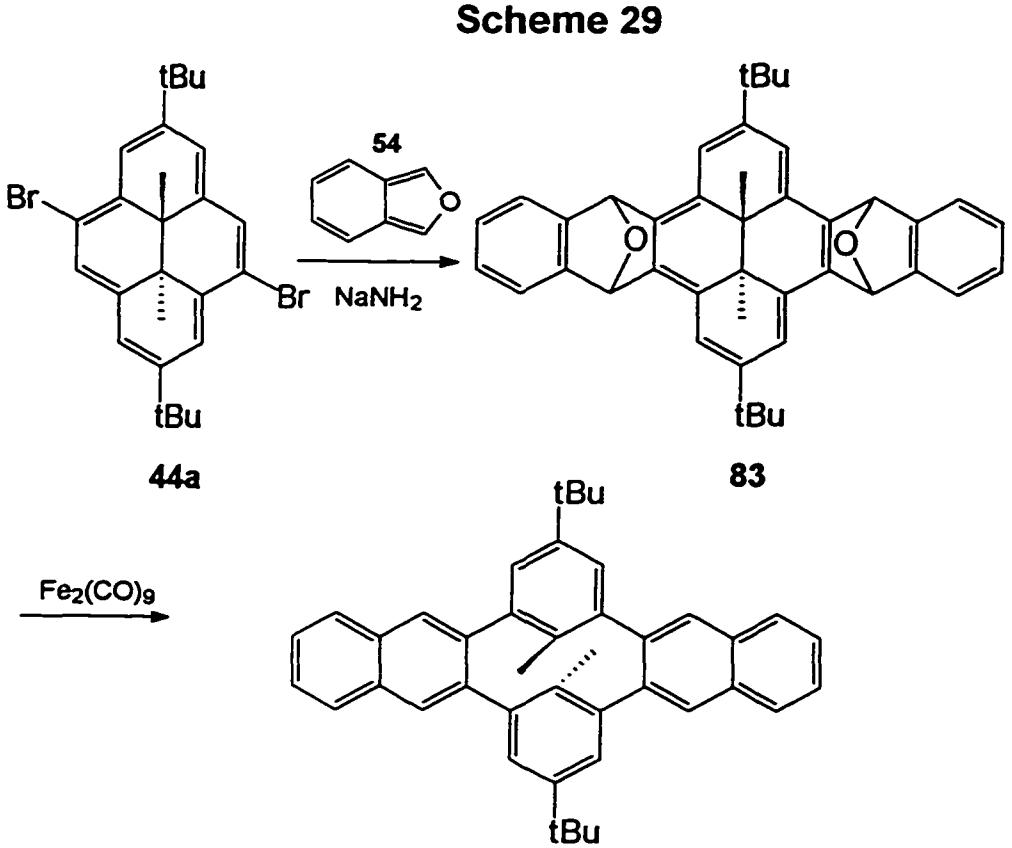


80 **81**

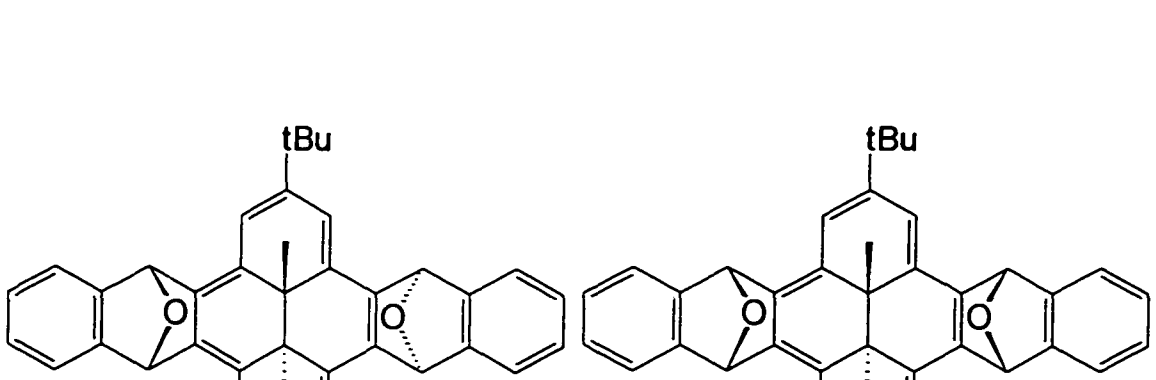
Reaction of the bis-adducts **81** with $Fe_2(CO)_9$ (Scheme 27) in benzene at 65 °C gave 68% of the colourless cyclophane **82a**, mp 231-232 °C. The structure of **82a** was proved by its CI mass spectrum, $MH^+ = 445$, and CH analysis, together with its ^1H NMR spectrum which showed the internal methyls protons shielded at δ 1.07, consistent with those of other cyclophanes and much different from that of dihydropyrenes. The *t*-butyl groups also are less deshielded in **82a** (δ 1.29) than in **81** (δ 1.67). Moreover, the compound only exhibited weak UV absorption beyond λ_{max} (cyclohexane) 287 nm (12,000), unlike the dihydropyrenes which are all intensely coloured and have very strong absorption above 300 nm. The cyclophanediene form, **82a**, is then the thermodynamically stable isomer in this case. This is consistent with our AM1 calculations,[47,62] which suggests that **82a** has an enthalpy of formation about 18 kcal/mole lower than that of **82b**. Quantitatively, this calculation result agrees well with our experimental one, i.e., that the cyclophane form **82a** is 20 kcal/mol lower in enthalpy than **82b** (See below)

We next tried to prepare the naphthalene fused system. Reaction of **44a** with an excess of isobenzofuran **54** generated in situ from 1-methoxy-phthalan **52** (See Scheme 16) in THF in the presence of excess of $NaNH_2$ yielded 33% of the bis adducts **83** with some 35% of mono adduct **84** (Scheme 29). For the bis adducts, two isomers were found, with the internal methyl protons of the C_i isomer **83a** at δ -4.39 and those of C_s isomer **83b** δ -3.66 and -5.17 respectively. (Note this is an even larger difference than for **81b**). Although the

Scheme 29



44a **83** **85**



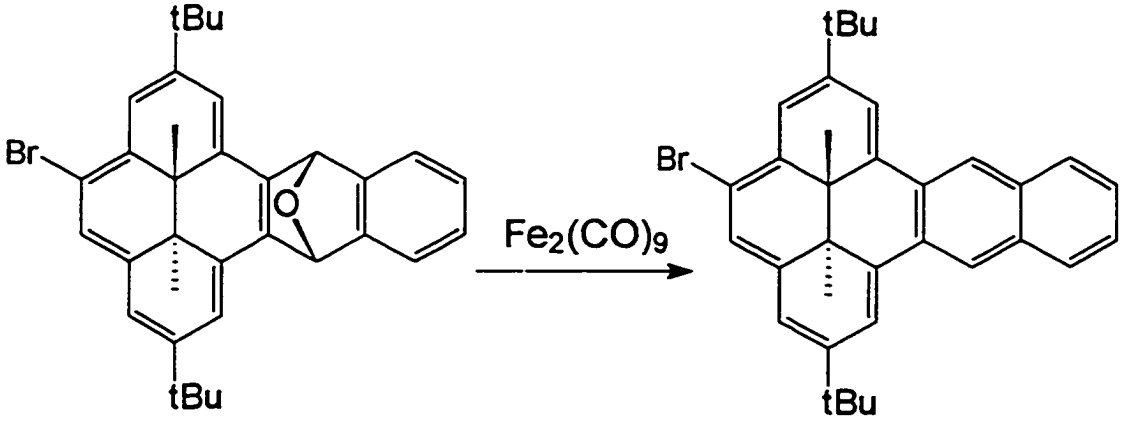
83a **83b**

two isomers could not be separated from each other, the mixture gave a correct CI mass spectrum and CH analysis.

The deoxygenation of **83** with $Fe_2(CO)_9$ in benzene gave the colourless cyclophane **85a**, mp 340-342 °C, in 95% yield. The structure of this compound was indicated by its proton NMR spectrum with the peak for its internal methyl protons at δ1.06, consistent with the benzene fused compound **82a**, together with its CI MS (MH^+ 545) and a satisfactory CH analysis. Like **82a**, the cyclophane form **85a** was the isomer isolated.

The mono adducts **84** when treated with $Fe_2(CO)_9$ in benzene gave the deoxygenated product **86** in pyrene form (Scheme 30). The chemical shift of the internal methyl protons is

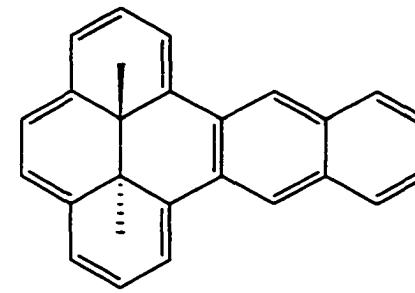
Scheme 30



84 **86**

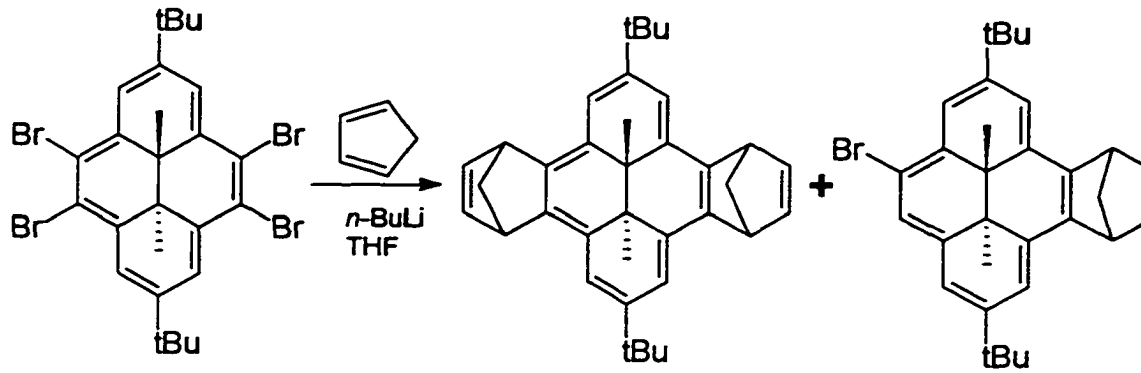
δ -0.43, very close to the parent mono naphtho-fused system **87** (δ-0.49).[63]

We thought it would be worthwhile to react cyclopentadiene with the [14]annulyne intermediate derived from **44a** to generate compounds like **81** in which the O was replaced by a CH_2. However dibromide **44a** might not be suitable for this reaction, since the strong base ($NaNH_2$) used would deprotonate the acidic protons of cyclopentadiene



87

Scheme 31

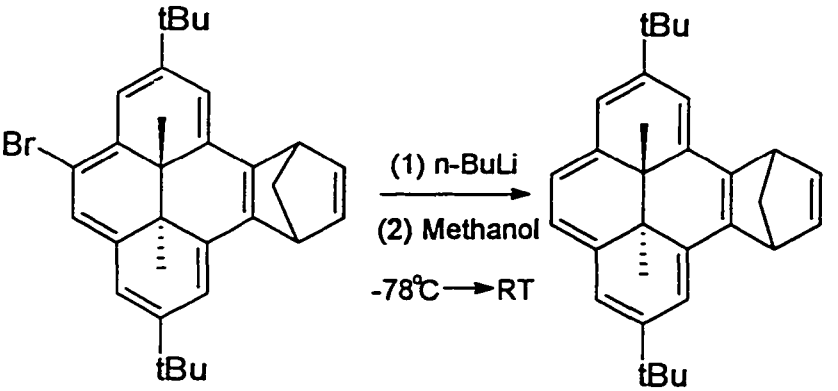


80 **88a,b** **89**

first.[64] We thus reacted the tetrabromide **80** [55]with BuLi at low temperature to give the annulyne which then was reacted with freshly distilled cyclopentadiene[64] (Scheme 31) to give the desired bis adducts **88a,b** (1:1) in 89% yield. Some mono adduct **89** (~5%) was also isolated. As expected, for the bis adducts **88a** and **88b**, **88a** has C_i symmetry and hence has one singlet for its two internal methyl protons at δ -4.12 and the C_s isomer, **88b**, has two singlets at δ -3.83 and -4.42. These two isomers were not separable by recrystallization or chromatography. The CI MS ($MH^+ = 473$) and satisfactory CH analysis combined with the NMR spectrum confirm their structures.

The mono-adduct **89** consists of two pairs of enantiomers, corresponding to the two positions for the bromine atom shown, each pair shows two singlets for the internal methyl protons at δ -3.50, -3.75 for one pair and δ -3.51, -3.76 for the other pair. We also saw trace amounts of the mono adducts **90**. Compared with the similar mono adducts, **81c** (δ -3.12 to -

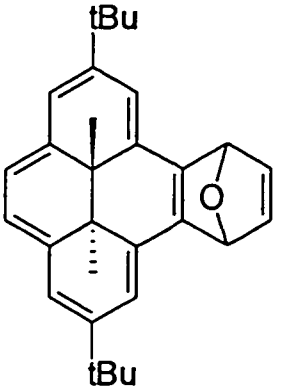
Scheme 32



89 **90**

3.42 for the internal methyl protons) from furan addition, compound **89** has more negative chemical shifts for its internal methyl protons. This means that the cyclopentadiene adduct fragment affects the chemical shifts (therefore the ring current of the [14]-macrocyclic ring) less than for the furan adduct. We present a more detailed discussion about this issue in the next chapter.

To prove that the bromine atoms have no significant effect on the ring current, we reduced compound **89** with *n*-BuLi/MeOH at -78 °C to give compound **90** (Scheme 32). The latter shows its internal methyl protons at δ -3.52 and -3.77, almost unchanged from those in the bromides **89**. The structure



91

of compound **90** is supported from its CI MS ($MH^+ = 409$) and HR MS (408.2826 consistent with the calculated 408.2817 for $C_{31}H_{36}$).

Similarly, bromide **81c** was reduced to compound **91**.

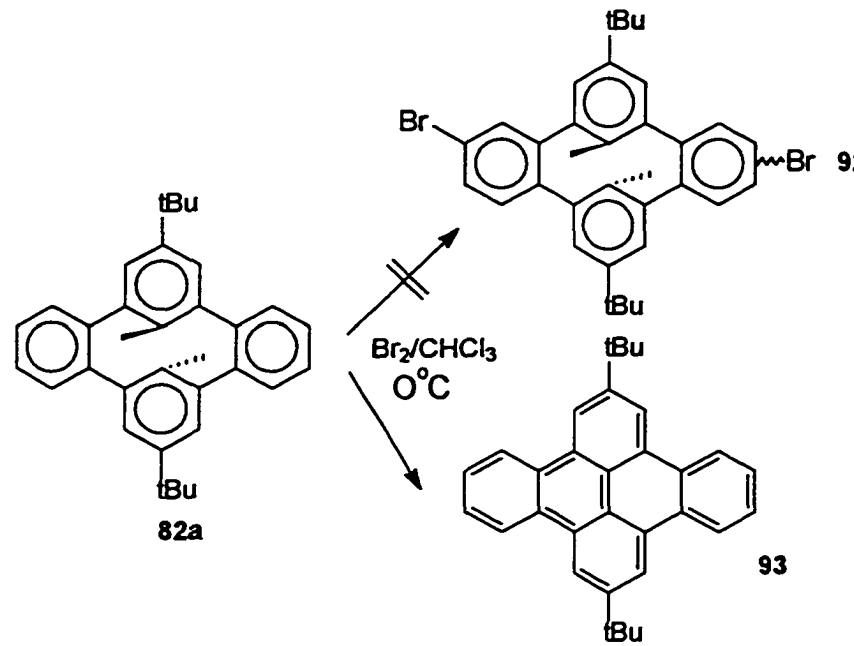
Hydrogenation of compounds **90** and **91** using H_2/PtO_2 yields compounds **90a** and **91a** respectively (see the structures in the Experimental).

2.4 Synthesis of the Substituted Bis [e] Fused Dihydropyrenes

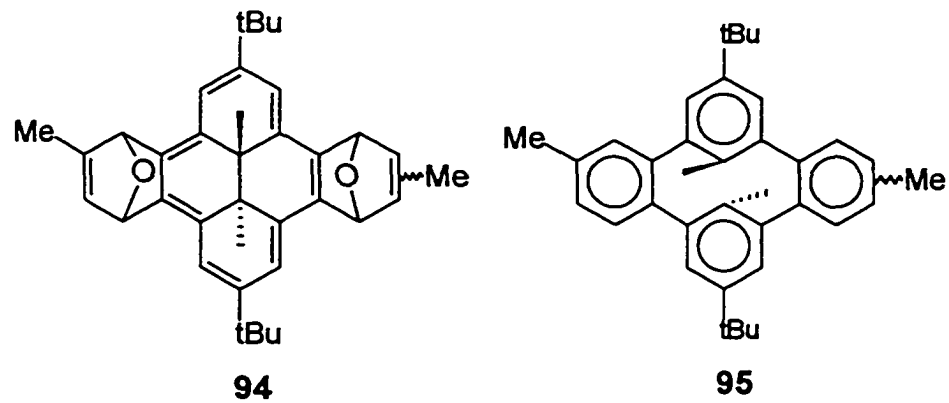
One goal of this project was to produce photoswitchable molecules. Indeed, compound **82** does show this interesting property both in solution and in the *solid state* (see the next chapter). However, its pyrene form **82b** reverts to its cyclophane form **82a** at room temperature thermally. For a better photoswichable molecule, we possibly need to functionalize compound **82** (See the next chapter for reasons). We thus first tried to prepare the bromide **92** (Scheme 33). Disappointingly, **82a** on bromination gave **93** in almost quantitative yield. Obviously the driving force for this reaction is the release of strain on the removal of the internal methyl groups and formation of the highly aromatic dibenzopyrene. The colourless dibenzopyrene **93**, mp 286-288 °C, shows an AA'MM' splitting (δ 8.85 and 7.72) and a singlet at δ 8.95 for its aromatic protons in its proton NMR spectrum. They are

all deshielded compared with those in the cyclophane **82a** due to the stronger ring current

Scheme 33



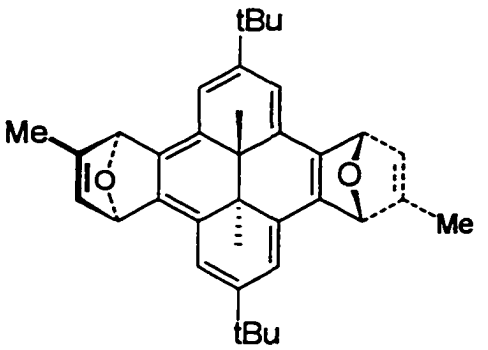
deshielding effect in **93**. No peaks were seen in the upfield region above 0 ppm. Compound **93** also shows a typical dibenzopyrene UV-Vis spectrum (with fine structure) .[24] Its structure



was confirmed by the CI MS MH^+ peak at 415 and HR MS = 414.2375 (calc 414.2347 for $C_{32}H_{30}$).

Next, the milder $I_2/CuCl_2$ conditions[65] was tried. But again compound **93** was obtained in 83% yield.

We thus decided to introduce the substituent at an earlier stage. Reaction of 3-methylfuran, made from methyl chloroacetate and 4,4-dimethoxy-2-butanone in a four-step process,[66] with tetra bromide **80** gave the bis adducts **94** in 42% yield. Theoretically, there are



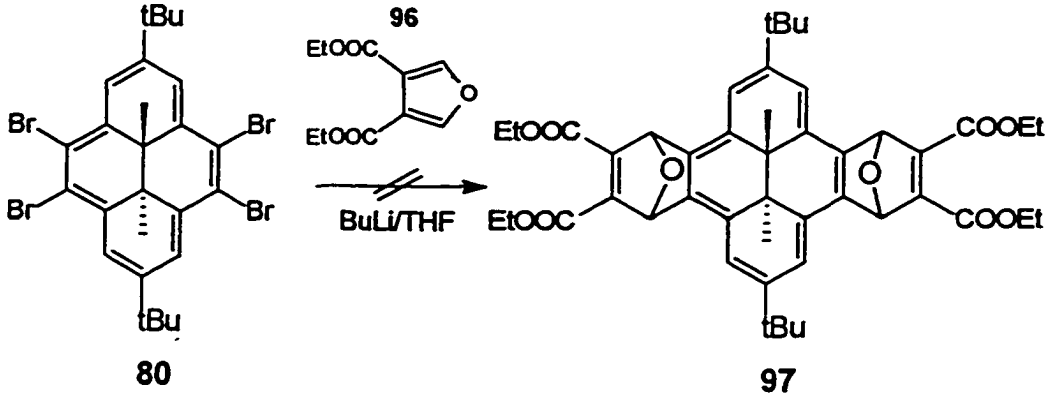
94a

seven isomers of the bis adducts possible and nine singlet peaks for their internal methyl protons. Indeed, in the proton NMR of the mixture of bis adducts, we saw 9 singlets in three groups centred at -3.67 , -3.93 and -4.21 ppm respectively. By fractional recrystallization, we were able to isolate one pure *anti-anti*-isomer **94a**. Its structure was easily established by its CI MS and CH analysis and NMR spectrum, which showed just one singlet for its internal methyl protons due to its C_i symmetry. Both the pure isomer and the mixture of the bis-adducts gave a CI MS MH^+ peak at 505 as expected and a satisfactory CH analysis.

These bis-adducts, **94**, underwent deoxygenation under the standard conditions with $Fe_2(CO)_9$ to generate the colourless cyclophane **95** in 98% yield. Again its structure was

apparent from its CI MS, NMR spectra and CH analysis. Like that of **82a**, its UV-Vis spectrum does not show any significant absorption above 280 nm. Compound **95** shows the same photochromic property as compound **82**.

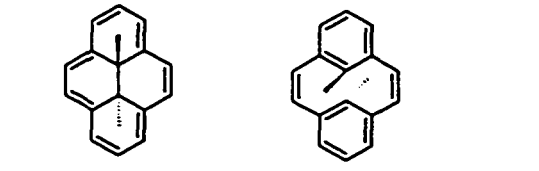
Scheme 34



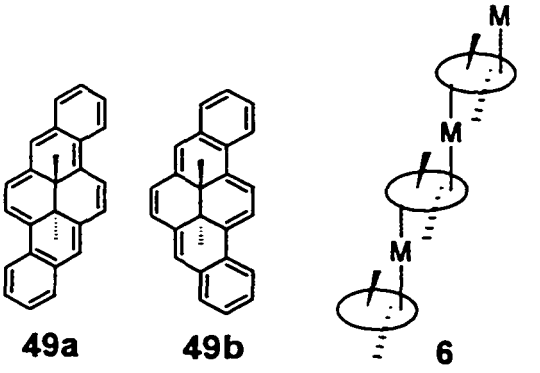
We also attempted the Diels-Alder reaction using diethyl-3,4-furandicarboxylate **96**.[67] However this failed, probably because diene 96 is too electron poor. Most of the diene **96** was recovered from the reaction, but the pyrene **80** decomposed. So obviously the annulyne was generated.

2.5 Synthesis of Metal Complexes

Another main synthetic goal of this project was to synthesize metal complexes of the bis-fused pyrene systems. Very few metal complexes of large ring annulenes are known,[68] and the only reported metal complexes of benzannulenes are from this group.[69] There is no report on the metal complexes of bis benzannulenes or bis metal complexes of benzannulenes. This in part is probably because of the limited accessibility and the stability of both the annulenes and their metal complexes. The synthesis in reasonable quantities of bis benzannulenes in this thesis makes it possible to study the metal complexation of these bis fused benzannulenes. Furthermore, it has been postulated that polymers of π-complexed metal



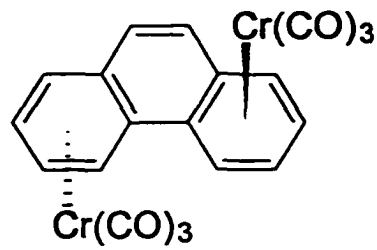
5a, pyrene **5b, cyclophane**



49a **49b** **6**

complexes such as **6** are potential organic conductors.[23] Inclusion of a dihydropyrene unit as part of the complexing unit is especially attractive because dihydropyrene **5a** and its

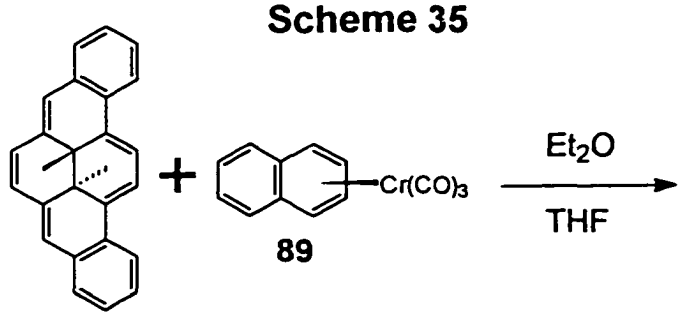
derivatives are photo-switchable to the "stepped" cyclophanediene valence isomer **5b**,[46,47] and moreover this conversion is reversible either thermally or photochemically (see Scheme 7 in Chapter one). And thus a photo-switch could be built in to such a conductor, i.e. the switch arising from the conducting "on" state (a flat fully delocalized dihydropyrene) and the non-conducting "off" state (a stepped cyclophane with non-communicating benzene sextets).[23a] Attempted bis-complexation of **49** is the first step down this path.



99

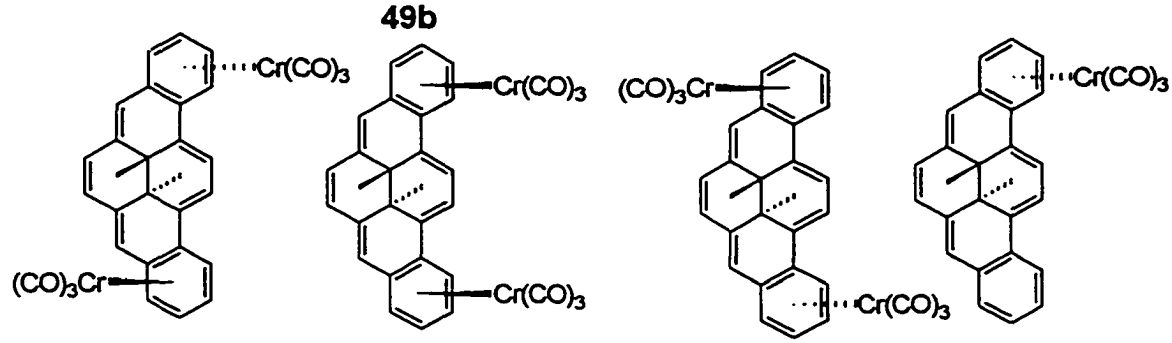
Dihydropyrenes do not survive the rather harsh conditions necessary with use of $Cr(CO)_6$.[69a] The mild ligand exchange reaction using (tricarbonylchromium)naphthalene **98**

Scheme 35



89

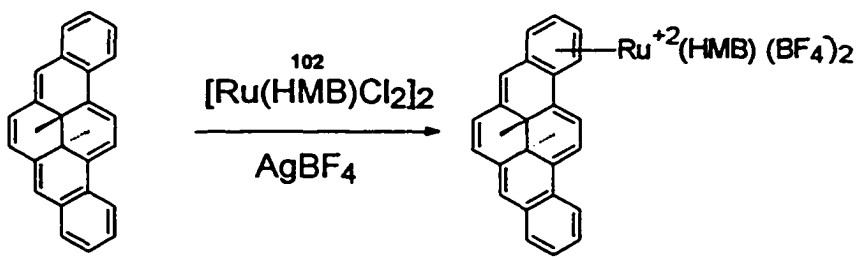
49b



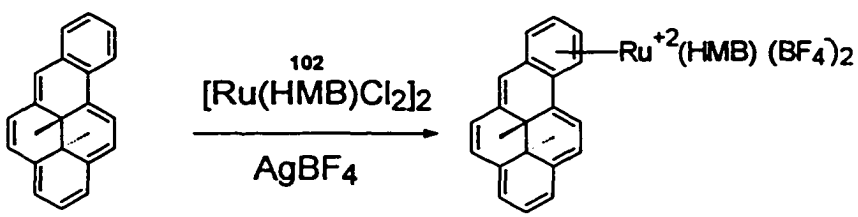
100a **100b** **100c** **101**

is better suited, providing the sextet containing ring to be complexed is more delocalized than in naphthalene itself.[69] As a model reaction, phenanthrene with (tricarbonylchromium)naphthalene **98** at 60 °C for 15 hours yielded 80% of the bis-complex **99** in better yield than the literature method.[70a] Similar reaction of **49b** gave 50% of the bis-complex **100** as a mixture of the three isomers in a ~12:4:1 ratio (Scheme 35). The major isomer would be expected to be **100a**, and this could be fractionally crystallized pure, mp 219-220 °C. It and the minor isomer **100c**, are symmetrical and thus show only one type of methyl proton at δ +0.64 and + 0.99 respectively, while the nonsymmetrical isomer **100b** shows two peaks at δ +0.86 and +0.42. The ratio of these three bis isomers indictes that the methyl groups do have orientional function in the complexing as predicted (see in the

Scheme 36



49b **103**



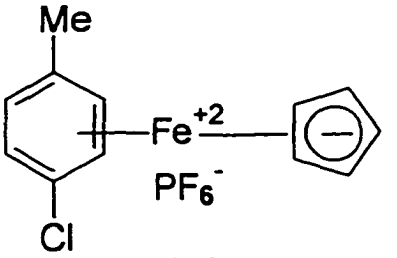
104 **105**

Introduction earlier). A small amount of mono complexed product **101** is also formed, whose

structure was supported by CIMS MH^+ peak at 484 . Disappointingly, the less stable *transoid*-isomer **49a** decomposes under these complexing conditions, and no complexed product could be isolated.

Attempted formation of the bis Ru complexes of **49a** or/and **49b** by using (hexamethylbenzene)ruthenium(II) complexes, **102**,[71b] failed, only the mono-complex **103** of **49b** could be obtained as a mixture of two isomers (Scheme 36).[70b] Although we could not get a satisfactory CH analysis for this mixture (due to the existance of starting material **102** in the product and the product's decomposition), the FAB MS (Peaks at 682 = M^+-BF_4, as well as fragment peaks) and its NMR spectrum supported their structure clearly. Two isomers (~ 1:1) were seen from the NMR spectrum with the internal methyl protons at δ 0.68 and 0.29 for one isomer and δ 0.58 and 0.20 for the other isomer. Similarly, we obtained the mono complexes **105** as a mixture of the two isomers from the mono-fused pyrene **104**. FAB MS gave a clear peak at 632 for (M^+-BF_4) fragment. In the proton NMR spectrum (d_6-acetone), one isomer shows its internal methyl protons at δ -0.49 and -0.85, and the other one at δ -0.50 and -0.91. Note the chemical shifts are different in different solvents. For instance, in $CDCl_3$, δ = - 0.52 and - 0.86 for one isomer and - 0.56 and - 0.89 for the other isomer.

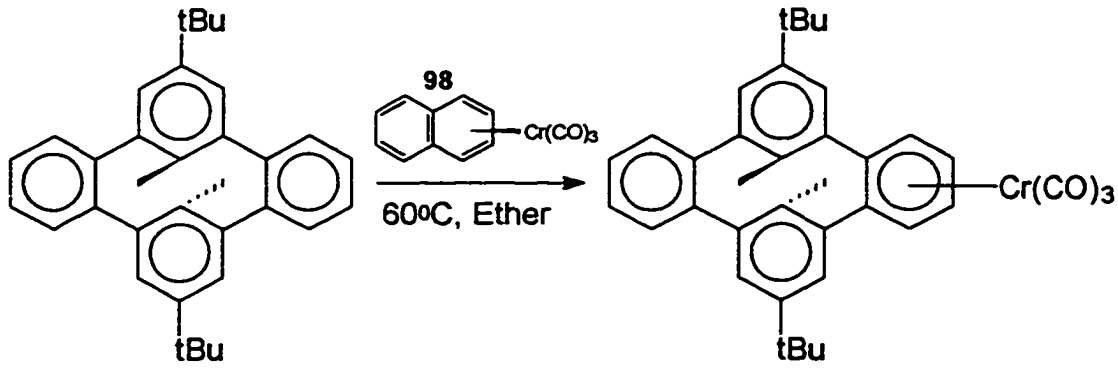
We then tried to make the similar iron complexes. Two major methods for the synthesis of iron complexes of cyclophane and fused aromatic systems have been widely used.[71-73] The first one is Bennett's photochemical exchange procedure for preparing arene-metal complexes.[71] The



106

second is the direct complextion reaction between ferrocene and the aromatic compounds

Scheme 37

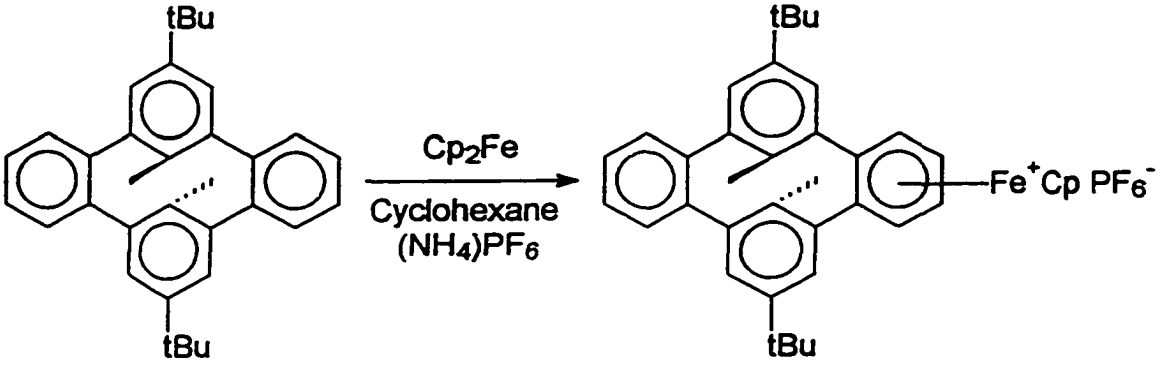


82a **107**

under lewis acid catalysis, such as $AlCl_3$.[72] Since the dihydropyrene compounds are not able to survive the harsh conditions of the ferrocene-$AlCl_3$ procedure, we decided to use the photo-catalyzed procedure.[71] Unfortunately both the reactions from **49b** and **104** with **106** failed. Only starting materials were recovered. Success of the synthesis and the photochromic properties of the [*e*] fused cyclophanedienes drove us to make the metal complexes of these cyclophanes. The reaction (Scheme 37) between an excess of (η^6-naphthalene)$Cr(CO)_3$, **98**, and the bis-fused cyclophane **82a** gave some orange solid, which in its LSI MS gave a group of peaks at 580.2 (calculated for $C_{37}H_{36}CrO_3$: 580.7). It seems some mono-complexed compound, such as **107**, was formed. But attempts to purify and characterize this product failed, probably due to the loss of the internal methyl groups and two possible complexing positions of the ligand. The reaction between $Cr(CO)_6$ and **82a** in Bu_2O gave a similar result.

Same as the [*a*] fused systems, the reaction between cyclophane **82a** with (η^6-toluene)-(η^5-cyclopentadienyl)iron hexafluorophosphate **106**, also gave recovered starting materials. Since cyclophane **82a** is much more stable than the pyrene compounds, the rather harsh conditions using Nesmeyanov's method was tried[72,73] (Scheme 38). Reaction of **82a** with

Scheme 38



82a **108**

ferrocene and $AlCl_3$/Al in cyclohexane at 110 °C yielded a mixture of metal complexes, but we were not able to purify and characterize them. But a strong peak at 565.2 (= M-PF_6) from LSI MS indicated that we may has some of the mono metal complex **108**.

Chapter Three

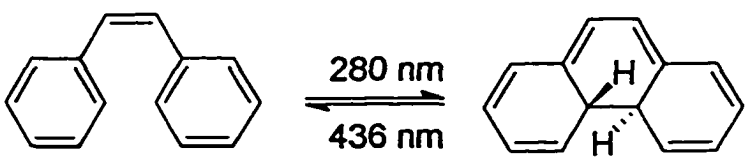
Results and Discussions

3.1 Photochromic Properties

3.1.1 Photocyclization

The photochemical process from the cyclophane compound **82a** to the pyrene-like compound **82b** is similar to that in the electrocyclization reaction from cis-stilbene to 4a,4b-

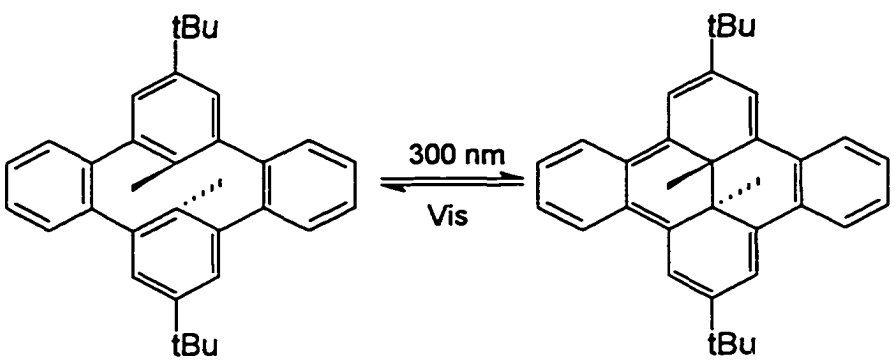
Scheme 39



109a **109b**

dihydrophenanthrene (Scheme 39).[74] Photochemical cyclization (Scheme 40) of the open

Scheme 40



82a **82b**

forms **82a** and **95a** to the closed forms **82b** and **95b** were followed directly by both ^{1}H NMR and UV spectroscopy. The solutions of the open isomers in normal glassware (NMR tube) were irradiated with UV light of 300 nm. Since the closed form isomers **82b** and **95b** tend to go back to the open form cyclophanes at room temperature, the pyrene forms were characterized at - 50 ^{0}C when the thermal return is essentially stopped.

An NMR tube containing the solution of the cyclophane (in d_8-THF) was first cooled to about - 80 ^{0}C in a cooling bath of pentane, which was cooled by liquid nitrogen outside. Then the NMR tube in a small pentane cooling bath was transferred immediately into a photochemical reactor and irradiated with light of 300 nm for ~ 1 min. We noted that a very heavy frost formed very quickly on the cooling bath and on the NMR tube and this probably blocked further photons from entering the solution for the photocyclization. The NMR tube was then transferred into the NMR instrument and the NMR spectrum was immediately recorded at the desired temperature.

The chemical shift data for both open and closed isomers of compounds **82a/b** and **95a/b** are given in Table 1 (For the ^{1}H NMR spectra, see Appendix I).

A trend is apparent from this NMR data: photocyclization of **82a** results in a considerable upfield shift of the internal methyl protons from ~ +1.07 to - 3.41 ppm ($\Delta\delta$ = 4.48) and a downfield shift of all other protons outside the rings. This clearly shows that a strongly aromatic dihydropyrene **82b** was formed. Similarly **95a** was converted into the dihydropyrene **95b** after the photocyclization and **95b** shows the same change in its NMR

Table 1. ^{1}H NMR Chemical Shift Data (360 MHz) for Dihydropyrene and Cyclophane Forms of Compounds **82** and **95**

Compounds	δ_{Me} (inside)	t-Bu	ArH	δ_{Me} (outside)
82a (open)	1.07 (s)	1.29 (s)	7.79 (q), 7.39 (q), 6.95 (s)	
82b (closed)	-3.41 (s)	1.79 (s)	9.37 (q), 7.59 (q), 9.45 (s)	
95a (open)	1.030 (s)	1.290 (s)	7.57 (s), 7.55 (s), 7.50 (m)	2.42 (s)
	1.035 (s)	1.283 (s)	7.18 - 7.21 (m), 6.92 (m)	
	1.040 (s)	1.275 (s)		
95b (closed)	-3.27 (s)	1.76 (s)	9.28 (s), 9.26 (s), 9.12 (s)	2.67 (s)
			9.09 (s), 8.95 (s), 7.40 (m)	
			7.22 (m)	

spectrum compared to **95a**. The chemical shift of the internal methyl protons of compound **82b** is in complete agreement with the predicted value (-3.31 ppm) using the average deviation of the calculated π - SCF bond orders.[27]

The photochemical conversions of the colourless cyclophanes to the deeply coloured cyclized dihydropyrene isomers were calculated using the relative integrals of corresponding pairs of proton signals for the two isomers in NMR spectra. Under the conditions mentioned above, the highest conversion of **82a** to **82b** was ~35% and for **95a** to **95b** ~20%. This is

discussed further below.

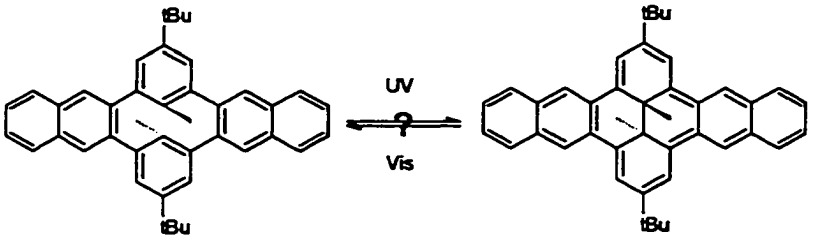
To record the UV-Vis spectrum of the dihydropyrene form **82b** on a normal UV-Vis instrument without a low temperature cell is difficult. A solution of cyclophane **82a** (~ 1 x 10^{-5} in cyclohexane or THF) was cooled to about - 50 ^{0}C in a UV cell and then was irradiated with the light of wavelength 300 nm for about 15 sec, and then the cell was transferred into the UV-Vis instrument and the scanning started immediately. The UV absorption spectra of these two isomers are very different both in the pattern and absorption coefficient (see Appendix II for the UV spectra of compounds **82a** and **82b**). The molar absorption coefficient of the dihydropyrene **82b** was *estimated* based on the conversion from the NMR spectra. Compound **82a** only shows a weak absorption maximum of λ_{max} (THF) 295nm (11,000; the molar absorption coefficient is in the unit of "mol^{-1} cm^{-1}"; same below). However the dihydropyrene isomer **82b** shows many stronger peaks with λ_{max} (THF) = 431 nm (150,000). It has a much stronger absorption than its isomer **82a**.

The conversion was not very reproducible and the highest was ~ 35% for **82a** and 20% for **95a**. Several factors may prevent us from obtaining a higher conversion. First the heavy frost on the cooling bath and on the NMR tube blocked the passage of photons into the sample. This would not only limit the conversion but also make it somewhat irreproducible. Another factor contributing to the low conversions could come from the wavelength of the light used for the photocyclization. To obtain maximum conversion of **82a** to **82b**, the light used should have wavelength of the maximum of absorption for compound **82a**, but also where **82b** has the minium absorption at the same wavelength. Compound **82a** has its maximum absorption at λ_{max} = 295 nm (ϵ_{295} = 11,000), but at the same wavelength compound

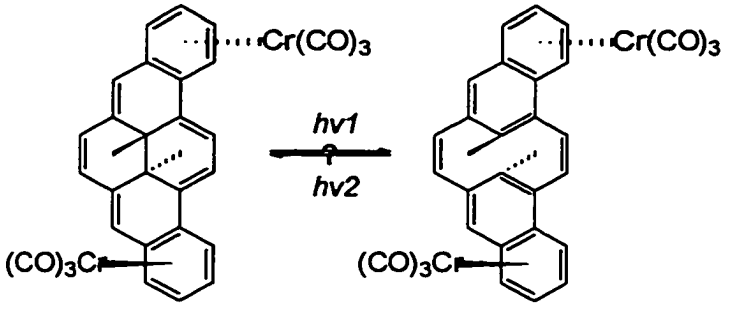
82b has a much stronger absorption (ϵ_{295} = ~ 60,000). This means most of the photons arriving into the solution were absorbed by the product **82b** and hence drove the reaction back to the starting compound **82a**. Compound **82b** has less absorption under 300 nm, and thus it might be better to use light of wavelength under 300 nm, but then a quartz NMR tube or flask is required otherwise most of the photons below 300 nm would not pass though the normal glassware to photoactivate the compound **82a**. Another factor which may affect the conversion is the ratio of the quantum yields of the two directions of the photochemical process.

In summary, we believe at least three factors may have prevented us from obtaining a higher (complete) conversion: 1) The frost on the cooling bath and NMR tube; 2) The

Scheme 41



85a **85b**



100a **100d**

closed isomer **82b** has a much higher absorption than open isomer **82a**; and 3) The normal glass has absorbed many photons below 300 nm. For more detailed studies, the proper instruments are necessary.

For the bis naphtho-fused compound **85a**, no photocyclization product dihydropyrene **85b** could be detected using NMR or UV (Scheme 41). No colour change was seen when a solution of **85a** was irradiated with 300 nm light even at - 80°C. When irradiated with visible light, the bis [a] fused products **49** and the bis metal complexes **100** also did not give any detectable photo opened cyclophane products. Note for the metal complexes **100**, the isolated forms are the dihydropyrene isomers **100a**. Further discussion is presented below.

3.1.2 Photochemical Opening and Photofatigue

Photochemical decolourations of the dihydropyrenes **82** and **95** were carried out by irradiating solutions of mixtures of the closed isomers (**82b** or **95b**) and the open isomers (**82a** or **95a**) generated from the photocyclization reactions with visible light (tungsten lamp) in a chamber at -40 to -50°C. Clean and complete conversion of the closed isomer to the open one was observed in all cases for both **82b/82a** and **95b/95a**. Unlike the photocyclization form **82a/95a** to **82b/95b**, the reverse reaction, photochemical opening reaction from **82b/95b** to **82a/95a** is a complete conversion reaction. In all cases, the complete decolouration needed less than 1 min. From these results, one can conclude that the photochromic processes are fully reversible (see the NMR and UV spectra after decolouration in Appendices I and II).

For the pair **82a/82b**, further photofatigue was tested. After over ten colouration-decolouration cycles were carried out in solution, no detectable decomposition was observed from the NMR spectra.

No decomposition (from NMR spectra and UV) was observed from the solution of **82a** in cyclohexane stored at -7°C after about six months and the solution still showed the same photoswitchable properties. This indicates that at this temperature the cyclophane form has good thermal stability.

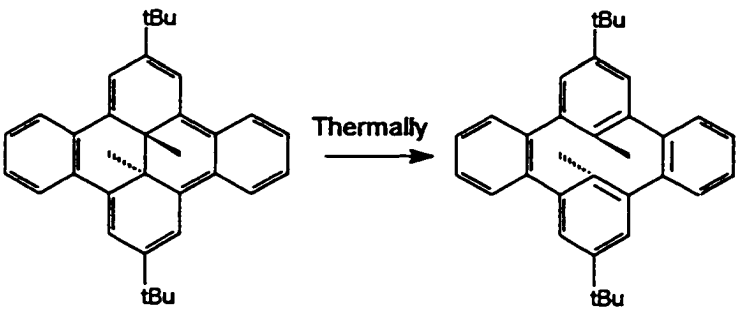
For practical applications, it is more important that the compound shows photoswitchable properties in the solid state. So we prepared a polymer based film of compound **82a** in polystyrene. Very impressively, the film shows the same reversible photochromic properties. Even after ~15 cycles (no more cycles were tested), the film still showed the same reversible colour change. Furthermore in the solid state it seems that the thermal return to **82a** is much slower than that in solution, since now the colour of **82b** lasts about 2-3 seconds at room temperature before it reverted to the colourless **82a**. After more than one year at 7°C, this film still shows the reversible photoswiching process and no decomposition is observed. We have also made a casting of compound **82a** on Silica gel and Alumina. Although the reversible photochromic process can be seen, significant decomposition was obtained after a couple of cycles.

In summary, these results show the two pairs of compounds **82a/b** and **95a/b** have reversible photochromism with fatigue resistance both in the solution and in the solid state and these make them potential candidates for photo memory units and other applications.

3.1.3 Thermal Decay of the Dihydropyrene Isomers 82b/95b to the Cyclophanes Isomers 82a/95a

The shortcoming of these photochromic compounds are that the dihydropyrene isomers thermally return back to the cyclophane isomers. In solution, the dihydropyrene forms can not be detected at room temperature using UV or NMR spectroscopy. No typical green colour of the dihydropyrene was seen either at this temperature when a solution of **82a** was irradiated. The lifetime of the dihydropyrene isomer must therefore be very short at

Scheme 42



82b **82a**

room temperature. As mentioned earlier, the photochromic films made from polystyrene with compound **82** show much slower thermochromism and the life time of the dihydropyrene isomer **82b** in the solid state is much longer, in the range of 2-3 seconds at room temperature as now the green colour lasts several seconds. So clearly, the polymeric matrix could stabilize the dihydropyrene forms.

The thermal decay of **82b/95b** to their cyclophane forms (Scheme 42) was monitored

using VT NMR. Table **2** shows the kinetic rate constants and the half-lifes of the dihydropyrene isomers of **82**. The thermodynamic data E_{act}; $\Delta H^{\ddagger}$; $\Delta S^{\ddagger}$ were generated from plotting ln k *vs* 1/T and ln (k/T) *vs* 1/T (see Appendix III for a set of VT-NMR spectra used for the plotting and the plots for rate constants and the thermodynamic data calculations).

Table 2. First Order Rate Constants and Half-lives for the Thermal Opening of the Dihydropyrene form **82b**[a]

T (± 2 K)	k (s^{-1})	$t_{1/2}$ (sec)
233	$(2.86 \pm 0.19) \times 10^{-5}$	$(2.42 \pm 0.18) \times 10^{4}$
243	$(2.16 \pm 0.12) \times 10^{-4}$	$(3.21 \pm 0.17) \times 10^{3}$
253	$(9.45 \pm 0.11) \times 10^{-4}$	$(7.33 \pm 0.09) \times 10^{2}$
263	$(4.26 \pm 0.08) \times 10^{-3}$	$(1.63 \pm 0.03) \times 10^{2}$
298[b]	$(3.97 \pm 0.08) \times 10^{-1}$	$(1.70 \pm 0.03) \times 10^{0}$

E_{act} = 20.1 (± 0.7) kcal/mol; $\Delta H^{\ddagger}$ = 19.6 (± 0.7) kcal/mol; $\Delta S^{\ddagger}$ = 5.5 (± 2.7) cal/mol K.

(a): For solution in d_8-THF. (b): Data at T = 298 K are estimated.

For the pair **95a** and **95b**, NMR studies gave similar results with E_{act} = 16.9 (± 2.5) kcal/mol; $\Delta H^{\ddagger}$ = 16.4 (± 2.5) kcal/mol; $\Delta S^{\ddagger}$ = 1.2 (± 9.8) cal/mol K. Since the conversion of compound **95a** to **95b** is lower, the accuracy of the calculation results is very limited, especially the value of $\Delta S^{\ddagger}$.

From the spectra of NMR and UV after the decolouration, both the photo and thermal ring opening of **82b/95b** to **82a/95a** were quantitative (see the spectra in Appendix I and II).

Although the stable form of the bis naphtho[e] compound **85** is the cyclophane form **85a**, irradiation of the **85a** even - 80 ^{0}C with 300 nm light leads to no detectable dihydropyrene **85b**.

From our previous studies in all the [a] fused compounds, the thermodynamically preferred isomers are the dihydropyrene forms.[47] When the solutions of these [a] fused dihydropyrenes (including the mono and bis fused systems) are irradiated with visible light at room temperature, no detectable diene isomers of these dihydropyrenes were recorded. For the mono [e] fused systems such as **87** and **109**, the isolated forms are the dihydropyrene forms **87b** and **109b**. But when these compounds are irradiated with visible light, the diene isomers **87a** and **109a** form quantitatively. The latter revert to **87b** and **109b** both thermally or on irradiation with UV light.

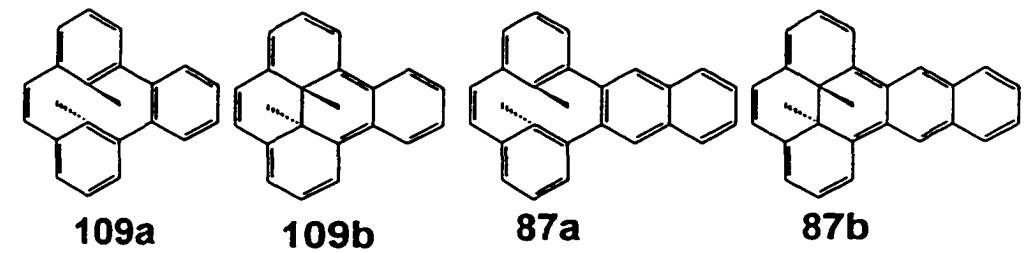
The thermodynamically preferred isomers can be estimated by calculation of H_f for the dihydropyrenes and the cyclophanes. This was carried out using Hyperchem 4.5 to do an AM1 computation (see the computation section in the Experimental).[48a]

The calculation results from AM1 for H_f with the available experimental E_{act} are summarized in Table 3. The absolute values of the calculation depend upon the parameters used in the calculation, but the differences in H_f between similar compounds are fairly reliable (± 2 Kcal/mol). Note for the parent compound **5a** and **5b** the calculated result of $\Delta H_f = 3.4$ kcal/mol is in good agreement with the experimental result (3.0 kcal/mol). This leads us to believe that the following trends are reliable: 1) for [e] fused systems, increasing fusion makes the cyclophane forms relatively more stable than the corresponding dihydropyrene forms; 2)

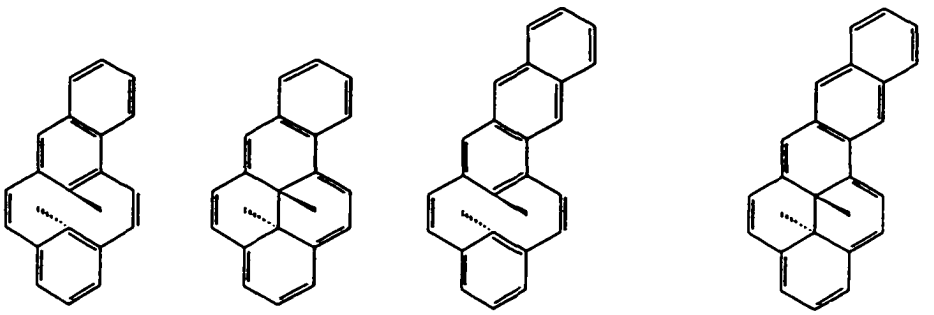
Table 3. AM1[48a] Calculations of H_f and ΔH_f (CPD-DHP) and the experimental E_{act} for Selected Compounds (kcal/mol) (For the structures, see next page)

Compd	H_f(CPD)		H_f(DHP)		ΔH_f(CPD-DHP)	E_a(CPD→DHP)	E_a(DHP→CPD)
parent	**5a**	107.8	**5b**	104.4	3.4	23	
benzo[e]	**109a**	119.5	**109b**	118.4	1.1	25	
naphtho[e]	**87a**	137.9	**87b**	137.2	0.7	25	
benzo[a]	**110a**	127.3	**110b**	116.7	10.6		
naphtho[a]	**111a**	149.5	**111b**	135.5	13.5		
bis-benzo[e]	**82a**	93.9	**82b**	111.8	- 17.9		20
bis-benzo[e]	**16a**	131.2	**16b**	149.3	- 18.1		
bis-naphtho[e]	**95a**	167.9	**95b**	194.8	- 26.9		
bis-benzo[a,e]	**112a**	139.2	**112b**	130.4	8.8		
bis-benzo[a,h]	**113a**	140.7	**113b**	150.5	- 9.8		
benzo[e]	**114a**	108.5	**114b**	111.9	- 3.4		

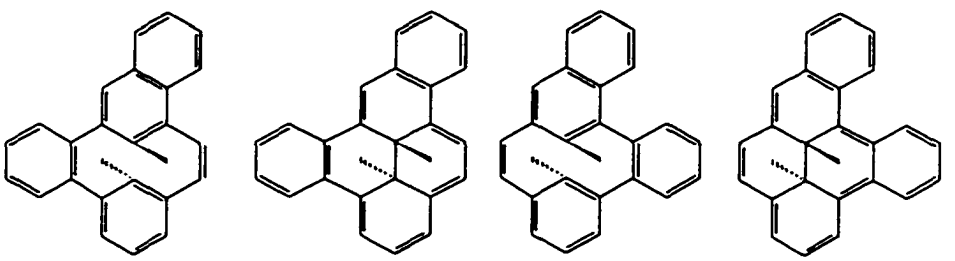
(Note for Table 3: H_f (CPD) = the heat of formation for the related cyclophane isomer; H_f (DHP) = the heat of formation for the related dihydropyrene isomer; ΔH_f (CPD - DHP) = [H_f (CPD) - H_f (DHP)]; E_a(CPD → DHP) is the activation energy for the thermal reaction from the cyclophane isomer to the dihydropyrene isomer; E_a(DHP → CPD) is the activation energy for the thermal reaction from the cyclophane isomer to the dihydropyrene isomer. See the Computation section in the Experimental).



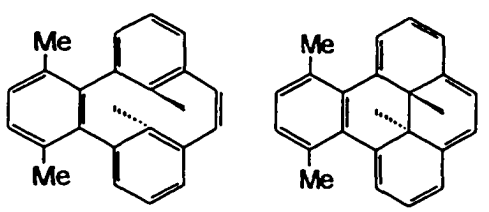
109a **109b** **87a** **87b**



110a **110b** **111a** **111b**

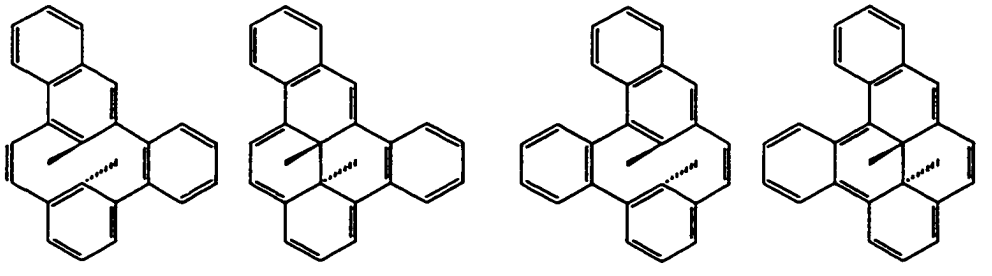


112a **112b** **113a** **113b**



114a **114b**

for [a] fused, the reverse is true, e.g. the dihydropyrene forms tend to be more stable; 3) for the same fusion, the difference in H_f between the cyclophane form and the dihydropyrene form is smaller in the [e] fused systems than that in the [a] fused systems; this indicates that the [e] fused is probably more likely to show reversible photoswiching properties; 4) although both compounds **112** and **113** are bis fused dihydropyrenes with one fused ring at the [a]

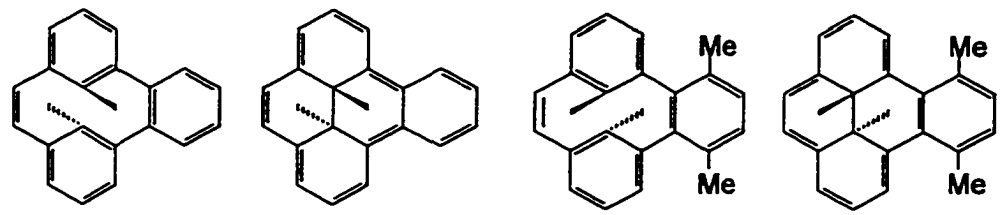


112a **112b** **113a** **113b**

position the other one at a side position, AM1 calculations indicate that the former has the dihydropyrene form to be the thermally stable one, while the latter has the cyclophane form the more stable one.

A partial energy analysis[47] based on π-SCF/MM2-type calculations (see the Computation section in the Experimential for more) using PCMODEL V5.0,[48b] indictes that for DHPs the same ring fusion causes more strain in the [*e*] series than in [*a*] series. This is probably because of increased H-interactions between the two sets of "bay" hydrogens in the [e] series, but only one set in the [a] series. In the CPDs, on the other hand, the strain energies of [a] and [e] fused isomers are almost same. Thus the main difference in the total energies of the CPDs is from the difference of the π-energies of the [e] and [a] fused isomers. Combining this with the conclusion from the AM1 calculations, it is clear that at least the increased strain energy in [*e*] series is one major driving force to stabilize the CPD forms.

Lai's work provides experimential evidence.[75] For the pair of compounds **109a** and **109b**, the dihydropyrene isomer **109b** is the thermodynamically more stable one.[47] But among the pair



109a **109b** **114a** **114b**

of compounds **114a** and **114b** synthesized by Lai and coworkers, the diene form **114a** is the thermodynamically more stable isomer.[75] Actually this is consistent with our calculation results shown in Table 3. Obviously, the adverse steric interactions between the external methyl groups and the hydrogens on the dihydropyrene moiety in the near-planar **114b** destabilize the dihydropyrene form.

The experimental and calculation results suggest that the reason no diene forms are detected when the [*a*] fused dihydropyrenes are irradiated is due to the small E_{act} for the thermal return reactions (diene → dihydropyrene). No detectable quantity of the dienes accumulate.[47] We have measured the E_{act} for the thermal return of **82b** to **82a** as 20 kcal/mol and the calculated ΔH_f between **82b** and **82a** is 18 kcal/mol. For the bis naphtho[e] compound **95**, the calculated ΔH_f between **95b** and **95a** increases to 27 kcal/mol. Since the photocyclization reaction from **95a** to **95b** should have the same mechanism as that from **82a** to **82b**, there is no obvious reason why the former photochemical cyclization to the dihydropyrene should not occur. If the suggestion that the transition state is more reactant like in this thermal decay is correct,[46,47] then one would expect the thermal E_{act} for the

dihydropyrene **95b** going to **95a** will be substantially less than that for **82b** to **82a**, and thus following the same argument for the [*a*] fused systems,[47] no appreciable quantity of **95b** will accumulate when **95a** is irradiated with UV light. Laser flash photolysis studies are under way to test this hypothesis.

Table 3 shows that compounds **112** and **113** have much closer H_f for their dihydropyrene and cyclophane forms than that of bis benzo[*e*] compound **82**. Both the dihydropyrene and cyclophane isomers of **112** and **113** should thus be detectable with normal NMR/UV methods at room temperature. Therefore these compounds probably have the better bistability required for the practical photoswitchable molecules.

Due to the rigid structure and the two *anti* internal methyl groups, the reversible photoisomization of **5a** to **5b** and of their derivatives can only proceed rotationally, i. e. with the preservation of the two axes of rotation.[76] According to the Woodward-Hofmann rules this process is allowed by symmetry in the electronically excited state, i.e., only is allowed photochemically and forbidden thermally if a concerted process. Surprisingly, the isomerization **82b/95b** (dihydropyrenes) to **82a/95a** (dienes) can also proceed thermally with a *low* E_{act} and it leads to the same product as the photochemical reaction.

From electronic configuration-correlation analysis,[76a] Schmidt has concluded that the symmetry-forbidden thermal return from the diene form **5b** to its dihydropyrene **5a** is via a doubly excited singlet of **5a**, and vice versa. The process is still a synchronous reaction rather than a biradical mechanism, since there is no effect on the rate constants/quantum yields from changing solvent or adding iodine, etc.[76a] Thus the thermal return from **82b/95b** to **82a/95a** should follow the same mechanism, that is, the ground configuration of **82b/95b** gets excited

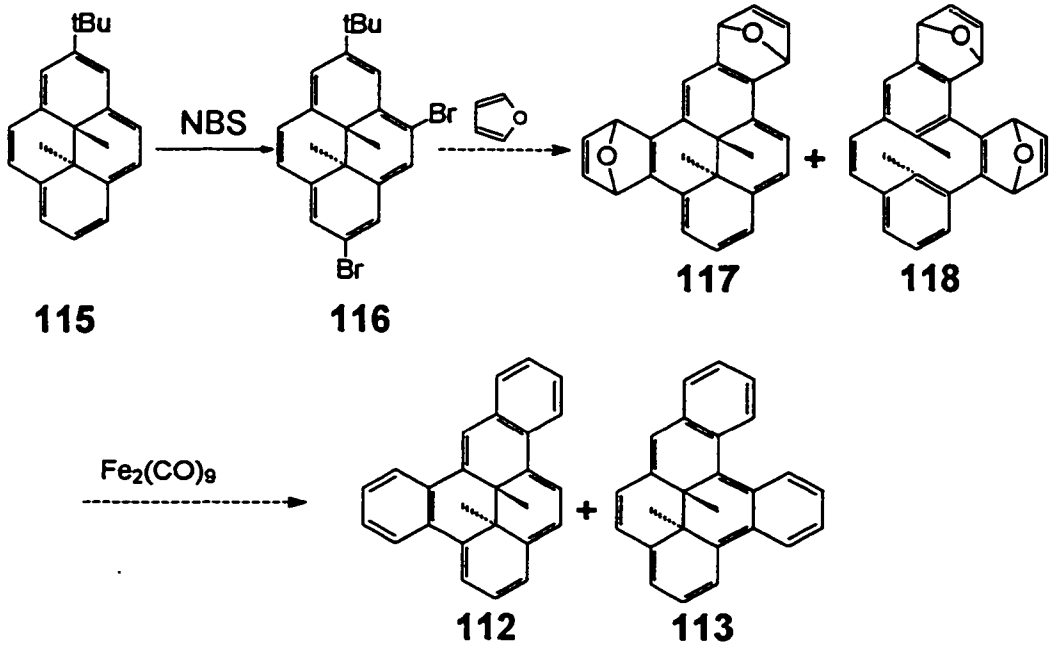
thermally - avoiding electronic relaxation - to a doubly excited singlet configuration of **82a/95a** which then goes to the ground state of **82a/95a**.

Although we did not study solvent effects of the photochemical process, we expect the processes between **82a/95a** and **82b/95b** probably proceed only via the singlet state as between **5a** and **5b**.[46]

3.1.4 For a Better Photoswich - Modification of the Current Molecules

Although compounds **82** and **95** show the photo-switch process we expected, the shortcoming of these compounds is that their dihydropyrene forms **82b/95b** thermally revert to the cyclophanes. For a practical application, this has to be overcome. Two possible

Scheme 43

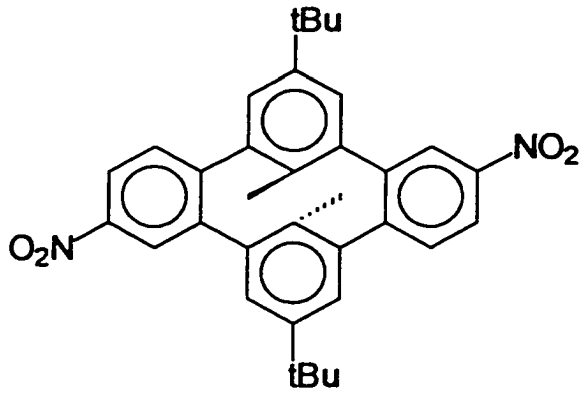


strategies are: 1) Modification of the switchable molecules and 2) utilization of polymer-matrix.

For the first strategy, compounds **112** and **113** are the immediate and obvious targets. Their synthesis should be straightforward (Scheme 43). If these compounds follow the same mechanism for the photochemical/thermal ring cyclization/opening, they should show similar photo-switch properties to those of **82/95**. Furthermore the smaller difference in H_f (see Table 3) between their dihydropyrene and diene forms should at least slow down the thermal decay (have a larger E_a) and hence make them better candidates for a photo molecular switch.

Substitutents on the rings might affect the thermal rate constants too.[46] From the detailed studies of substituted DMDHP's derivatives from Blattman and Schmidt,[46] it is seen that electron withdrawing groups increase the rate constants of the thermal return to the dihydropyrene forms. This is also true for the mono [*e*] fused systems.[60a] This indicates that although all the dihydropyrene forms are the more stable form in the above systems, electron withdrawing groups tend to stabilize the dihydropyrene forms and increase the thermal rates of return from the cyclophane form to the dihydropyrene form. Thus for the bis [*e*] fused systems we have synthesized in this thesis, we might expect a similar effect, that the rates from dihydropyrene form to the cyclophane form in our bis [e] fused systems might be slowed down by electron withdrawing groups. This may be understood as follows: the dihydropyrene forms are always relatively electron rich compared to the cyclophane forms and hence electron withdrawing groups tend to stabilize the dihydropyrene more than cyclophanes. More compounds, such as the nitrated compound **119**, are needed to test this hypothesis.

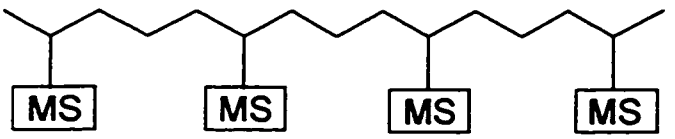
There are many reports which use polymers as the matrices for advanced materials to



119

improve their properties, including photochromic properties and stability.[20d, 35a] The typical properties of polymers like ease of processibilty, mechanical strength, long-term stability combined with the properties of the functional molecules, such as photo-switch molecules, could offer an incredible opportunity for molecular devices.

To take advantage of polymers with our molecules, three directions are worthy of pursuit. First, to slow down/stop the thermal decay from the pyrene **82b** to **82a**, the switchable molecules could be chemically bound onto the polymeric chain. In this structure, the polymer works as an "anchor" and locks the dihydropyrene forms mechanically due to their now large inertia as part of the huge polymeric backbone. This technique has been widely used to stabilize many photochromic molecules.[35a] To support this idea, we have tested and found that the thermal return rate of **82b** to **82a** has been slowed down dramatically in the solid state (a thin film made with polystyrene or alumina). Thus we want to make polymer-based compounds, such as **120**. To do this, the rings in the compounds have to be functionalized to have a handle for manipulation. Scheme **44** shows one possible route to

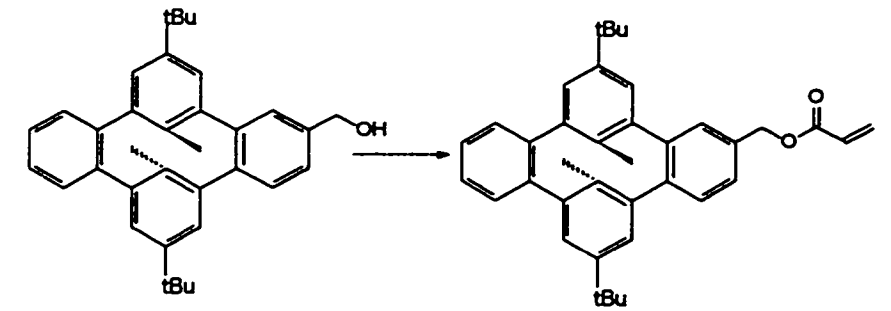


120

MS = Molecular Switch Units

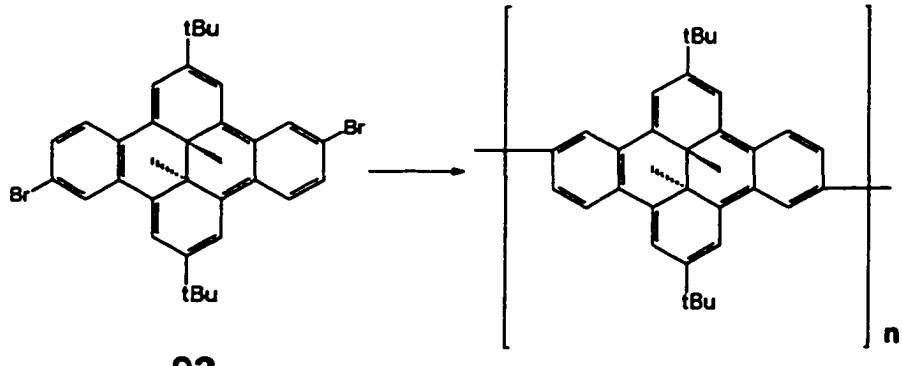
make such a copolymer. The copolymer shown should give a transparent and flexible film with good mechanical and processing properties for practical application as that of the polymer poly(methylmethacrylate)) (PMMA).

Scheme 44



An alternate strategy is to use the switchable molecule as the monomer, and directly use it to make polymers, such as **124** (Scheme 45). As far as we know, no such photochromic polymer has yet been reported. Unfortunately attempts to synthesize the precursor for this

Scheme 45

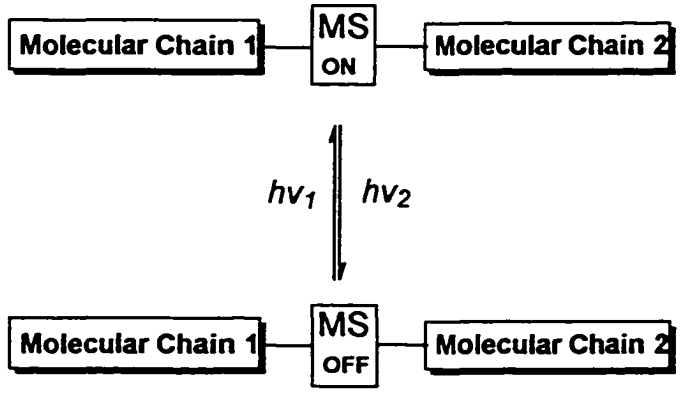


92 **124**

polymer, compound **92**, has not yet been successful. The direct halogenation of compound **82a** has only yielded compound **93** with loss of the two internal methyl groups (See Scheme 33 earlier).

The switchable molecules could also be incorporated into functional polymeric/molecular chains, e.g. to use the photo-switch molecule as the controlling gate to

Scheme 46



MS = The Molecular Switch (e.g. compounds 82 and 95)

control physical properties such as NLO properties , electronic conducting properties etc.

(Scheme 46). This is possible since the dihydropyrene form of our molecule has complete π conjugation which allows electrons to flow through it and hence works as the "on" in a switch, but the cyclophane form does not have such conjugation and therefore is the "off" state in the switch.

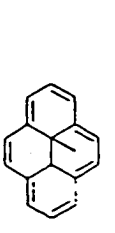
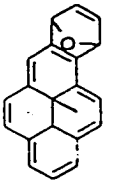
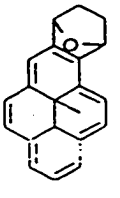
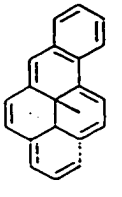
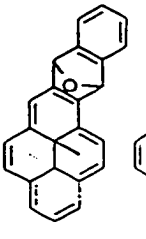
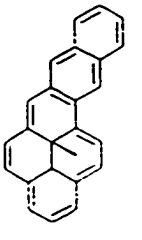
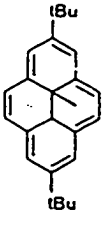
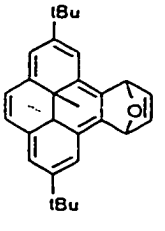
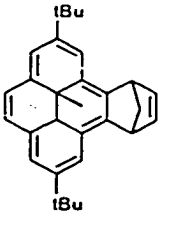
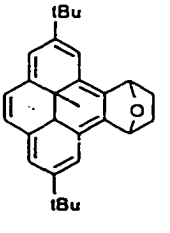
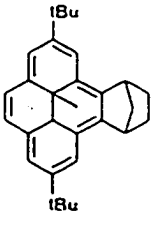
3.2 Ring Current and Relative Bond Fixing Ability (RBFA)

3.2.1 Space Anisotropy Effect of Fusion Species

Extensive work from our group has proven that the changes in chemical shifts of the internal methyl protons in compound **5a** and its derivatives is mostly caused by ring current changes in the [14] annulene.[21,22] That is, if a fusion of any fragment on the [14] ring causes any bond localization and therefore ring current change, we could use the chemical shift change to measure the bond-fixing ability of the fused fragment. But central to this proposal is the assumption that the chemical shifts of the internal methyl protons are not affected anisotropically through space by the fused fragment. This is true for relatively planar systems such as compounds **110** and **59**.[21] But it is not necessary true for non - planar systems such as the furan adducts **46, 91** and complexed systems **100**. It would be expected for these non - planar systems that the anisotropy effects through space might be larger and then the two internal methyl groups should have different chemical shifts, since the two methyl groups have

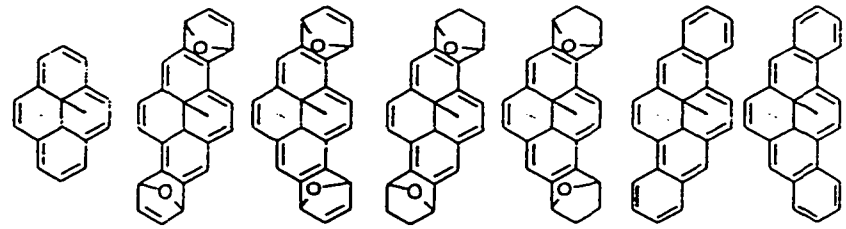
relatively very different position with respect to the fused species in these non - planar systems. Surprisingly, it can be seen from Tables 4 and 5 that the chemical shift differences between the methyl groups in these compounds are really rather small, especially in comparison to the average shifts of the two internal methyl groups from the parent pyrene **5a**.

Table 4. The Chemical Shifts of the Internal Methyl Protons for Monofused DMDHPs[a]

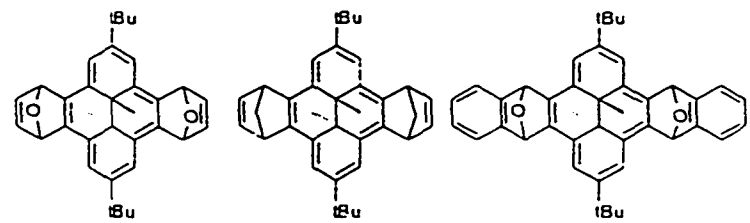
					
-4.25	-3.34 -3.51	-4.23 -4.13	-1.62 -1.63	-3.66 -4.01	-0.44
5a	46c	70	110a	58	59a
					
-4.06	-3.13 -3.38	-3.52 -3.77	-3.94 -4.12	-4.00 -4.17	
43	91	90	91a	90a	

[a] All data is from this work, except that for **5a**, **46c**, **58**, **59**, and **110a**, which can be found in ref 21 and that for compound **43** in ref 55.

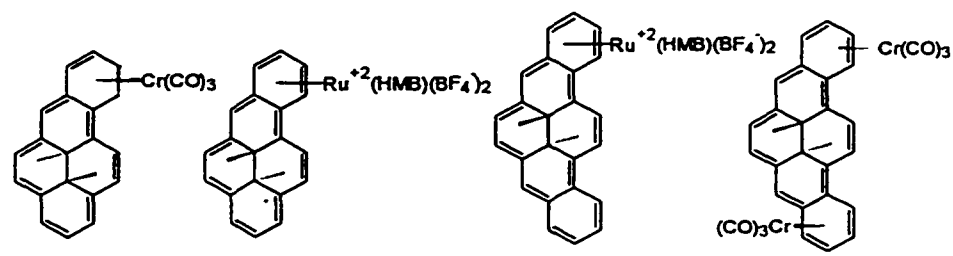
Table 5. The Chemical Shifts of the Internal Methyl Protons of Bis-fused DMDHPs and Metal Complexes[a]



- 4.25	- 4.0	- 4.3	- 3.94 to - 4.36	- 3.58	+ 0.02
5a	47	48	71a	49a	49b



- 3.99 and - 3.70, - 4.30	- 4.12 and - 3.83, - 4.42	- 4.39 and - 3.66, - 5.17
81a,b	88a,b	83a,b



- 0.87, - 0.98 - 0.81, - 1.16	- 0.52, - 0.86 - 0.56, - 0.89	+ 0.68, + 0.30 + 0.57. + 0.21	+ 0.64
125a,b	105	103	100

[a] All the data is from this work, except that for **5a**, **49a**, **49b**, and **125a**, which can be found in ref 21.

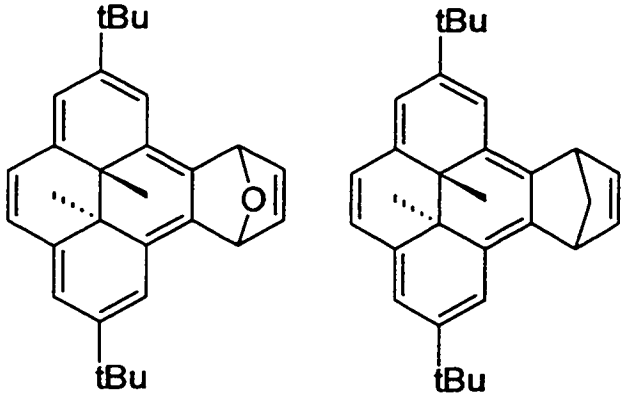
For example, in compound **125a** (Table 5), the chemical shift difference between the two methyl protons is only 0.11 ppm; while the chemical shift change of the internal methyl protons from the parent pyrene **5a** to compound **125a** is 3.32 ppm.

Based on McGlinchey's work,[77] we have proven computationally (see Appendix IV for the calculation using McGlinchey's equation) that the metal complexing group does not have a large through space anisotropic effect on the methyl protons.[78]

This result is supported by experimental results. For example, the chemical shift difference of the two internal methyl protons in compound **125a** is only 0.11 ppm while the calculated value from McGlinchey' equation[77] for the through space effect of the $Cr(CO)_3$ group in this compound is + 0.12 ppm and - 0.10 ppm for the proximal and distal methyl groups respectively. A further anisotropy effect could come from the fused ring. This through space anisotropy effect can be calculated using the Memory equation.[79a] The results show such an anisotropy is again negligible. For example, the through space deshielding of the benzene ring in compound **110a** is 0.062 ppm and 0.047 ppm for the closest and furthest methyl group respectively.[79b] They actually differ by 0.008 ppm.[21] For other metal complexes shown in Table **5** we see similar results.[78] Thus we believe that the change in chemical shift of the internal methyl protons on going from the reference molecule **5** to **110** and **125a** and other metal complexes shown in Table **5**, reflects a real change in ring current and hence bond localization in the macrocyclic ring. Thus we could use this chemical shift change to measure the bond fixing ability of the fused metal complex species.

For the furan adducts **91**, **91a** (Table 4) and similar compounds, the only likely appreciable through space anisotropy effect might come from the oxygen atom in the

fragments. Again experimental data suggests it is negligible. This is clearly seen from the chemical shifts of compounds **70**, **90a** and **91a**. These three compounds have the chemical shifts of the internal methyl protons around -4.0 ppm, very close to the parent pyrene **43** (-4.06 ppm)[55]. More convincingly, the chemical shift difference of the two internal methyl protons in compound **91a** is almost the same (0.18 ppm) as that in compound **90a** (0.17 ppm). Since the two internal methyl groups have relatively very different positions to the bridge oxygen atom in compound **91a**, if the oxygen has any considerable through space anisotropy effect on these two internal methyl protons, the chemical shifts of these protons in compound **91a** should be more different than that in **90a**. As the difference (0.18 - 0.17 =



-3.13
-3.38

91

-3.52
-3.77

90

0.01 ppm) of the chemical shift difference of the two internal methyl protons in compounds **90a** and **91a** is small, we will use the chemical shifts of these furan adducts directly to calculate the bond-fixing ability of the fused species.

3.2.2 Relative Bond Fixing Ability (RBFA)

Table 6 gives for related compounds both the average values (δ_{ave}) of the internal methyl proton chemical shifts and the calculated anisotropy free values (δ_{calc}). The anisotropy free shifts of the fused metal complexes species are calculated after removal of the through space anisotropy effect using the McGlinchey[77] and Memory[79a] equations. For the Diels-Alder adducts, such as **90** and **91**, the through space anisotropy is too small, so the average values of the two internal methyl chemical shifts were used directly.

The RBFA of the fused species can now be calculated using equation[21] (**3.1**)

$$RBFA = [4.25 - \delta(Me_{ave})] / 2.63 \quad (3.1)$$

Table 6. Average Chemical Shifts, δ_{ave} and δ_{calc}, Values for Use in the RBFA Calculations[a]

Compound	δ_{ave}	δ_{calc}
46c	-3.42	
90	-3.64	
90a	-4.08	
91	-3.26	
91a	-4.03	
105	-0.93	-0.92
125a	-0.69	-0.72

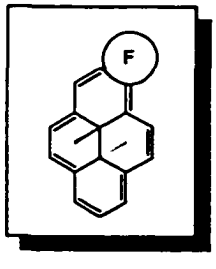
[a] For other related metal complexes, see ref 78.

Here benzene is used as the reference and its RBFA is defined as one unit. The results are shown in Table 7. As can be seen, the order for RBFA is:

Benzene-Ru^{+2}-(HMB) > Benzene-$Cr(CO)_3$ > Benzene > Oxanorbornadiene > Norbornadiene

Table 7. Relative Bond-Fixing Ability (RBFA) Values for Selected Fused Species

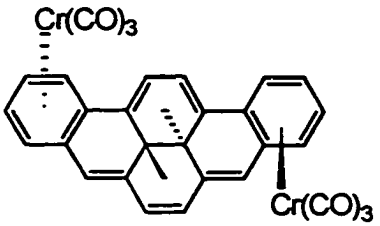
Compounds	Δδ	BFA
Cp-Ru-Cp*	3.63	1.46
Benzene-Ru^{+2}(HMB)	3.53	1.37
Benzene-$Mn(CO)_3$	3.49	1.35
Benzene-$Cr(CO)_3$	3.33	1.26
Benzene	2.63	1.00
	0.83	0.32
	0.42	0.16
	~0.0	0.0
	~0.0	0.0



$$BFA = [\ 4.25 - \delta(Me_{ave})] / 2.63$$

$$= \Delta\delta / 2.63$$

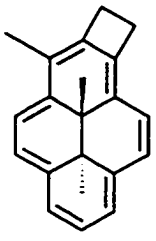
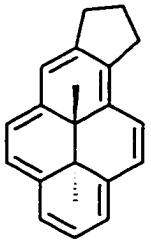
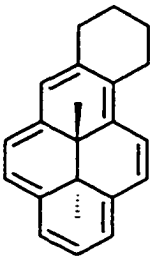
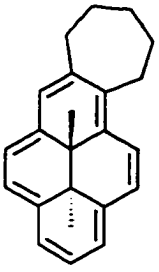
Clearly the metal complexed species have a greater bond fixing ability of the annulene ring than benzene itself.[80] The greatest bond fixing effect ability is from Benzene-Ru^{+2}-(HMB) species. In the bis-complexed compound **100a**, two strong bond-fixing groups, Benzene-$Cr(CO)_3$, almost annihilate completely the ring current, ie. only 7% (0.33/5.2) of the ring current is left compared to that in the parent pyrene **5a**.[23a]



100a

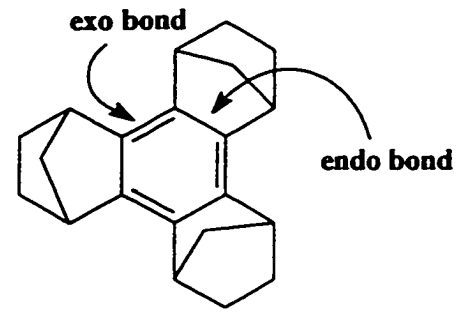
From Table 8, simple fused rings from four membered to seven membered rings, cause no appreciable bond alternation on the [14] ring as all the chemical shifts of the internal methyl protons of these compounds are very close to that of the parent pyrene **5a** as shown in Table 8.[22] These results are in a good agreement with the similar fused benzene systems.[82]

Table 8. The Chemical Shifts of the Internal Methyl Protons of the Simple Fused DMDHPs[a]

			
- 4.23	- 4.18 - 4.20	- 3.95 - 3.99	- 4.18 - 4.23
126	**127**	**128**	**129**

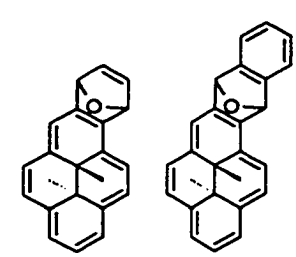
[a] For the data, see refs 22 and 81.

Siegel suggests that bicyclic annelation can induce significant bond localization.[8c-8f,83] However, not all bicyclic systems do so. For example, both bicyclo[2.2.1]norbornene and [2.2.1]oxanorbornene fusion on to **5** does not induce any significant bond localization on the [14] ring, as seen in compounds **70**, **71a**, **90a** and **91a** (Table 4 and 5), which for **70** and **71a** agree with calculation.[22] Interestingly, the same fusion on benzene, both experimentally and computionally suggest that they cause significant bond localization, e.g. in compound **130** (exo = 1.379 Å and endo = 1.417 Å, eg, Δr = 3.8 pm)[8c,84]



130

Since both [2.2.1]oxanorbornadiene and [2.2.1]norbornadiene species have significant bond fixing ability, and the reduced fragments [2.2.1]norbornene and [2.2.1]oxanorbornene do not, as seen in compounds **70**, **71a**, **90a** and **91a**, it can then be concluded that the oxygen atom does not have any significant role in the bond fixation. This further points out that the bond fixation must arise because of either a π-π interaction between the isolated double bond with the [14] π system or bond angle strain caused by the fusion or both. These results also indicate that a σ-π through space anomalous effect[85] must play a minor role in the bond localization in our systems and the angle strain probably plays the major role as suggested in other similar systems.[8d,83] In the adduct of isobenzofuran (**58**, Table 4) the bond localization decreases greatly as seen from its chemical shift of the internal methyl protons and the



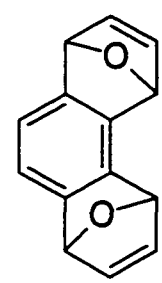
-3.34 -3.51 -3.66 -4.01

46c **58**

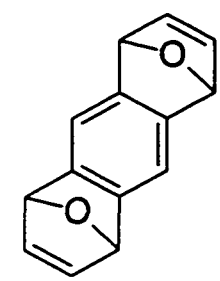
H-2 and the coupling constants in their proton NMR spectra (in compound **58**, J_b/J_a = 1.18 compared with J_b/J_a = 1.23 in compound **46c**, also for H-2, δ = 7.72 in **46c**, while the δ = 7.86 in **58**).[21] Since it has similar fusion as that of the furan adduct **46c** (Table 4), it is not obvious why. Obviously, more work needs to be done to explain the real reasons for the bond localization. We present a possible explanation below.

3.2.3 Different Resonance Structures Make a Difference

It is interesting to note that although both compounds **47** and **48** (Table 5) are bis adducts from furan, the former has no bond localization, but the latter loses about 40 % of its ring current in the [14] annulene. In the benzene series, such as compounds **126** and **127**, the same results are seen,[8c] that is, compound **126** shows significant bond localization but **127** does not. This can be explained by Resonance Theory. The most stable resonance structures of compound **47** and that of compound **48** are shown in Scheme **46**. The two resonance structures **47A** and **47B**

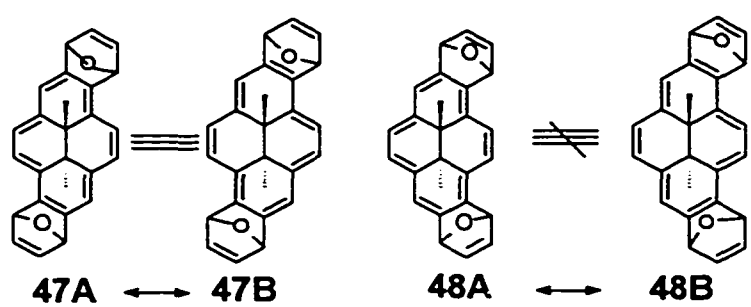


126



127

Scheme 46

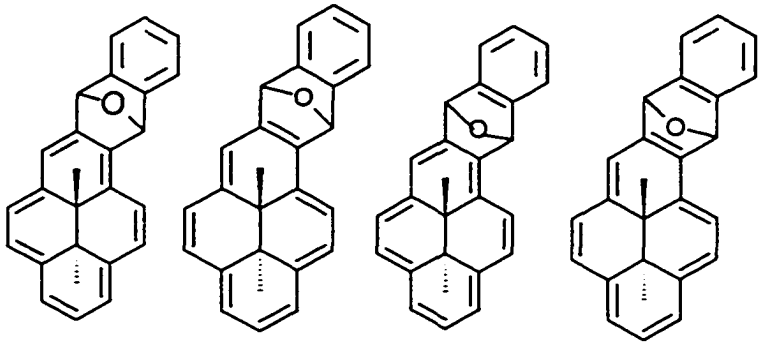


of compound **47** are equivalent and therefore have the same energy. They thus have identical contributions to the real structure of the molecule **47**. If no other resonance structure makes a significant contribution to the real structure, we would then expect that the structure of compound **47** will not show significant bond localization. However for compound **48**, the two resonance structures **48A** and **48B** are different and therefore must have different contributions to the real molecule's structure. Based on the X-ray data of the mono adduct **46c** and the coupling constants in its proton NMR spectrum, we believe that structure **48A** is the preferred one for this bis-adduct. Regardless of which structure is the preferred one, the real structure of compound **48** must have significant bond localization. We expect X-ray data to confirm this.

Applying the same principal to compounds **81** and **83**, one would expect no bond localization on these bis adducts, and none is observed.

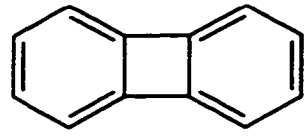
We mentioned earlier that the NMR implication of compound **58** is in contrary to the explanation of the reasons for the bond localization in compounds **46c** and **90**, eg, no similar

Scheme 47



58A **58B** **58C** **58D**

bond localization was seen in compound **58** as that in **46c** since both have similar fusion onto the [14] annulene ring. Again resonance theory could remove this conflict. The four most reasonable resonance structures of **58** are shown in Scheme 47.



131

Among them we would expect that **58A** is the most favoured one based on the X-ray and NMR data of similar compound **46c**,[21] that is, in this structure, the two π-systems are more isolated. Thus the benzene π system and the [14] π systems try to avoid face to face direct interaction with each other as that in **58D** which has an unfavored local homo-antiaromatic 4π system. The double bond prefer the **exo** positions on both π systems. Thus if a π-π interaction through the bridge ring between the two π systems plays a major role in the bond localization, the weaker π-π interaction in compound **58** might reduce the bond localization in the [14] π systems and on the benzene ring too. A similar preferred structure is seen in biphenylene **131**.[86] We need X-ray data to confirm this hypothesis.

Chapter Four

Conclusions

4.1 Synthesis

DMDHP's containing bromines at the less usual 4 and 5 positions, compounds **44a** and **44b**, have been synthesized for the first time using NBS/DMF or NBS/$CHCl_3$. A new method was developed for the synthesis of 2,7-dibromodimethyldihydropyrene **21a** starting from bromide **27**, which itself was made by the bromination of diacid **26** using dibromoisocyanuric acid (DBI).

Applying the aryne route to dibromide **21a** gave the bis furan adducts, compounds **47** and **48**. Deoxygenation of these two compounds with $Fe_2(CO)_9$ yielded the dibenzannulenes **49a** and **49b**. Thus we have shown that the aryne (Diels-Alder) route can be used to synthesize bis fused DMDHPs.

This new synthesis gave reasonable amounst of compounds **49a/49b** such that we have been able to study the synthesis of their Fe, Ru and Cr complexes. The ligand exchange reaction of **49b** with $Cr(CO)_3$Naph (compound **89**) gave the bis chromium complexes **100a/100b/100c** as well as the mono chromium complex **101**. These are the first bis complexes of a large annulene. The ratio of the three bis isomers **100a/100b/100c** is ~12:4:1. This ratio indicates that the internal methyls in the DHDMP do have orientational function as we suggested in the introduction. For the Fe and Ru complexes, only the mono Ru

complex **103** of **49b** and the mono Ru complex **105** of **104** were synthesized successfully using $[Ru(HMB)Cl_2]_2$ (compound **102**).

Applying the same aryne synthetic strategy to bromides **44a**, **44b** or **80**, we have synthesized bis [e] fused furan adducts **81** and **94** and isobenzofuran adducts **83**. These compounds gave the dibenzo- and dinaphtho-[2.2]metacyclophanes **82**, **85** and **95** after the deoxygenation by using $Fe_2(CO)_9$ in the cyclophanediene form. These are the first known compounds in the series of the bis fused metacyclophanes.

Attempts via several routes to synthesize the Cr and Ru complexes of the metacyclophane **82a** yielded some products which could not be purified and characterized, probably due to the loss of the internal methyls and the two different complexing positions for the mono metal complexes.

4.2 Photoswitch Properties

Among the bis [e] fused compounds, pairs **82a/82b** and **95a/95b** show reversible and repeatable photo-switching properties both in solution and in the *solid state*. In solution, when the cyclophane forms **82a** and **95a** are irradiated with 300 nm of light at low temperature (<-20 ^{0}C), they are converted to the dihydropyrene forms **82b** and **85b** and when the pyrene forms **82b** and **95b** are irriadiated with visible light these dihydropyrenes go back to the cyclophanes forms **82a** and **95a**. This process was repreated for more than ten times without any detectable decomposition by NMR. The pyrene forms **82b** and **95b** were characterized at low temperature and they thermally return to their cyclophane forms **82a** and **95a** at room

temperature. From VT NMR data, the activation energies (20 and 17 kcal/mol repectively) of the thermal return reactions of **82b** to **82a** and **95b** to **95a** have been calculated by plotting ln k vs 1/T.

A polystyrene based film (<0.1% of **82a**) of **82** shows much better bistability and photofatigue resistance required for photo-switching units. More than 15 cycles of colouration/decolouration have been tested and no decomposition was observed. After more than one year at 7 °C, the film still shows the same reversible photoswitchable process. These properties make them potential candidates for optical memory units. For the similar naphtho[*e*] fused compound **95a**, no pyrene isomer **95b** was detected upon irradiation with UV light.

Proposals have been made for better (bistability and processing properties) photoswitchable molecules. These include the unsymmetrical bis fused compounds **113**, and the polymer-based compounds such as **123** and **124**.

4.3 Relative Bond Fixing Ability

Fusion of different ring systems to the parent dihydropyrene **5** causes different bond fixation in the dihydropyrene part of the molecule. Both the experimental NMR data and the computional results using McGlinchey's equation indicated that the fused species had little through space anisotropy effect on the internal methyl protons in the various fused dyhydropyrene compounds. Thus the resultant NMR data were used to measure the relative bond fixing abilities (RBFA) of such fused species.

The order observed was:

Benzene-Ru^{+2}(HMB) (1.37) > Benzene-$Cr(CO)_3$ (1.26) > Benzene (1.00) > Oxanorbornadiene (0.32) > Norbornadiene (0.16)

The reduced species, oxanorbornene and norbornene, do not induce any significant bond localization on the [14] annulene ring.

The strongest bond localization was observed in the bis chromium complexed compound **100**, where the ring current in the [14] annulene ring was almost completely annihilated (7% left).

Chapter Five

Experimental

5.1 General Experimental Conditions

Melting points were determined on a Reichert 7905 melting point apparatus integrated to a chrome-alumel thermocouple. Infrared spectra, major peaks only, calibrated with polystyrene were recorded on a Bruker IFS25 FT-IR or on a Perkin-Elmer 283 spectrometer as KBr disks unless otherwise stated, Ultraviolet-visile spectra were recorded on a Perkin-Elmer Lambda-4B spectrometer in the stated solvents, Proton NMR spectra were reorder at 90 MHz on a Perkin-Elmer R-32, at 250 MHz on a Bruker WM 250, at 300 MHz on a Bruker AC 300, or at 360 MHz on a Bruker AMX 360 using $CDCl_3$ or other solvents as stated and either TMS as internal standard or the $CDCl_3$ peaks at 7.24 ppm. Carbon NMR spectra were recorded at 62.9 MHz or at 90.6 MHz in $CDCl_3$ or other stated solvent using the solvent peak for calibration. Mass spectra were recorded on a Finnigan 3300 gas chromatography-mass spectrometer using methane gas for chemical ionization (CI) or electron impact (EI) at 70 eV. FAB or LSI mass spectra and exact mass measurement used a Kratos Concept-H instrument with perfluorokerosene or mMBA as the calibrants. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous $MgSO_4$, Na_2SO_4 or K_2SO_4 as appropriate. PE refers to distilled petroleum ether, bp 30-60 ^{0}C. Hexanes refers to

the comerical product from Aldrich, which is a mixture of isomers of hexane. Photonic irradiation was carried out on a Raynet Photochemical Reactor. All reagents as commerical unless otherwise specified. All reported MH^+ or M^+ peaks from MS spectra for bromides are based on the isotope ^{79}Br.

5.2 PCMODEL MMX and HyperChem AM1 Computations

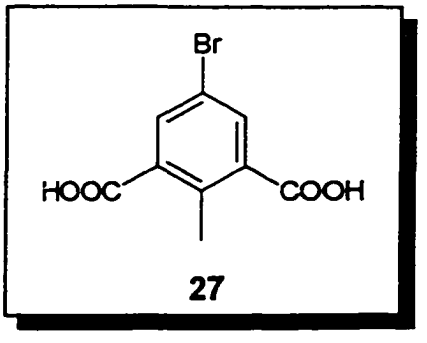
PCMODEL is a Molecular Mechanics modeling program. The force field used in PCMODEL is called MMX and is derived from the MM2 force field of N. L. Allinger, with the pi-SCF routines taken from MMP1, also by N. L. Allinger. The main calculation function of this modelling program is the geometry optimization, which gives the minimized energy and the heat of formation. In its structure output, it give the optimized structure with minimized energy and the required bond length and/or bond angle, dihedral angle and so on by using the "Query" command. In its minimized energy output, it lists the total energy, as well as a breakdown by component, dipole moment, heat of formation (H_f) and strain energy (SE). The components of the strain energy are Str (stretching), Bnd (bending), StrBnd (stretch-bend cross term), Tor (torsion), VdW (Van der Waal interactions), and QQ (charge-charge electrostatic interaction). We have found this program gives good results for the geometry of both cyclophanes and DMDHPs, which agrees well with X-ray data. However, PCMODEL does not give good values of H_f for DMDHPs and cyclophanes, although the difference in energies of the same series of compounds seems more reliable. We use this program mainly to obtain the optimized structure (for McGlinchey's calculations) and the strain energy differences for the same series of molecules in this thesis, which we found are

reliable. To ensure a global minimization, for the same compound we started with very different initial structures for the minimization and took the one with lowest H_f as the global minimim. The literature (ref 47) has a more detailed discussion about the stain energy and the pi energy of the related compounds. In this thesis, we use the conclusion about the contribution of strained energy and pi energy to the total energy of the molecule directly from the literature.[47]

AM1 (Austin Model 1) is a modified MNDO method proposed and developed by M. J. S. Dewar and co-workers at the University of Texas at Austin. This is a Semi-empirical Quantum mechanical and SCF method. It can calculate electronic properties, optimized geometries, total energy, and heat of formation and so on. In this thesis we use this method to calculate the heats of formation and find the results are in good agreement with experimental results. For example, the calculated result of ΔH_f (3.4 kcal/mol) for the parent DMDHPs **5a** and **5b** is in good agreement with the experimental result (3.0 kcal/mol). However, the AM1 calculation gives a bond alternate structure for DMDHPs, which is not the experimental result. Also, compared with PCMODEL (MMX), AM1 is much more time consuming. The AM1 calculation results for H_f of the related compounds are summarized in Table 3. We then use these Hf results to predict the thermally stable isomers of the pyrene/cyclophane pairs and then to compare the result with the experimental results.

5.3 Synthesis

5-Bromo-2-methyl-benzenedicarboxylic acid (27)[53]



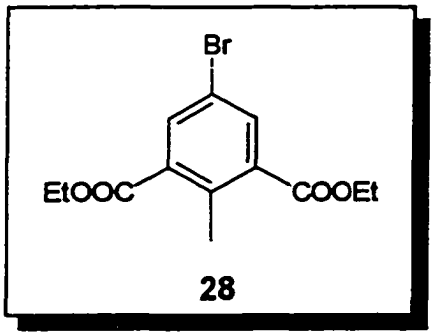
27

A solution of dibromoisocyanuric acid (DBI)[57a] (16 g, 55.7 mmol) in concentrated sulfuric acid (150 mL) was added over 30 min to a stirred solution of 2-methyl-1,3-benzenedicarboxylic acid **26**[87] (18 g, 100 mmol) in concentrated sulfuric acid (100 mL). After stirring 2 h at room temperature the mixture was poured over crushed ice (600 g). The white solid was collected by suction filtration, washed twice with water and then resuspended in saturated $NaHCO_3$ solution (600 mL). The undissolved solid (cyanuric acid) was filtered away, rinsed with a small portion of saturated $NaHCO_3$ solution, and discarded. The filtrate was made acidic by addition of 50% sulfuric acid with ice-bath cooling. The white precipitate was collected by suction filtration , washed with water and dried under vacuum to yield 25g (~100%) of 5-bromo-2-methyl-1,3-benzenedicarboxylic acid **27**, mp 255-257 ^{0}C; ^{1}H NMR (d_6-DMSO, 250 MHz) δ 13.1 - 13.8 (b, 2, -COOH), 7.93 (s, 2, ArH), 2.12 (s, 3, $-CH_3$); ^{13}C NMR (d_6-DMSO, 62.9 MHz) δ 167.6 (-COOH), 136.2, 135.9, 133.8, 118.0 (aryl carbons), 17.1 ($-CH_3$); CI MS m/z 259 (100, MH^+, correct isotope pattern), 243 (13), 215 (2.9), 173 (4.8).

Anal. calcd for $C_9H_7O_4Br$: C, 41.73; H, 2.72. Found: C, 42.24; H, 3.01.

Diethyl 5-bromo-2-methyl-benzenedicarboxylic acid (28)

The diacid **27** (34.0 g, 0.13 mol) , absolute ethanol (50 mL) and concentrated surfuric acid (10 mL) and *p*-TsOH (1 g) was added sequentially to benzene (300 mL) with stirring. After refluxing using a Dean-Stark water separator for 24 h, the cooled mixture was poured onto crushed ice (100 g) and extracted with ether (2 × 200mL). The combined organic layer was washed with water and $NaHCO_3$ solution, and then was dried with $MgSO_4$, and then evaporated to yield white crystals 26.4 g (~100%) of diethyl 5-bromo-2-methyl-benzenedicarboxylic acid **28** which was used directly in the next step. Recrystallization from hexanes yielded colourless crystals, mp 61.5-62.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.95 (s, 2, ArH), 4.35 (q, J = 7.1 Hz, 4, $-CH_2-$), 2.61 (s, 3, $-CH_3$), 1.38 (t, J = 7.1 Hz, 6, $-CH_2\underline{CH_3}$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 166.5, 139.4, 138.3, 134.7, 118.7, 61.6, 30.9, 17.6, 14.2; CI MS m/z 315 (MH^+, 100, correct isotope pattern), 271 (11.5).



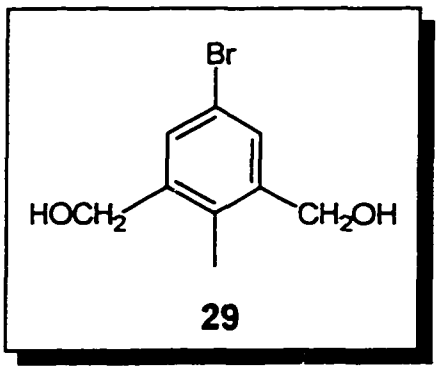
28

Anal. calcd for $C_{14}H_{15}O_4Br$: C, 49.54; H, 4.80. Found: C, 49.40; H, 4.76.

2,6-Bis(hydroxymethyl)-5-bromo-2-methylbenzene (29)[88]

A solution of diester **28** (26.0 g, 91.5 mmol) in dried THF (100 mL) was added

dropwise to a suspension of $LiAlH_4$ (5 g, 132 mmol) in dried THF (200 mL) over 30 min under N_2. The mixture was stirred at a gentle reflux for 4-5 h, cooled, and then quenched successively with H_2O (4 mL), 15% NaOH (4 mL) and H_2O (4 mL). The inorganic precipitate was removed by hot filtration. Evaporating the solvent from the filtrate yielded 14 g of white soild **29** which was used directly in the next step. The solid collected by hot filtration after the quench was also extracted with ether (3 × 100 mL) and gave another 3 g product to make the total yield 81%. A small portion was recrystallized from THF to yield colourless crystals, mp 168-169 °C; ^{1}H NMR (d_6-DMSO, 250 MHz): δ 7.42 (s, 2, ArH), 5.24 (t, J = 5.5 Hz, 2, -OH), 4.48 (d, J = 5.5 Hz, 4, $-CH_2-$), 2.04 (s, 3, $-CH_3$); ^{13}C NMR (d_6-DMSO, 62.9 MHz) δ: 142.9, 131.4, 127.4, 118.3 (aryl carbons), 60.6 ($-CH_2-$), 12.5 ($-CH_3$); CI MS m/z 231 (MH^+, 100, correct isopte pattern), 197 (13.5), 195 (12.7), 185 (55.2), 183 (49.8) 119 (17.4).

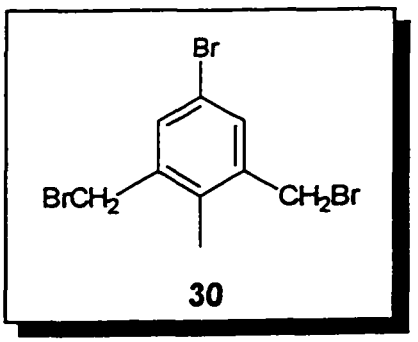


29

Anal. calcd for $C_9H_{11}O_2Br$: C, 46.70; H, 4.80. Found: C, 46.74; H, 4.86.

2,6-Bis(bromomethyl)-4-bromo-1-methylbenzene (30)

The di-alcohol **29** (14 g, 60.6 mmol) was added to a mixture of 48% hydrobromic acid (150 mL) and concentrated sulfuric acid (1 mL) and benzene (50 mL)



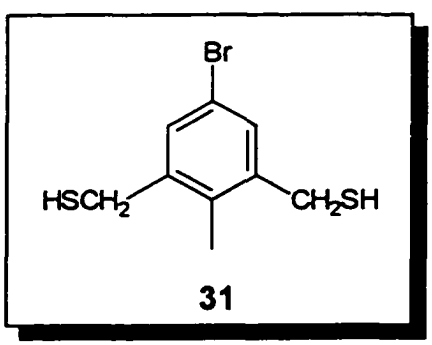
30

with good stirring. The mixture was then stirred under a reflux for 24 h. After the mixture was cooled, 5.2 g of analytical pure product **30** was collected directly by suction filtration. The filtrate was extracted with $CHCl_3$ (2 × 100 mL), and the combined extracts were washed with water (50 mL), dried by $MgSO_4$, and then evaporated to yield white crystals for a total yield of 21 g (99%). For characterization, a small portion was recrystallized from hexanes, mp 162-162.5 ^{0}C; ^{1}H NMR ($CDCl_3$, 250MHz) δ 7.41 (s, 2, ArH), 4.43 (s, 4, -CH_2-), 2.35 (s, 3, -CH_3); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 138.9, 135.6, 133.3, 119.2 (aryl carbons), 31.0 (-CH_2), 14.0 (-CH_3); CI MS m/z 361 (1.9), 359 (7.0), 358 (2.0), 357 (MH^+, correct isotope pattern, 7.3), 356 (1.5), 355 (2.7), 279 (50.4), 277 (100.0), 275 (56.0).

Anal. calcd for $C_9H_9Br_3$: C, 30.29; H, 2.54. Found: C, 30.41; H, 2.62.

2,6 -Bis(mercaptomethyl)-4-bromotoluene (31)[89]

A mixture of bromide **29** (5 g, 14.0 mmol) and thiourea (2.18 g, 28.6 mmol) in 95%ethanol (80 mL) was refluxed under nitrogen with stirring for 3 h. After the solution was cooled, half of the solvent was evaporated and the remainder cooled in the freezer. The precipitated bis-thiouronium salt was collected and dried. The salt was then added to a KOH solution (15 g , 85 % KOH in water, 70 mL) under nitrogen and refluxed for 5 h. The cooled solution was then added to crushed ice (50 g) and was acidified by 50% sulfuric acid. The mixture was



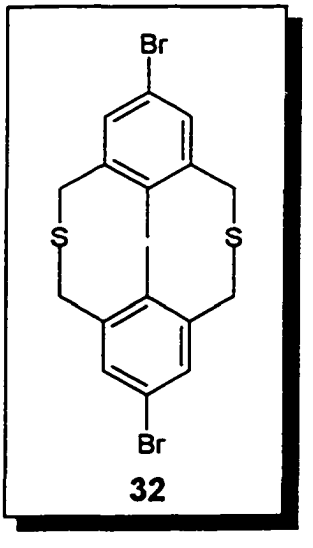
31

then extracted with ether (3 × 100 mL). The ether layer was washed, dried and evaporated to yield 3.4 g (97 %) the bis-thiol **31**. A portion of the product was recrystallized from hexanes to yield colourless needles, mp 74.5-75.0 ^{0}C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.27 (s, 2, ArH), 3.67 (d, J = 7.3 Hz, 4, -CH_2-), 2.31 (s, 3, -CH_3), 1.68 (t, J = 7.3 Hz, 2, -SH); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 142.0, 132.7, 130.6, 119.3 (aryl carbons), 26.9 (-CH_2-), 14.0 (-CH_3); CI MS m/z 265 (2.9), 264 (2 .0), 263 (4.4), 262 (MH^+, 2.0, correct isotope pattern), 233 (2.6), 231 (11.6).

Anal. calcd for $C_9H_{11}S_2Br$: C, 41.07; H, 4.21. Found: C, 40.67; H, 4.15.

***anti*-6,15-Dibromo-9,18-dimethyl-2,11-dithia[3.3] metacyclophane (32)**

A solution of the di-bromide **30** (4.64 g, 13 mmol) and the di-thiol **31** (3.42 g, 13 mmol) in N_2-degassed benzene (500 mL) was added dropwise over 36 h with vigorous stirring under nitrogen to a solution prepared by dissolving KOH (2.57 g, 85 %, 39 mmol) in water (100 mL) and ethanol (800 mL). After a further 2-4 h stirring at room temperture, most (3.18 g) of the anti-isomer product **32a** was separated directly by simple filtration. The solution was concentrated to 300 mL under reduced pressure and then was extracted with water (150 mL) and $CHCl_3$ (4 × 150 mL). The organic layer was then washed with water, dried, and evaporated and the residue (2.50 g, a



32

mixture of *anti* and *syn* isomers) was pre-absorbed on silica gel and chromatographed using $CHCl_3$/PE (1:1) as the eluant to elute first the *anti* isomer and then the *syn* isomer of **32**. The overall ratio of *anti /syn* isomers is about 4:1, with total yield 5.68 g (95%). *Anti*-isomer **32a** (4.45 g, 78%) mp 290-292 °C (decomp.); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.40 (s, 4, ArH), 3.64 and 3.61 (ABq, J = 14.2 Hz, 2 each, -CH_2-), 1.37 (s, 6, -CH_3); ^{13}C (360 MHz, $CDCl_3$) δ 137.7, 137.3, 132.7, 118.8 (aromatic carbons), 31.0 (-CH_2-), 14.5 (-CH_3); CI MS m/z 487 (11), 462 (6.9), 461 (55), 459 (100), 457 (MH^+, 47), 229 (13), 227 (14), 225 (10) , 199 (23), 197 (26), 133 (20).

Anal. calcd for $C_{18}H_{18}Br_2S_2$: C, 47.18; H, 3.96. Found: C, 46.80; H, 3.79

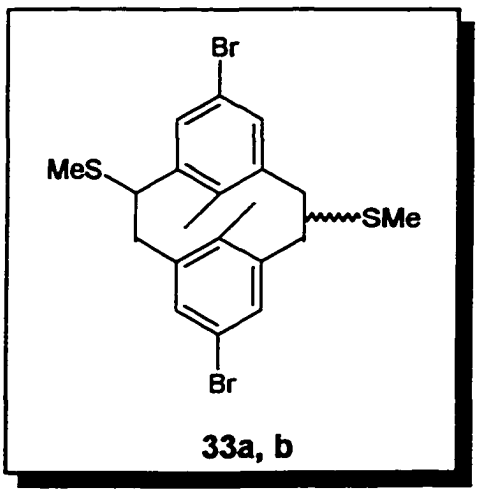
Syn-isomer **32b** (1.23 g, 22%); mp 268-270 °C (decomp.); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.92 (s, 4, ArH), 3.96 and 3.77 (ABq, J = 15.2 Hz, 2 each, -CH_2-), 2.43 (s, 6, -CH_3); ^{13}C NMR δ 137.9, 134.7, 132.1, 119.4 (aryl carbons), 36.1 (-CH_2-), 16.9 (-CH_3); CI MS m/z 457 (MH^+, correct isotope pattern).

Anal. calcd for $C_{18}H_{18}Br_2S_2$: C, 47.18; H, 3.96. Found: C, 47.42, H, 3.92.

Stevens rearrangement of the *anti*-thiacyclophane 32a to the *anti*-isomers 33a

Borch reagent $(MeO)_2CHBF_4$[90] (7.2 g, 85% oil, 37 mmol) was added to a solution of *anti*-dimer **32a** (4.87g, 10.6 mmol) in dried CH_2Cl_2 (45 mL). This mixture was stirred for 24 h. Ethyl acetate (40 mL) then was added, and stirring continued for 24 h. The upper clear

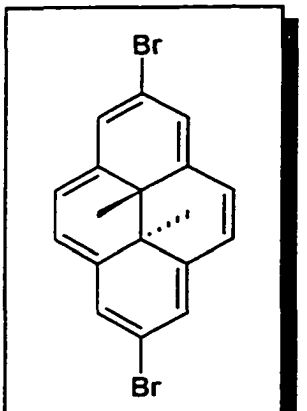
solvent was decanted after standing. The solid was washed again with ethyl acetate until clean powdered salt was produced by filtration. Then KOBu^t (2.89 g, 25.8 mmol) was added to a suspension of this salt in THF (70 mL) under nitrogen. After 2 h stirring at room temperture under nitrogen, the mixture was quenched with HCl (5 mL, 2 M) and water (50 mL), and then the mixture was extracted with CH_2Cl_2 (2 × 150 mL) and the combined organic layer was washed with water, dried with Na_2SO_4 and evaporated to yield the thioether ***anti*-33a** as a mixture of steroisomers (4.67g, 91%). This was used directly in the next step, the Hofmann elimination. ^{1}H NMR ($CDCl_3$, 250 MHz): complicated due to the steroisomers, but clear peaks for internal methyl protons at 0.6-1.1 ppm and at 2.0-2.2 ppm for SMe groups. CI MS m/z 485 (MH^+).



33a, b

***trans*-2,7-Dibromo-10b,10c-dimethyl-10b,10c-dihydropyrene 21a** (method A)

Borch reagent (6.5 g, 85% oil, 34 mmol) was added to a solution of the mixed isomers **33a** (4.67g, 9.60 mmol) in CH_2Cl_2 (100 mL) from the Stevens rearrangement above and then the mixture was stirred at room temperature for 2 days. Ethyl acetate



21a

(40 mL) was then added, and stirring continued for 4 h. The upper clear solvent was decanted after standing and then ethyl acetate (40 mL) was added and stirring continued for 2 h. This salt was then collected, dried and added to a solution of $KOBu^t$ (1.7g, 24 mmol) in dry THF (200 mL) at 0 °C. After 3 h stirring at room temperature, the mixture was quenched with water (10 mL), HCl (2 mL, 2M) and PE (50 mL). The aqueous layer was further extracted with PE (3 x 100 mL), and the combined extracts were washed, dried, and then preabsorbed on silca gel (20 g) and flash chromatography was applied to yield 3.1 g (81%) of deep green (black) crystals of *trans*-isomer **21a**. A sample was recrystallized from chloroform to give dark green crystals, mp 213-215 °C (lit.[49] mp 213-214 °C); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.68 and 8.51 (s, 4 each, ArH), -4.03 (s, 6, internal methyl); ^{13}C NMR (90.6 MHz) δ 136.7, 126.8, 123.9, 118.5, 29.2, 14.2; CI MS m/z 394 (8.4), 393 (47), 392 (46), 391 (100), 390 (64), 389 (53, MH^+), 388 (28), 312 (36), 311 (74), 310 (37), 309 (66), 225 (13), 112 (16), 91 (34).

HR MS (E.I.) calcd for $C_{18}H_{14}Br_2$: 387.9462. Found: 387.9469.

***trans*-2,7-Dibromo-10b,10c-dimethyl-10b,10c-dihydropyrene 21a** (method B)

A pre-cooled (in freezer) solution of NBS (1.54 g, 8.62 mmol) in dry DMF (70 mL) was added slowly over 30 min to a pre-cooled (in freezer) solution of pyrene **5a** (1.00 g, 4.31 mmol) in dry DMF (50 mL) at 0 °C and then the reaction was stirred without cooling for 2 h. Diethyl ether (200 mL) was added, and then the mixture was poured into ice-water. The

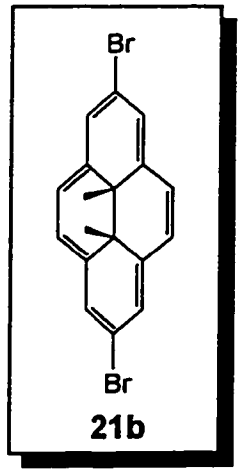
ether extract was washed well with water and dried with $MgSO_4$, and then a flash chromatography gave the identical green product as in method A, 1.18 g (70%), which could then be recrystallized from chloroform, mp 212-214 °C (lit.[49] mp 213-214°C).

Stevens rearrangement of the *syn*-thiacyclophane 32b to the *syn* isomers 33b

Borch reagent $(MeO)_2CHBF_4$[90] (0.65 g, 85% oil, 4.0 mmol) was added to a solution of *syn*-dimer **32b** (46 mg, 0.10 mmol) in dried CH_2Cl_2 (20 mL). After stirring at room temperature under nitrogen for 2 h, ethyl acetate (10 mL) was added to the mixture. The mixture was stirred at room temperture for 2 h again and the upper clear solvent was decanted after standing. The solid was washed again with ethyl acetate until the powdered salt was produced by filtration. Then $KOBu^t$ (25 mg, 0.22 mmol) was added to the suspension of this salt in THF (20 mL) under nitrogen. After 2 h stirring at room temperture under nitrogen, the mixture was quenched with HCl (2 mL, 2 M) and water (20 mL), then the mixture was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic layer was washed with water, dried with Na_2SO_4 and evaporated to yield 40 mg (82%) of the thioether ***syn*-33** as a mixture of steroisomers, which was used directly in the next step for the Hofmann elimination. CI MS m/z 485 (MH^+).

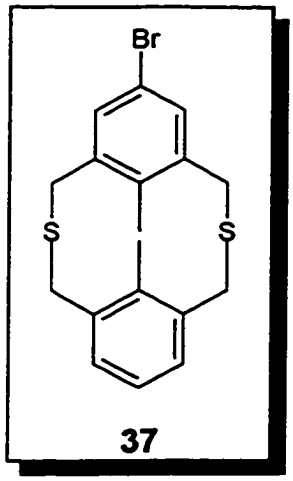
Hofmann elimination of 33b to *trans*-2,7-dibromo-10b,10c-dimethyl-10b,10c-dihydropyrene 21a and *cis*-2,7-dibromo-10b,10c-dimethyl-10b,10c-dihydropyrene 21b

Borch reagent[90] (0.26 g, 85% oil, 1.4 mmol) was added to the solution of **33b** (40 mg, 0.082 mmol) in 20 mL CH_2Cl_2 under nitrogen. The mixture was stirred for 1 h at room temperature and then ethyl acetate (20 mL) was added and stirring continued. The solvent was decanted after 1 h, and the oily residue was stirred with ethyl acetate (40 mL) for 4 h. This gave a crystalline product, which was filtered and dried under vacuum to give the *syn* salt **34b** (45 mg , 83 %). This salt was then added to a solution of $KOBu^t$ (22 mg, 0.2 mmol) in THF (50 mL) at room temperature. After 2 h stirring the mixture was quenched with water (10 mL), HCl (1 mL, 2 M) and PE (50 mL). The organic layer was washed with water (3 × 15 mL), dried with Na_2SO_4, and then evaporated to yield deep green (black) crystals, 25 mg (77%), a mixture of the *cis* and *trans* isomers (ratio = 4:6, determined by NMR). Chromatography using PE as eluant of this crude product separated these two isomers: Eluted first was *trans*-isomer **21a**, 15 mg, identical to the samples above. Eluted second was the *cis*-isomer **21b** (10 mg), mp 204-205 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.69 and 8.40 (s, 4 each, ArH), -1.95 (s, 6, internal methyl); CI MS m/z 391(28.4), 390 (57.2, MH^+, correct isotope pattern), 312 (41), 311 (100), 310 (42).



21b

anti-6-Bromo-9,18-dimethyl-2,11-dithia[3.3]metacyclophane (37)



37

A solution of dibromide **30** (2.72 g, 7.61 mmol) and dithol **36**[87] (1.40 g, 7.61 mmol) in de-airated benzene (500 mL) was added dropwise over 2 days to a solution of KOH (1.5g, 85%, 22.8mmol) in ethanol (1000 mL) and water (100 mL) under N_2 with vigorous stirring. After a further 2 h stirring, the solution was evaporated and the residue was extracted with water (200mL) and CH_2Cl_2 (3 x 150 mL). The organic extract was washed with water, aq. $NaHCO_3$, water, and then was dried and evaporated. Flash chromatography of the residue using PE gave 1.8 g (63%) of *anti-* and *syn-* isomers (~ 6:1). The mixture was recrystalized from benzene to yield 0.56 g of colourless crystals of *anti-* isomer **37a**, mp 199-200 °C; NMR ($CDCl_3$, 360 MHz): δ 7.41(s, 2, H-5,7), 7.26 (d, J = 7.6 Hz, 2, H-14, 16), 7.07 (t, J = 7.6 Hz, 1, H-15), 3.69 (bs, 4, H-3,10), 3.60 (s, 4, H-1,12), 1.40 and 1.25 (s, 3 each, $-CH_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 138.3, 137.79, 137.76, 135.3, 132.6, 130.2, 125.5, 118.6 (aromatic carbons), 31.41, 31.01(bridge carbons), 14.57, 14.54 (internal methyl carbons); CI MS m/z 379 and 381(1:1, 100, MH^+).

Anal. calcd for $C_{18}H_{19}BrS$: C, 56.99; H, 5.05. Found: C, 56.72; H, 4.91.

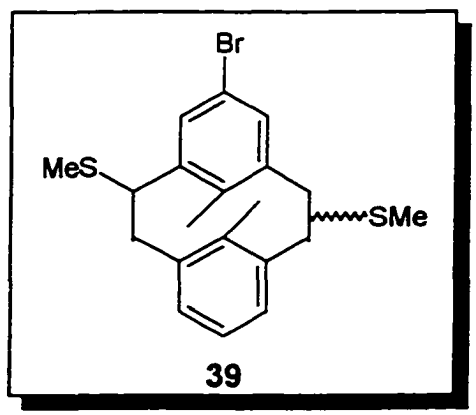
The mother liquor was chromatographed over silca gel using CH_2Cl_2-PE (1:5) as eluant. Eluted first was 0.21 g of *anti-*isomer **37a**. Eluted second was *syn-*isomer, **37b** (0.12

g), mp 154-155 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 6.99 (t, J = 7.7 Hz, 1, H-15), 6.70 (s, 2, H-5,7), 6.66 (d, J = 7.6 Hz, 2, H-10,14), 4.02-3.77 (m, 8, H-1,3,10,12), 2.51 and 2.46 (s, 3 each, $-CH_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 137.7, 135.7, 135.6, 134.6, 132.5, 130.1, 124.7, 119.7 (aromatic carbons), 37.0, 36.5 (bridge carbons), 17.2, 16.7 (internal methyl carbons); CI MS m/z 379 and 381 (1:1, 100, MH^+), The bromine isotope pattern was correct (1:1).

Anal. calcd for $C_{18}H_{19}BrS$: C, 56.99; H, 5.05. Found: C, 56.17; H, 4.85.

Stevens Rearrangement of 37a to 39

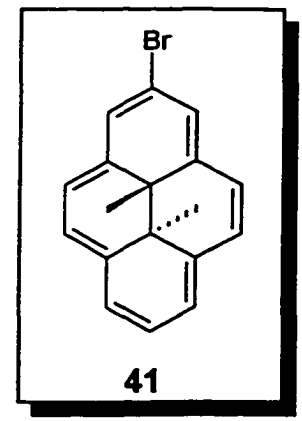
Borch reagent $(MeO)_2CHBF_4$[90] (2.6 g, 85% oil, 14 mmol) was added to a solution of *anti*-dimer **37** (0.900 g, 2.37 mmol) in dried CH_2Cl_2 (30 mL). After stirring at room temperture under nitrogen for 24 h, ethyl acetate (20 mL) was added to the mixture. The mixture was stirred at room temperture for 24 h again and the upper clear solvent was decanted. The solid was washed with ethyl acetate until the powdered salt (1.4 g) **38** was produced, which was used directly in the next step for the Steven rearrangement. Then KOBu^t (0.63 g, 5.7 mmol) was added to a suspension of **38** (1.4 g, 2.4 mmol) in THF (70 mL) under nitrogen. After 10 h stirring at room temperture under nitrogen, the mixture was quenched with 2 M HCl (5 mL) and water (50 mL). The



39

mixture was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was washed, dried, and evaporated to yield 0.91 g (95%) of **39** as a mixture of steroisomers. It was then used directly for Hofmann elimination in the next step; CI MS m/z 407 (MH^+, correct isotope pattern).

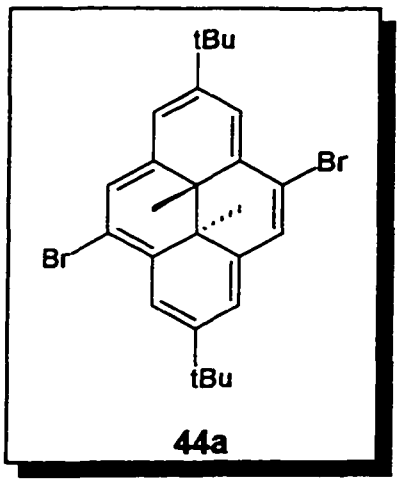
trans-2-Bromo-10b,10c-dimethyl-10b,10c-dihydropyrene (41)



41

Borch reagent[90] (1.3 g, 85% oil, 6.8 mmol) was added to a solution of **39** (910 mg, 0.44 mmol) in CH_2Cl_2 (50 mL) under nitrogen. The mixture was then stired for 4 h at room temperture and then ethyl acetate (40 mL) was added and stirring continued for overnight. The solvent was decanted after standing, and the oily residue was stirred with ethyl acetate (40 mL) for 4 h. This gave the salt **40**, which was then collected and dried under vacuum to give 1.4 g of product. Then KOBu^t (0.56 g, 5.0 mmol) was added to a suspension of this salt (1.4 g, 2.3 mmol) in THF (80 mL) under nitrogen at 0°C. After 3 h stirring the mixture was quenched with water (10 mL), 2 M HCl (1 mL) and PE (50 mL). The organic layer was washed by with $NaHCO_4$ solution, water, dried with Na_2SO_4 and then preabsorbed on 2 g silca gel and flash chromatography using PE as eluant to yield 0.41 g (60%) deep green (black) crystals of *trans*-isomer **41**, identical sample as in literature,[50] mp 110-111 °C. (lit.[50] mp 111-112 °C); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.70 (s, 2, H-1,3), 8.65-8.50 (m, 6, H-4,5,6,8,9,10), 8.07 (t, 1, J = 9.0 Hz, H-7), -4.07 and -4.08 (s, 3 each, $-CH_3$).

trans-4,9-Dibromo-2,7-di-*t*-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene (Method A)



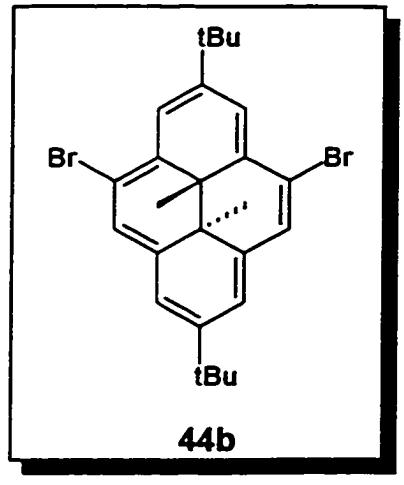
44a

A pre-cooled (in freezer at -7 °C) solution of NBS (1.10 g, 6.17 mmol) in dry DMF (100 mL) was added slowly over 1 h to a pre-cooled (in freezer at -7 °C) solution of pyrene **43**[55a](1.01 g, 2.94 mmol) in dry DMF/CCl_4 (350 mL/50 mL) at 0°C and then the reaction was stirred without cooling for 2 h. Hexanes (200 mL) was added, and then the mixture was poured into ice-water. The hexanes extract was washed well with water and dried with $MgSO_4$, and then flash chromatography gave the dark green product **44a**, 1.3 g (88%), which could be recrystallized from hexanes, mp 220-222 °C; ^{1}H NMR ($CDCl_3$, 360 MHz): δ 8.81 (bs, 2, H-3,8), 8.64 (bs, 2, H-5,10), 8.49 (bs, 2, H-1,6), 1.68 (s, 18, *t*-Bu), -3.83 (s, 6, -CH_3); ^{13}C NMR ($CDCl_3$, 90.6 MHz) δ 148.2, 137.2, 132.4, 126.9, 121.9, 121.5, 116.5, 36.3, 32.2, 31.9, 14.3; CI MS m/z: 500 (MH^+, correct isotope pattern); IR (KBr) 3036, 2961, 2860, 1329, 777 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 201 (123 000), 350 (73 000), 388 (39 000), 485 (5 500).

Anal. calcd for $C_{26}H_{30}Br_2$: C, 62.17; H, 6.02. Found: C, 61.06, H, 6.01. HR MS (E.I.) calcd: 500.0714. Found: 500.0715.

trans-4,9-Dibromo-2,7-di-_t_-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene (Method B) and _trans_-4,10-dibromo-2,7-di-_t_-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene

A solution of NBS (3.53 g, 19.8 mmol) in $CHCl_3$ (150 mL) was added to a solution of pyrene **43**[55a](3.1 g, 9.01 mmol) in $CHCl_3$ (250 mL) at room temperature and then the reaction was stirred overnight. Then the solution was poured onto ice-water and extracted with chloroform (2x 100 mL). The extracts were washed with water and dried with $MgSO_4$, and then evaporated to yield 4.5 g (~ 100%) of green product as a mixture of **44a** and **44b** (4:6).



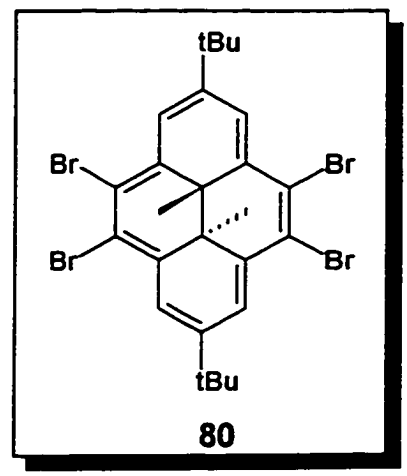
44b

Attempts to separate these two isomers by recrystallization or chromatography failed. **44b**: ^{1}H NMR ($CDCl_3$, 360 MHz): δ 9.00 (d, J = 1.4 Hz, 2, H-6,8), 8.96 (d, J = 1.2 Hz, 2, H-1,3), 8.85 (d, J = 1.2 Hz, 2, H-5,9), 1.70 (s, 9, _t_-Bu),1.67 (s, 9, _t_-Bu), -3.67 (s, 3, $-CH_3$), -3.71 (s, s, $-CH_3$); ^{13}C NMR ($CDCl_3$, 90.6 MHz) δ 149.5, 137.9, 133.7, 133.5, 133.0, 127.4, 124..6, 124.1, 122.9, 117.1, 36.6, 36.3, 34.5, 32.1, 31.8, 26.9, 14.6, 14.0; CI MS m/z 500 (MH^+, correct isotope pattern).

trans-4,5,9,10-Tetrabromo-2,7-di-_t_-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene (80)[55a]

A solution of Br_2 (166 mL, 0.0772 mmol Br_2/mL in CCl_4, 12.8 mmol) was added

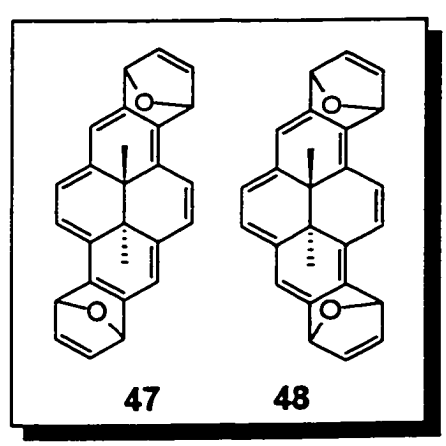
dropwise to a stirred solution of 2,7-di-t-butylpyrene **43**[55] (1.10 g, 3.20 mmol) in CCl_4 (200 mL) at 0 °C in 1 h . After further stirring for 1 h, the solution was poured onto ice-water (200 g) and the organic layer was extracted with CH_2Cl_2 (3 x 100 mL). The CH_2Cl_2 extracts were washed, dried and evaporated to yield 2.0 g (95%) of the product. Flash chromatography using hexanes or recrystallization from hexanes gave green crystals, identical properties to those reported in the literature,[55a] mp 227-229 °C (lit.[55a] mp 228-230 °C).



80

Furan adducts 47 and 48 from dibromide 21a: *trans*-1,4,8,11,13b,13c-hexahydro-13b,13c-dimethyl-1,4:8,11-diepoxydibenzo[b,def]chrysene (47) and *trans*-1,4,9,12,13c,13d-hexahydro-13c,13d-dimethyl-1,4:9,12-diepoxydibenzo[a,def]chrysene (48)

$NaNH_2$ (150mg, 3.85 mmol) and KOBu^t (2 mg, 0.018 mmol) were added to a solution of **21a** (122mg, 0.31 mmol) in dried furan (4 mL) and THF (4 mL) at room temperature with stirring. After 48 h, methanol (0.5 mL) was added, followed by silica gel (2 g). The solvent was evaporated and the residue was

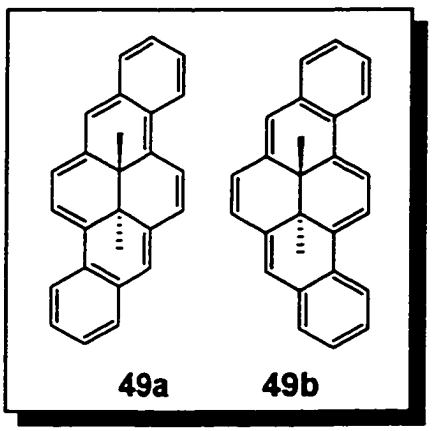

47 **48**

chromatographed over silica gel using PE to first elute small amounts of unchanged dibromide **21a** and parent pyrene **5a** and then PE: ether (4 : 1) to elute the products, 70 mg (62%), as a mixtures of six isomers of *transoid*[66b] **47** and *cisoid* **48** (~3.5/1). The mixture was chromatographed using PE/ether and fractionally recrystallized from CH_3OH/CH_2Cl_2 to produce 30 mg of a mixture of the three *transoid* isomers **47**. ^1H NMR ($CDCl_3$, 360 MHz): **47uduu**[56c] δ 8.46, (s, 2, H-5,12), 8.43-7.96 (m, 4, H-6,7,13,14), 7.23-7.16 (8 lines, 2, H-4,11), 7.16-7.13 (8 lines, 2, H-2,9), 6.59 (bs, 2, H-1,8), 6.25 (bs, 2, 4,11), -3.80 and -4.15 (s, $-CH_3$); **47udud + 47 uudd** δ 8.46 (s, 2, H-5,12), 8.43-7.96 (m, 4, H-6,7,13,14), 7.39-7.36 (6 lines, 2, H-2,9), 7.34-7.31 (6 lines, 2, H-3,10), 6.61 (bs, 2, H-1,8), 6.23 (bs, 2, H-4,11), -3.96 and -4.01 (s, 3 each, $-CH_3$)-see text; ^{13}C NMR ($CDCl_3$, 90.6 MHz) δ 144.3, 143.7, 143.6, 143.9, 142.8, 142.3, 142.0, 141.9, 141.3, 140.8, 140.4, 137.2, 137.1, 136.2, 129.7, 129.3, 128.0, 123.3, 123.2, 123.1, 118.2, 117.8, 117.7, 117.1, 116.5, 84.0, 83.54, 83.50, 81.5, 81.3, 81.2, 32.7, 32.6, 32.3, 14.9, 14.4, 14.1-each type of carbon showed three resonances, e.g., the internal methyl carbons: 14.9, 14.4, 14.1; CI MS m/z 393 (5.5), 365 (MH^+, 100), 364 (47), 349 (18), 348 (4.6), 337 (3.3), 335 (6.6), 298 (3.4).

HR MS (E.I.) Calcd for $C_{26}H_{20}O_2$: 364.1463; Found: 364.1485.

Cisoid isomers **48**: ^1H NMR ($CDCl_3$, 360 MHz, peaks after subtracting *transoid* isomers): δ 7.80 and 7.42 (s, 2, H-5,8), 7.70-7.61 (m, 4, H-6,7,13,14), 7.05-6.81 (m, 4, H-2,3,10,11), 6.27 (bs, 2, H-1,12), 5.92 (bs, 2, H-4,9), -2.13, -2.27, -2.31, -2.45 (s, $-CH_3$)-see test; The protons were assigned by ^1H NMR COSY and NOESY (see appendix V).

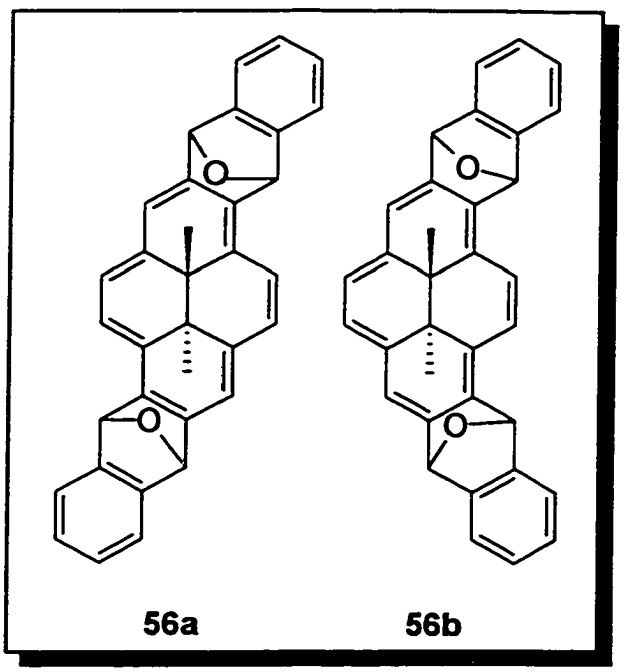
Deoxygenation of 47/48 to bisbenzannelated dihydropyrenes (49a) and (49b): *trans*-13b,13c-dimethyl-13b,13c-dihydrobenzo[*b,def*]chrysene (49a) and *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*rst*]pentaphene (49b)



A mixture of mixed isomers of 47 (12mg, 0.033 mmol) and $Fe_2(CO)_9$ (29 mg, 0.080 mmol) in benzene (4 mL, distilled from sodium under argon) was stirred at 60 ^{0}C under Ar for 1 h. The cooled mixture was quickly chromatographed on silica gel (5% water deactivated), using petroleum ether as eluant. The deep blue band yielded 6 mg (55%) of **49a**. ^{1}H NMR ($CDCl_3$, 360 MHz) δ 9.30 (d, J = 7.4 Hz, 2, H-4, 11), 9.21 (d, J = 7.4 Hz, 2, H-5, 12) , 8.81 (s, 2, H-7, 14), 8.60 (d, J = 7.4 Hz, 2, H-1, 8), 8.31 (d, J = 7.4 Hz, 2, H-6, 13), 7.76-7.64 (m, 4, H-2, 3, 9, 10), -3.46 (s, -CH_3); CI MS m/z 333 (MH^+, 100.0), 332 (M^+, 60.7), 318 (weak), 317 (weak), 303 (weak). The data are identical with the literature.[56a]

When mixed isomers of **47/48** were used, both benzannulenes **49a,b**[56a] were obtained.

Benzoisofuran adducts 56a and 56b and ***trans*-12-bromo-14b,14c-dimethyl-14b,14c-dihydronaphtho[2,1,8-qra]naphthacene 57**

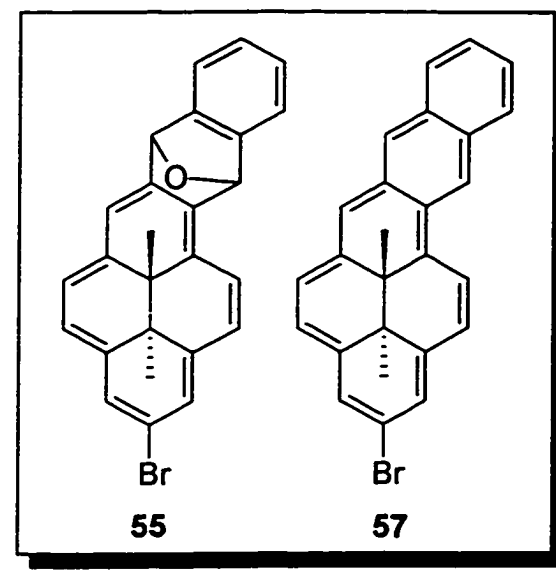


LDA (5 mL, 1.5M in hexane) was added to a solution of 1-methoxyphthalan **53**[57] (1.48 g, 10 mmol) in THF (10 mL) under Ar at room temperature. TLC indicated isobenzofuran **54** (which shows a strong fluorescence) is formed immediately. Then dibromodihydropyrene **21a** (200mg, 0.51 mmol) and $NaNH_2$ (80 mg, 2.04 mmol) were added immediately. The mixture was stirred at room temperature for 2 days, and then methanol (1 mL) was added. The mixture was preabsorbed and chromatographed on silica gel using PE/ethyl acetate as eluant. PE eluated first trace amounts of the dibromodihydropyrene **21a** and the debrominated pyrene **5a**. The second fraction (red) was 18 mg of the deoxygenated product **57** from the mono adduct **55** in about 10% yield, followed by a small amount of the mono-adduct **55** (always with small amount of the debrominated product **59** from **55**). **55**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.6-8.2 (m), 7.4-6.6 (m), -3.64, -4.01 (s, $-CH_3$,); CI MS m/z 427 (MH^+).

57: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.88 (s, 1, H-12), 8.19 (s, 1, H-7), 8.08-7.95 (m, 2, H-8,11), 7.65 and 6.78 (AB, J = 6.6 Hz, 2, H-13, 14), 7.56-7.54 (m, 2, H-9, 10), 7.18 and

7.00 (AB, J ~ 12 Hz, 2, H-4, 5), 7.66 and 6.86 (s, 2, H-1,3), -0.39 and -0.41 (s, 3 each $-CH_3$). CI MS m/z 441 (2.7), 439 (2.3), 414 (23), 413 (93), 412 (88), 411 (100, MH^+), 410 (67), 397 (3.3), 333 (22) 332 (32) 331 (54), 285 (14), 257 (12), 174 (28).

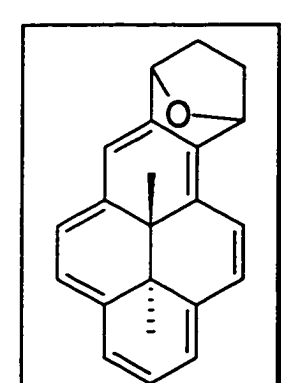
The following major fraction (80 mg, 23%) using PE/ethyl acetate (5:1) as eluant was collected and characterized as a mixture of the bis-adduct products **56a** and **56b**. The low stability of these adducts prevented a complete characterization. Theoretically there should be six isomers totally for **56**. **56a** and **56b**: ^1H NMR ($CDCl_3$, 300 MHz) δ 8.5-6.4 (m, ArH and -OCH-), -2.72, -3.08, -3.11, -3.48 , -3.55, -3.67, -3.96, -4.20 (s, $-CH_3$); CI MS m/z 466 (1.0), 465 (MH^+, 5.3), 464 (1.5, M^+), 449 (0.6), 448 (1.8), 253 (0.7), 238 (2.0), 237 (16.9), 147 (4.1), 135 (7.7).



55 **57**

Hydrogenation of furan adduct 46c to 70

A solution of the mono adduct **46c** (40 mg, 0.13 mmol) in ethyl acetate (10 mL) was added to pre-reduced PtO_2 (5 mg) in ethyl acetate (10 mL). Then the mixture was stirred under H_2 for 30 min. Direct chromatography of the product on silica gel using PE/ethyl acetate (4:1) as eluant gave 37 mg (93%) of the product

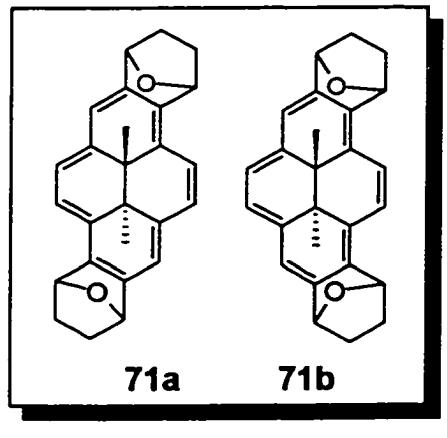


70

70, as green crystals from petroleum ether, mp 112-113 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63 (d, J = 8.0 Hz, 1), 8.55-8.49 (m, 5), 8.40 (s, 1), 8.02 (t, J = 7.8 Hz, 1), 6.37 (m, 1), 5.99 (m, 1), 2.36-2.31 (m, 2), 1.54-1.30 (m, 2), -4.13 and -4.23 (s, 3 each); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 142.2, 139.5, 139.3, 136.4, 136.1, 126.1, 124.0, 123.9, 123.3, 122.8, 122.5, 119.1, 114.4, 80.5, 78.1, 31.4, 30.3, 29.3, 27.9, 14.2, 13.7; CI MS m/z 329 (3.0), 309 (4.0), 303 (3.1), 302 (20.4), 301 (100.0, MH^+), 300 (51.1), 286 (5.8), 285 (12.4), 283 (3.4), 242 (2.6); IR (KBr, cm^{-1}) 2961, 2923, 2345, 1442, 1294, 990, 877, 811, 664. UV (cyclohexane) λ_{max} (ε_{max}) 342 (59 500), 379 (23 100), 473 (4 400), 640 (550).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.30; H, 6.76.

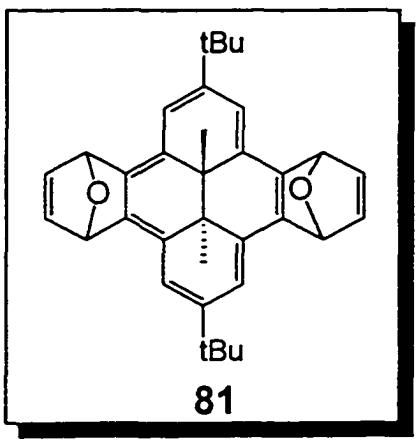
Hydrogenation of furan adduct 47/48 to 71a/71b



A solution of a mixture of the bis adduct **47/48** (~1.9 mg, 0.05 mmol) in ethyl acetate (5 mL) was added to pre-reduced PtO_2 (2 mg) in ethyl acetate (5 mL). Then the mixture was stirred under H_2 for 30 min. After filtration, direct chromatography of the solution on silica gel using petroleum ether as eluant gave ~2 mg (~100%) of the product, as a mixture of (total six isomers) **71a** and **71b**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.60-8.44 (m, 4), 8.31 (s, 1), 8.26 (s, 1), 6.39-6.31 (m, 2), 5.94-5.91 (m, 2), 2.52-2.08 (m, 2), 1.74-1.37 (m, 2). -3.94, -4.02, -4.18, -4.19, -4.20, -4.26, -4.36, and -4.43 (s, total 6, -

CH_3). These eight singlets should correspond to the six possible isomers which should have eight singlets for their internal methyl protons-see text; CI MS m/z 367 (MH^+).

Furan adducts of 44a to give 81: *trans*-6,13-di-*t*-butyl-1,4,8,11,14b,14c-hexahydro-14b,14c-dimethyl-1,4:8,11-diepoxydibenzo[*fg,op*]naphthacene (81) (Method A)



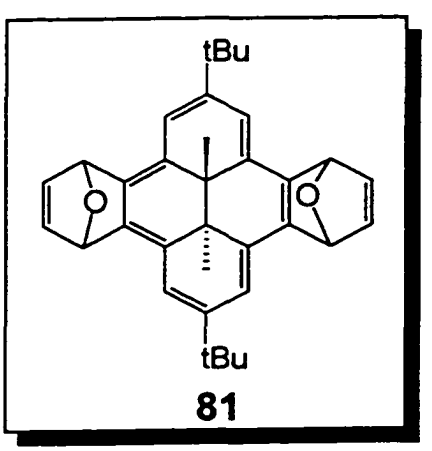
$NaNH_2$ (400 mg, 10 mmol) and $KOBu^t$ (2 mg) were added to a stirred solution of bromide **44a** (430 mg, 0.86 mmol) in dried furan (5 mL) and THF (0.5 mL), and then the mixture was stirred at 55°C for 4 days. Methanol (0.5 mL) and silica gel were added and the solvent was evaporated, then the residue was chromatographed over silica gel using PE - ethyl acetate (9:1) as eluant. Eluted first was the mono-adduct (~20 mg, 5%). Eluted next was bis-adduct **81**, 241 mg (59%) as a mixture (1:1) of two isomers **81a** and **81b**. In its ^1H NMR spectrum, the internal methyl protons appeared at δ -3.99 for isomer **81a** and at -3.70 and -4.30 for isomer **81b**. Isomer **81a** could be fractionally crystallized from hexanes, mp 236-238 °C; ^1H NMR (360 MHz) δ 8.34 and 8.31 (bs, 4, ArH), 7.29 and 7.19 (dd, J = 5.5 and 1.9 Hz, 4, -CH=CH-), 6.67 and 6.65 (m, 4, OCH), 1.67 (s, 18, *t*-Bu) and -3.99 (s, 6, $-CH_3$); ^{13}C NMR (90.6 MHz) δ 145.1, 141.7, 139.2, 138.9, 128.4, 128.3, 115.8, 115.7, 115.2, 82.0, 81.7, 36.0, 31.9, 31.3, 14.2; UV

($CHCl_3$) λ_{max} nm (ϵ_{max}) 284 (5 100), 377 (53 000), 391 (36 100), 446 (6 900), 665 (800); IR (KBr) cm^{-1} 2961, 2932, 2848, 1467, 1254, 1027, 864; CI MS m/e 477 (MH^+).

Anal. calcd for $C_{34}H_{36}O_2$: C, 85.94; H, 7.60. Found: C, 85.67; H, 7.61.

The mono-adduct **81c**: This side product easily decomposed during workup and purfication; ^1H NMR (300 MHz) δ 8.48 (d, J = 3.2 Hz, 1), 8.41 (s, 1), 8.09 (m, 3), 7.16 and 7.05 (m, 1 each), 6.52 (m, 2), -3.12, -3.13,- 3.38 and -3.42 (s, 6 total, $-CH_3$); CI MS at 489 and 491(MH^+, 1:1 for bromine isotope).

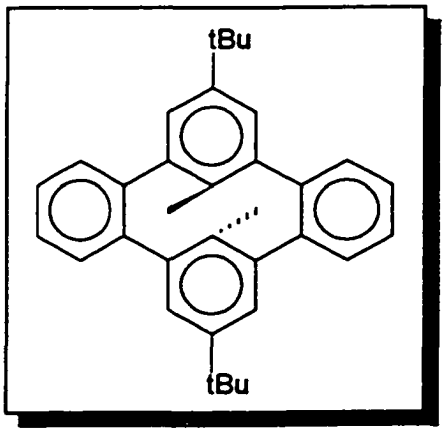
Furan Adducts of 44a to give 81: *trans*-6,13-di-*t*-butyl-1,4,8,11,14b,14c-hexahydro-14b,14c-dimethyl-1,4:8,11-diepoxydibenzo[*fg,op*]naphthacene (81) (Method B)



n-BuLi (0.92 mL, 2.3 mmol, 2.5 M in hexane) in hexane (15 mL) was added dropwise to a stirred solution of the tetrabromide **80**[55a] (0.684 g, 1.04 mmol) in furan (50 mL) and THF (5 mL) at -78 °C over 30 min under Ar. Then the cooling bath was removed and the mixture was stirred further for 2 h at room temperature. Methanol (2 mL) was added to quench the mixture and ether (100 mL) and ice-water (100 g) were added. A simple filtration at this stage yielded 0.16 g bright green crystals, which was identified as pure isomer **81a**. The filtrate was extracted with ether (2 x

100 mL). The ether extracts were then washed, dried, and evaporated to yield a further 0.19 g (total yield: 71%) of the product, mainly isomer **81b**. Fractional recrystallization or chromatography was used as in method A to separate the two isomers completely and yield the identical sample as in **Method A**.

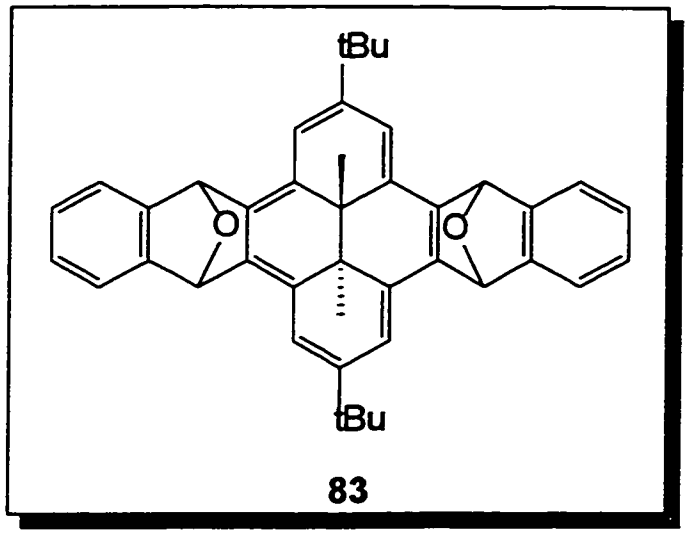
Deoxygenation of 81 to give 82: *anti*-[1,2;9,10]-dibenzo-5,13-di-*t*-butyl-8,16-dimethyl[2.2]metacyclophane



The mixture of adducts **81** (100mg, 0.21 mmol) and $Fe_2(CO)_9$ (190 mg, 0.53 mmol) in benzene (10 mL) was stirred under Ar at 65-70 °C for 6 h. The mixture was cooled and silica gel (2 g) was added. Direct chromatography using hexanes gave 40 mg (68%) of colourless product **82**, which was recrystallized from hexanes, mp 231-232 °C; ^{1}H NMR (360 MHz) δ 7.69 and 7.39 (AA'XX', 8, H-4,5,6,7,11,12,13,14), 6.95 (s, 4, H-1,3,8,10), 1.29 (s, 18, t-Bu), 1.07 (s, 6, $-CH_3$); ^{13}C NMR (90.6 MHz) δ 150.9, 144.6, 140.6, 138.9, 129.4, 129.2, 129.0, 34.7, 31.6, 18.7; UV (cyclohexane) λ_{max} nm (ϵ_{max}) 288 (12 000), 378 (2 400), 392 (2 000); IR (KBr) cm^{-1} 3049, 2961, 2860, 1567, 1467, 1417, 1354, 1254, 1228, 877, 730; CI MS m/z 445 (MH^+).

Anal. calcd for $C_{34}H_{36}$: C, 91.84; H, 8.16. Found: C, 91.24; H, 8.36.

Benzoisofuran adduct of 80 to 83



83

LDA (15 mL, 1.5 M in cyclohexane, 22.5 mmol) was added to a solution of 1-methoxyphthalan (3.0 g, 20 mmol) in THF (35 mL) under Ar at room temperature. After 5 min, the dibromide **44a** (1.0 g, 2.0 mmol) and sodium amide (400mg, 10 mmol) were added, and stirring continued for 4 days. After methanol (2 mL) was added, the total mixture was pre-absorbed onto silica gel and chromatographed with PE-ether. PE eluted first trace amounts of pyrene **5b** and **41a** and then PE-ether (20:1) eluted the mono-adduct **84** (~0.21g, 20%). This was not able to be purified properly due to presence of the debrominated product from **84** and the deoxygenated product **86**; ^{1}H NMR (300 MHz) δ 8.5-7.1 (m, ArH), 6.6 (m, OCH), 1.72 (s, *t*-Bu), -3.68 and -4.22 (s, -CH_3); LSI MS (Matrix: mNBA) calculated: 539.6 (MH^+). Found: 539.2.

Next was eluted a mixture (1:1) of the two bis-adduct isomers **83a** and **83b** (0.38g, 33%). Recrystallization and chromatography failed to separate these two isomers completely but yielded an **81b** enriched mixture. Their ^{1}H NMR spectra were assigned by COSY and

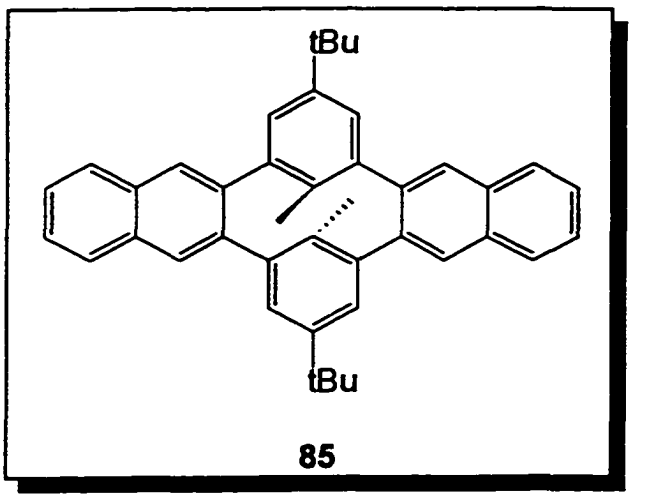
NOSEY. ^{1}H NMR (360 MHz, d_8-THF) **83a**: δ 8.65 (bs, 4, H-1,3,10,12), 7.48-7.45 and 7.40-7.37 (m, 2 each set, H-5,8,14,17), 7.03 (s, 4, H-4,9,13,18), 6.86-6.84 (m, 4, H-6,7,15,16), 1.73 (s, 18, *t*-Bu), -4.39 (s, 6, $-CH_3$). **83b**: 8.61 (bs, 4, H-1,3,10,12), 7.41-7.39 and 7.32-7.30 (m, 2 each set, H-5,8,14,17), 7.02 (s, 4, H-4,9,13,18), 6.78-6.75 (m, 4, H-6,7,15,16), 1.750 and 1.746 (s, 9 each, *t*-Bu), -3.66 and -5.17 (s, 3 each, $-CH_3$); ^{13}C NMR (mixture of **83a** and **83b**, 90.6 MHz) δ 145.0, 249.7, 146.4, 146.1, 145.7, 141.5, 141.1, 140.9, 140.8, 129.0, 128.8, 128.5, 128.4, 126.0, 125.9, 125.84, 125.78, 120.4, 120.2, 120.1, 119.9, 117.5, 116.6, 116.5, 83.1, 83.0, 82.64, 82.57, 36.7, 35.0, 32.8, 32.2, 30.9, 16.4, 14.3, 12.1; UV (CH_2Cl_2) λ_{max} nm (ϵ_{max}) 229 (15 000), 250 (18 000), 273 (16 000), 368 (58 000), 399 (52 000), 461 (12 000) 480 (6 900); IR (KBr) cm^{-1} 3049, 2988, 2961, 2910, 2860, 1605, 1454, 1341, 1254, 864, 751, 626; LSI MS (Matrix: mNBA) calculated: 577.3 (MH^+); Found: 577.3.

Anal. calcd for $C_{42}H_{40}O_2$: C, 87.45; H, 6.99. Found: C, 86.19; H, 6.95; HR MS (E.I.) calcd for $C_{42}H_{40}O_2$: 576.3028. Found: 576.3029.

Deoxygenation of 83 to 85: *anti*-[1,2-b;9,10-b]-dinaphtho-5,13-di-*t*-butyl-8,16-dimethyl[2.2]metacyclophane (85)

The mixture of adducts **83** (68 mg, 0.12 mmol) and $Fe_2(CO)_9$ (130 mg, 0.35 mmol) in benzene (30 mL) was stirred under Ar at 65-70 °C for 8 h. The mixture was cooled and silica gel (2 g) was added. Direct chromatography using hexanes yielded 38 mg (59%) of colourless **85**. Recrystallization of **85** from cyclohexane gave needles, mp 340-341 °C

(sublimed); ^{1}H NMR (360 MHz, d_8-THF) δ 8.22 (s, 4, H-4,9,13,18), 7.96 and 7.50 (AA'XX', 8, H-5,6,7,8,14,15,16,17), 7.14 (s, 4, H-1,3,10,12), 1.31 (s, *18*, *t*-Bu), 1.06 (s, 6, -CH_3); ^{13}C NMR (90.6 Mhz, d_8-THF) δ 150.6, 143.1, 140.3, 138.4, 134.7, 130.5, 128.5, 128.0, 126.8, 34.8, 31.7, 18.6; UV (THF) λ_{max} nm (ϵ_{max}) 261 (550 000), 287 (470 000); IR (KBr) cm^{-1} 3047, 2964, 2862, 1690, 1639, 890, 739; CI MS m/z 545 (MH^+).



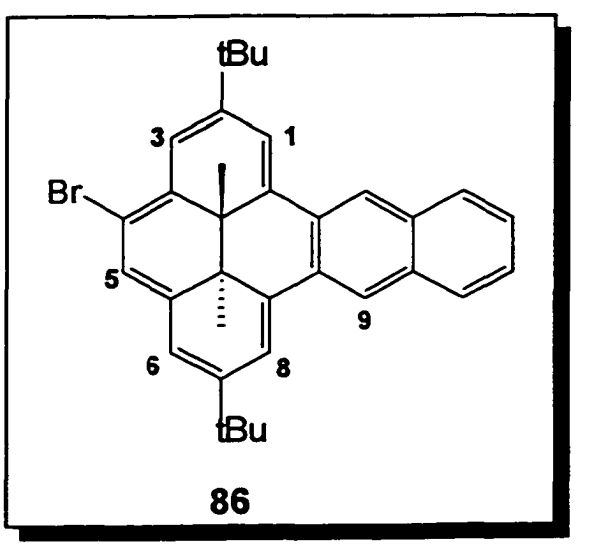
85

Anal. calcd for $C_{42}H_{40}$: C, 92.59; H, 7.40; Found: C, 92.12; H, 7.60.

Eluted next was starting material **83**, 25 mg (37%).

Deoxygenation of 84 to 86

The mixture of adducts **84** (250 mg, 0.46 mmol) and $Fe_2(CO)_9$ (410 mg, 1.13 mmol) in benzene (20 mL) was stirred under Ar at 65-70 °C for 8 h. The mixture was cooled and silica gel (2 g) was added. Direct



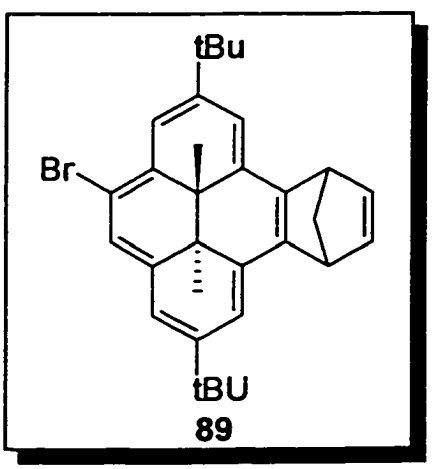
86

chromatography using hexanes gave 120 mg (50%) of red-brown product of **86**. Recrystallization of **86** from hexane gave dark red crystals, mp 185-186 °C; ^{1}H NMR (360 MHz, d_8-THF) δ 9.16 and 9.13 (s, 2, H-9,14), 8.157 and 8.153 (s, 2, H-1,8), 8.14-8.08 (m, 2, H-10,13), 7.55-7.50 (m, 2, H-11,12), 7.26 (s, 1, H-3), 6.94 (bs, 1, H-5), 6.67 (s, 1, H-6); UV (cyclohexane) λ_{max} nm (ϵ_{max}) 211 (66 800), 262 (50 200), 323 (33 700), 368 (26 200), 381 (41 000), 400 (50 400), 553 (4 100), 630 (420); IR (KBr) cm^{-1} 3055, 2950, 2854, 1609, 1442, 1352, 868, 734; CI MS m/z 521 and 523 (MH^+, 1:1 for one bromine).

HR MS (E.I.) calcd for $C_{34}H_{35}Br$: 522.1922. Found: 522.1917.

Cyclopentadiene adduct 88

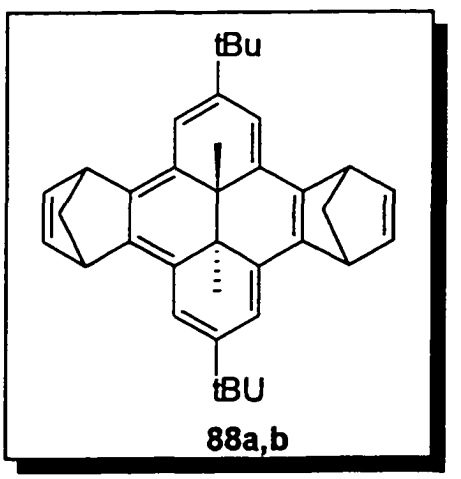
n-BuLi (1.0 mL, 2.5 mmol, 2.5 M in hexane) in hexane (15 mL) was added dropwise to a stirred solution of tetrabromide **80**[55a] (0.500 g, 0.758 mmol) and freshly distilled cyclopentadiene (1 mL) in THF (50 mL) at -78 °C over 30 min under Ar. Then the cooling bath was removed, and the mixture was stirred for a further 2 h at room temperature. After methanol (2 mL) was added to quench the mixture, hexanes (100 mL) and ice-water (100 g) were added. The mixture was further extracted with CH_2Cl_2. The extracts were then washed, dried, and concentrated to ~ 100 mL. Silica gel (10 g) was then added to pre-absorb the products and



89

then chromatography with hexanes/CH_2Cl_2 (3:1) eluted first a small amount of the mono-adduct **89** (~30 mg, two pairs of stereoisomers, 10%) together with some debrominated product **90**. **89** (with some **90**): ^{1}H NMR (300 MHz) δ 8.61-8.18 (m, 5), 6.95 and 6.84 (m, 2, -CH=CH-), 4.85 and 4.81 (m, 2, -CH-), 2.66-2.64 and 2.43-2.41 (m, 4, $-CH_2-$), 1.65 and 1.63 (s, 18, *t*-Bu), -3.497 and -3.746(s, 3 each $-CH_3$, one isomer), -3.503 and -3.754 (s, 3 each, $-CH_3$, the other isomer); CI MS m/z 487 and 489 (MH^+, 1:1, correct isotope pattern for one bromine).

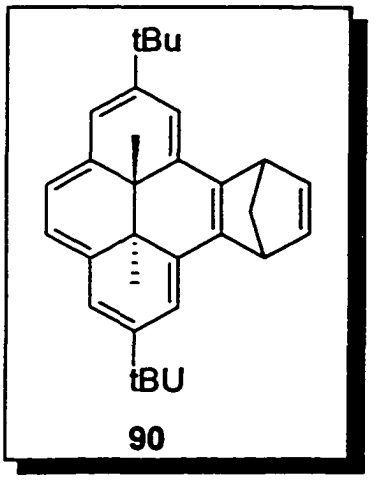
Eluted next was 0.32 g (89%) of the bis adduct product, as a mixture of both isomers **88a** and **88b** (1:1). Fractional recrystallization from cyclohexane failed to separate these two isomers. ^{1}H NMR (360 MHz) δ 8.40 and 8.38 (bs, 4, H-1,3,6,8, both isomers), 7.05-7.02 and 6.95-6.91 (m, 2 each set,-CH=CH-, both isomers), 4.91 and 4.88 (m, 2H each, -CH-, both isomers), 2.69 to 2.67 and 2.51-2.48 (m, 2 each, $-CH_2-$, both isomers), -4.12 (s, 6H, $-CH_3$, **88a**), -3.83 and -4.41 (s, 6H, $-CH_3$, **88b**)-see text; ^{13}C NMR (90.6 MHz) δ 143.7, 143.4, 143.2, 142.23, 142.16, 142.02, 141.99, 129.6, 129.2, 129.0, 114.7, 114.6, 114.5, 114.4, 67.7, 53.4, 48.8, 48.0, 35.9, 32.1, 32.0, 31.8, 22.6, 16.4, 14.1, 11.9; UV (hexane) λ_{max} nm (ϵ_{max}) 267 (9 500), 369 (95 000), 374 (66 000), 392 (52 000), 457 (7 900), 476 (5 500), 663 (610); IR (KBr) cm^{-1} 3061, 2961, 2923, 2860, 1605, 1440, 1341, 1254, 864, 855, 680; CI MS m/z 473 (MH^+).



88a,b

Anal. calcd for $C_{36}H_{40}$: C, 91.47; H, 8.53. Found: C, 90.81; H, 8.83.

Mono-cyclopentadiene adduct 90

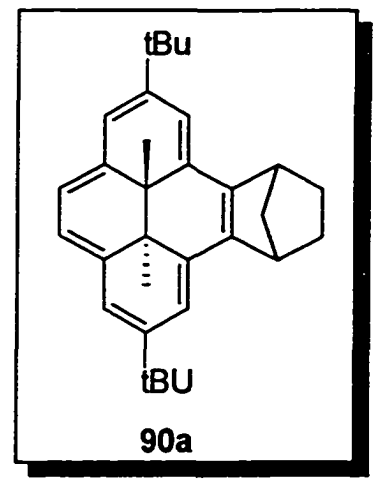


90

n-BuLi (0.4 mL, 2.0 M in hexane) was added by syringe to a stirred solution of **89** (5.0 mg, 0.010 mmol) in THF (10 mL) at -78 ^{0}C (the colour turned to red-brown immediately) and stirring continued for 15 mins. After methanol (1 mL) was added, the colour reverted to green. The cooling bath was then removed and the stirring was continued for 30 min. Ice-water (20 g) and PE (50 mL) was then added. The PE extracts were washed, dried and evaporated to yield 4 mg (~ 100%) product **90**. ^{1}H NMR (300 MHz) δ 8.28 and 8.27 (s, 2, H-1/3, 8/6), 8.243 and 8.235 (s, 2, H-3/1, 6/8), 8.19 (s, 2, H-4,5), 6.95 and 6.82 (dd, J = 5.6 Hz and 3.2 Hz, 2 each set, H-10, 11, -CH=CH-), 4.84 and 4.80 (bs, 2, H-9,12, -CH-), 2.66 and 2.42 (m, 2, H-9a, -CH_2-), 1.66 (s, 18, *t*-Bu), -3.52 and -3.77 (s, 6, -CH_3); CI MS m/z 409 (MH^+).

HR MS (EI) calcd for $C_{31}H_{36}$: 408.2817. Found: 408.2825.

Hydrogenation of 90 to 90a



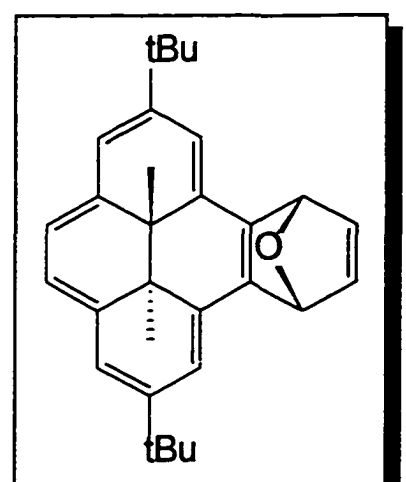
90a

The mixture of **90** (~ 4 mg, 0.010 mmol) and PtO_2 (2 mg) in ethyl acetate (10 mL) was stirred under H_2 for 30 min at room temperature. After a simple filtration on pepet, direct chromatography of the solution on silica gel using PE as eluant gave 4 mg (~ 100%) of product **90a**. ^1H NMR (300 MHz) δ 8.53-8.35 (m, broad, 6, H-1,3,4,5,6,8), 4.42 (bs, 2, , H-9,12, -CH-), 2.30-2.24 (m, 6, three sets of $-CH_2-$), 1.68 (s, 18, *t*-Bu), -4.00 and -4.17 (s, 6, $-CH_3$); CI MS m/z 411 (MH^+).

HR MS (E.I.) calcd for $C_{31}H_{38}$: 410.2974. Found: 410.2971.

Furan mono-adduct 91

n-BuLi (0.4 mL, 2.0 M in hexane) was added by syringe to a stirred solution of **81c** (45 mg, 0.092 mmol) in THF (10 mL) at -78 °C (the colour turned to red-brown immediately) and stirring was continued for 15 mins. After methanol (1 mL) was added, the colour reverted to green. The cooling bath was removed and the stirring continued for 30 min. Ice water (20 g) and PE (50 mL) was then added to the mixture. The PE extracts were washed, dried and evaporated to yield 30 mg (73%) of the product **91**. This compound



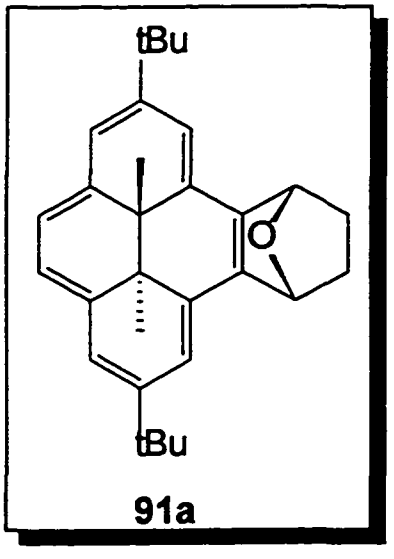
91

easily decomposed during work-up and in the $CDCl_3$ solution for NMR spectrum. ^1H NMR (300 MHz) δ 8.13 and 8.12 (s, 1 each, H-1,8), 8.09 (s, 2, H-4,5), 8.06 and 8.05 (s, 1 each, H-3,6), 7.16 and 7.03 (dd, J = 1.6 and 5.6 Hz, 2, H-10,11), 6.55 and 6.51 (m, 2, H-9,12), 1.66 (s, 18, *t*-Bu), -3.16 and 3.42 (s, 6, $-CH_3$); CI MS m/z 411 (MH^+).

HR MS calcd for $C_{30}H_{34}O$: 410.2609. Found: 410.2608.

Hydrogenation of 91 to 91a

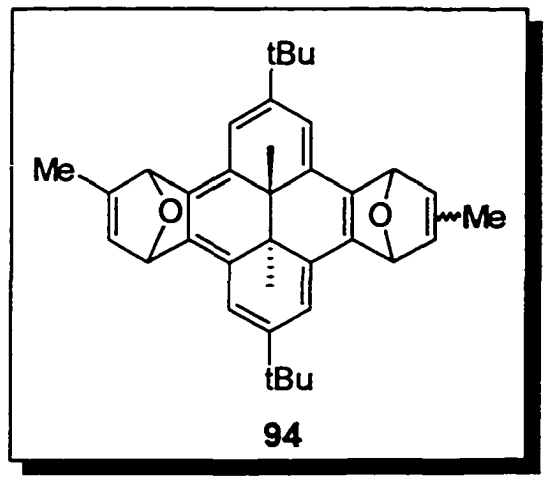
The mixture of **91** (~ 5mg, 0.012 mmol) and PtO_2 (2 mg) in ethyl acetate (10 mL) was stirred under H_2 for 30 min at room temperature. After the sample was pre-absorbed on silica gel, chromatography of the product using PE as eluant gave 5 mg (~ 100%) of product **91a**, together with some of the deoxygenated product: ^1H NMR (300 MHz) δ (8.9-8.4, m, ArH), 6.38 (m, -CH-), 3.00-2.97 (m, $-CH_2-$), 1.68 and 1.67(s, *t*-Bu), -3.94 and -4.12 (s, $-CH_3$); CI MS m/z 413 (MH^+).



91a

HR MS (E.I.) calcd for $C_{30}H_{36}O$: 412.2766. Found: 412.2759

Methylfuran adducts 94: *trans*-6,13-di-*t*-butyl-1,4,8,11,14b,14c-hexahydro-2,9(10),14b,14c-tetramethyl-1,4:8,11-diepoxydibenzo[*fg,op*]naphthacene (94)

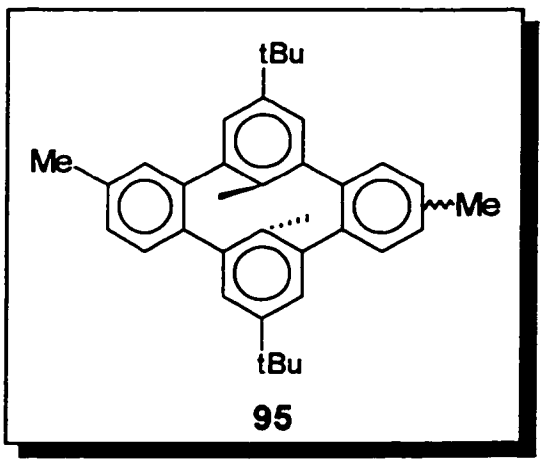


94

n-BuLi (2.0 mL, 4.4 mmol, 2.2 M in hexane) in hexane (10 mL) was added dropwise to a stirred solution of tetrabromide **80**[55a] (1.0 g, 1.52 mmol) and freshly distilled 3-methylfuran[66] (3 mL, excess) in THF (50 mL) at -78 °C over 40 min under Ar. Then the cooling bath was removed and the mixture was stirred further for 3 h at room temperature. After methanol (2 mL) was added to quench the mixture, silica gel (20 g) was added to the mixture and the solvent was evaporated. The residue was chromatographed directly with hexanes/ethyl acetate (5:1) to yield 0.32 g (42%) of the bis-adduct **94** (a mixture of diastereoisomers), which on recrystallization from cyclohexane/CH_2Cl_2 gave needles of pure isomer **94a**, mp 247-249 °C; ^{1}H NMR (360 MHz, d_8-THF) δ 8.52 and 8.38 (s, 2 each, H-1,3,8,10), 6.60 (m, 2, H-6,13, -CH=), 6.50 and 6.40 (bs, 2 each, H-4,7,11,14), 1.99 (bs, outside -CH_3), 1.68 (s, *t*-Bu), -3.92 (s, 6, inside -CH_3); ^{13}C NMR (90.6 MHz, d_8-THF) δ 154.7, 145.3, 143.3, 141.4, 135.5, 129.1, 128.4, 116.6, 115.7, 86.1, 83.0, 36.2, 33.1, 32.2, 27.7, 14.5, 13.5; UV ($CHCl_3$) λ_{max} nm (ϵ_{max}) 257 (22 000), 380 (83 000), 392 (60 000), 450 (13 000), 667 (910); IR (KBr) cm^{-1} 3023, 2948, 2860, 1595, 1425, 1330, 1266, 1240, 865; CI MS m/z 505 (MH^+).

Anal. calcd. for $C_{36}H_{40}O_2$: C, 85.67; H, 7.99. Found: C, 85.16; H, 8.00.

Deoxygenation of 94 to 95: *anti*-[1,2;9,10]-Dibenzo-5,13-di-*t*-butyl-8,16,18,22(23)-tetramethyl[2.2]metacyclophane (95)



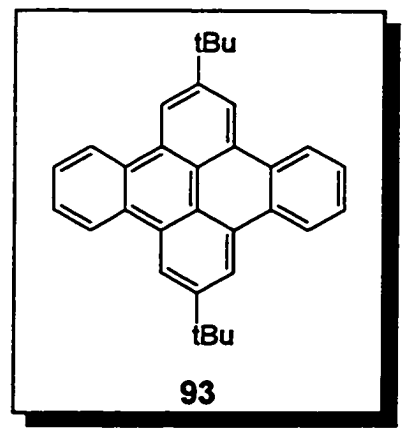
95

The mixture of adducts **94** (150 mg, 0.30 mmol) and $Fe_2(CO)_9$ (328 mg, 0.90 mmol) in benzene (50 mL) were stirred under Ar at 65-70 °C for 5 h. The mixture was cooled and silica gel (2 g) was added. Chromatography using hexanes gave 140 mg (98%) of colourless product of **95**, a mixture of the two isomers **95a** and **95b**. Fractional recrystallization of **95** from cyclohexane failed to separate these two isomers, but gave colourless crystals of the mixture, mp 235-237 °C; ^{1}H NMR (360 MHz, d_8-THF) δ 7.57 and 7.55 (s, 2 each), 7.50 (bs, 2, ArH), 7.21 and 7.20 (bs, 2, ArH), 6.91-6.94 (m, 4), 2.41 (s, outside -CH_3), 1.29 and 1.283 and 1.275 (s, *t*-Bu), 1.040 and 1.035 and 1.031 (s, inside -CH_3); ^{13}C NMR (90.6 MHz) δ 150.6, 144.5, 141.8, 140.8, 140.7, 140.6, 139.0, 138.5, 130.0, 129.6, 129.5, 129.2, 129.1, 128.99, 128.93 128.83, 34.7, 31.7, 27.7, 21.2, 18.7; UV (cyclohexane) λ_{max} nm (ϵ_{max}) 209 (41 000), 236 (62 000), 244 (62 000), 259 (56 000); IR (KBr) cm^{-1} 3017, 2954, 2854, 1623, 1595, 1478, 1373, 1280, 1250, 880, 820; CI MS m/z 473 (MH^+).

Anal. calcd for $C_{36}H_{40}$: C, 91.47; H, 8.53. Found: C, 91.14; H, 8.70.

Attempted bromination of cyclophane 82a: Formation of benzopyrene 93 (Method A)

Bromine (5.0 mL, 0.076 M in $CHCl_3$, 0.38 mmol) was added to a stirred solution of **82a** (44mg, 0.10 mmol) in $CHCl_3$ (5 mL) at 0 °C and stirring continued for 20 min. Then the mixture was extracted with water-CH_2Cl_2. The CH_2Cl_2 extract was washed, dried and then flash chromatographed and gave 40 mg (~100%) of colourless product **93**, which on recrystallization from cyclohexane gave colourless crystals, mp 286-288 °C; ^{1}H NMR (360 MHz) δ 8.95 (s, 4, H-1,3,8,10), 8.87-8.82 and 7.75-7.70 (m, 4 each, H-4,5,6,7,11,12,13,14), 1.65 (s, 18, *t*-Bu); ^{13}C NMR (90.6 MHz) δ 148.5, 130.4, 129.0, 127.2, 123.6, 122.0, 118.5, 35.6, 31.9; UV (hexanes) λ_{max} nm (ϵ_{max}) 225 (97 000), 234 (29 000), 267 (52 000), 277 (100 000), 288 (70 000), 316 (21 000), 330 (19 000); IR (KBr) cm^{-1} 3080, 3042, 2954, 2900, 2850, 1599, 1452, 1396, 708; CI MS m/z 415 (MH^+).



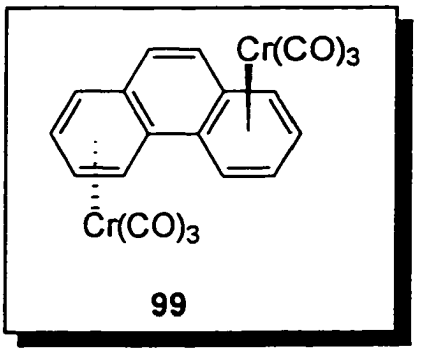
93

Anal. calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 91.11; H, 7.26. HR MS (E.I.) calcd for $C_{32}H_{30}$: 414.2348. Found: 414.2375.

Attempted iodination of cyclophane 82a: Formation of benzopyrene 93 (Method B)

Anhydrous $CuCl_2$ (14 mg, 0.1 mmol) and $AlCl_3$ (13 mg, 0.1 mmol) were added to a slurry of **82a** (45 mg, 0.1 mmol) and I_2 (25 mg, 0.1 mmol) in CH_3NO_2 (10 mL) at room temperature under Ar. The mixture was then stirred at 45-50 °C for 4 h. The cooled mixture was shaken with ice-water and CH_2Cl_2. The CH_2Cl_2 extract was washed, dried and evaporated to yield 34 mg (83%) of product **93**. Recrystallization from cyclohexane gave the identical sample as that in **Method A**.

Phenanthrene Bis-Chromium Complex (99)

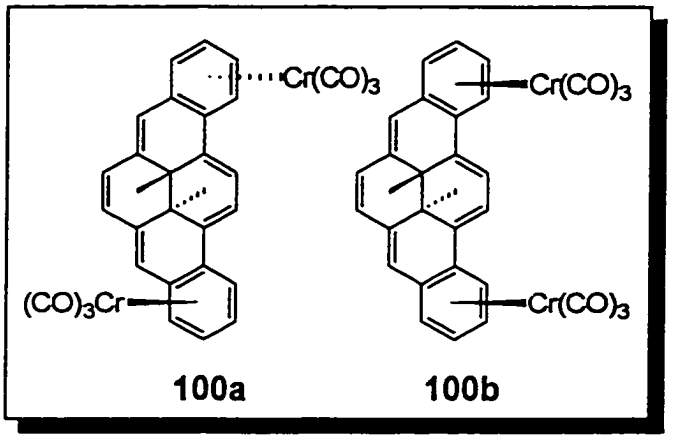


99

Naphthalenetricarbonylchromium **98**[80] (222 mg, 0.83 mmol) was added to a solution of phenanthrene (50 mg, 0.28 mmol) in Et_2O (1.5 ml) and THF (100µl) in a heavy vial, which was then sealed. After stirring magnetically at 60 °C overnight, the mixture was pre-absorbed onto silica gel and chromatographed using PE/CH_2Cl_2 as eluant. The first fraction was the starting material, naphthalene chromium complex **98** (35mg). The second orange fraction gave 100mg (80%) of the bis-metal complex **99**, mp 220-222 °C (decomp) (lit.[70] : 222 °C (decomp)); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.16 (s, 2), 6.20 (d, J = 6.6 Hz, 2), 5.84 (d, J = 5.9 Hz, 2), 5.56-5.51(m, 4); identical to the literature.[70] MS (C.I.) 453 (4.0), 452 (19.9), 451 (MH^+, 46.5), 450 (13.4), 449 (2.9), 316 (29.9), 315 (100), 314 (31.4), 313 (2.7),

Bis-chromium (0) complex of 49b to 100: *trans*-{μ-[(1,2,3,4,4a,14b-η:8a,9,10,11,12,12a-η)-12c,12d-dihydro-12c-12d-dimethylbenzo[rst]pentaphene]]hexacarbonyldichromium 100

A solution of **49b** (200 mg, 0.6mmol) and naphthalenetricarbonylchromium **98**[80](1.0g, 3.78 mmol) in ether (15 ml) and THF (1 mL) sealed in a heavy screw capped vial was stirred magnetically at 60 °C for 48 h. After cooling to room temperature, 15 mg of red-orange crystals was filtered directly, and were idientified as isomer **100a**.



The filtrate was then directly pre-absorbed on to silica gel and chromatographed using PE/ethyl acetate (10:1) as eulant. The first fraction was a small amount of the mono-metal complex, which was identified by MS(C.I. MH^+=469). Eluted next was a further portion of isomer **100a**, (115 mg, total 36%). Recrystallization from cyclohexane/THF gave red-orange crystals, mp 219-221 °C (decomp); ^{1}H NMR ($CDCl_3$, 360 MHz, assigned by COSY and NOESY) δ 6.85 (s, 2, H-13,14), 6.55 (s, 1, H- 6,7), 6.49 (s, 2, H-5-,8), 6.13 (d, J ~ 7 Hz, 2, H-1,12), 5.52 (d, J ~ 7 Hz, 2, H-4,9), 5.48 (d, J ~ 7 Hz, 2, H-3,10), 5.39 (t, J ~ 7 Hz, 2, H-2,11), 0.64 (s, 6, $-CH_3$); ^{13}C NMR (90.6 MHz) δ 232.9, 141.3, 134.0, 127.6, 122.9, 118.5, 101.5, 96.9, 91.9, 91.7, 90.7, 89.0, 41.0, 21.5; IR (KBr, cm^{-1}) 1950, 1875, 657, 629, 532, 469; UV (cyclohexane) λ_{max} nm (ϵ_{max}) 217 (33000), 341 (8400), 437 (4600); EI MS: 604

(M^+).

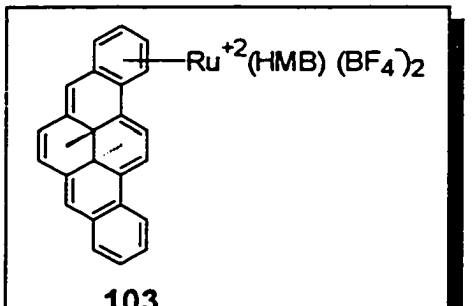
Anal. calcd for $C_{32}H_{20}Cr_2O_6$: C, 63.58; H, 3.34. Found: C, 62.91; H, 3.08. HR MS calcd for $C_{32}H_{20}Cr_2O_6$: 604.0070. Found: 604.0093.

Eluted next was isomer **100b** (52 mg, 14%). Recrystallization from cyclohexane/THF gave red-orange crystals, mp 214-216 ^{0}C (decomp); ^{1}H NMR (d_8-THF, 360 MHz, assigned by COSY, NOESY) δ 7.03 (s, 2, H-5,8), 6.72, 6.70, 6.67, 6.65 (s, 4, H- 6,7,13,14), 6.45 and 6.30 (d, J ~ 6.6 Hz, 2, H-4,9), 5.78 and 5.69 (t, J ~ 6.6 Hz, 2, H-2,11), 5.78 and 5.62 (d, J ~ 6.6 Hz, 2, H-1,12), 5.55 and 5.48 (t, J ~ 6.6 Hz, 2, H-3,10), 0.90 and 0.45 (s, 6, -CH_3); UV (hexane/CH_2Cl_2 : 4/1) λ_{max} nm (ϵ_{max}): 222 (44 000), 336 (20 000), 436 (10 200); IR (KBr, cm^{-1}) 2923, 1944, 1856, 664, 626; EI MS m/e 604.

Anal. calcd for $C_{32}H_{20}Cr_2O_6$: C, 63.58; H, 3.34. Found: C, 63.72; H, 3.69.

Ruthenium (II) Complexes 103

A solution of bisbenzannulene **49b** (25 mg, 0.075 mmol) in anhydrous propylene carbonate (5 mL) was added to a mixture of $[Ru(HMB)Cl_2]_2$ **102**[71b] (75 mg, 0.113 mmol) and $AgBF_4$ (110 mg, 0.565 mmol) in anhydrous propylene carbonate (5 mL). The mixture

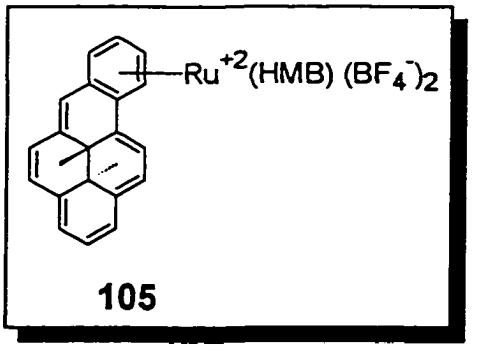


103

was stirred at room temperature for 12 h and then poured onto ether (200 mL) with stirring. The crude product was collected by filtration and then dissolved in a minimum of acetone. After filtration again, 25 mg (45%) dark red crystals of product **103** (as a mixture of two isomers: 1:1) was obtained by slow diffusion of ether into this clear acetone solution. Several times recrystallization by slow diffusion failed to separate the two isomers and remove small amounts of the starting material **102** (indictaed by a strong peak in the ^{1}H NMR spectrum for its methyl group protons at 2.18 ppm). ^{1}H NMR (d_6-Acetone$_3$, 360 MHz) δ 8.4-6.9 (m, ArH), 2.04 (s, outside -CH_3), 0.68 and 0.29 (s, inside -CH_3, one isomer), 0.58 and 0.20 (s, inside -CH_3, the other isomer); LSI MS (Matrix: mNBA) m/e 682.6 (M^+-BF_4).

Ruthenium (II) Complexes 105

A solution of benzannulene **104** (74 mg, 0.26 mmol) in anhydrous propylene carbonate (5 mL) was added to a mixture of $[Ru(HMB)Cl_2]_2$ **102**[71b] (88 mg, 0.13 mmol) and $AgBF_4$ (204 mg, 1.05 mmol) in anhydrous propylene carbonate (5 mL). The mixture



105

was stirred at room temperature for 12 h and then poured onto ether (250 mL) with stirring. The reaction flask was rinsed with acetone into the ether. The crude product was then collected by filtration. The solid residue was washed well with ether and then dissolved in a minimum of acetone. After filtration again, the acetone solution was added dropwise to ether (50 mL) with vigorously stirring. 100 mg (53%) dark red crystals of product **105** (as a

of two isomers: 1:1) was obtained by filtration. Two times recrystallization by this slow diffusion failed to separate the two isomers and removed trace amount of the starting material **102**. ^{1}H NMR (d_6-Acetone, 360 MHz) δ 8.49 (d, J = 6.6 Hz, ArH), 8.43 (d, J = 6.6 Hz, ArH), 8.09 (t, J = 5.0 Hz, ArH), 7.78-6.89 (m, ArH), 2.53 and 2.43 (s, outside -CH_3), -0.48 and -0.85 (s, inside -CH_3, one isomer), -0.50 and -0.92 (s, inside -CH_3, the other isomer); LSI MS (Matrix: mNBA) m/e 632.5 (M^+-BF_4). ^{1}H NMR ($CDCl_3$, 360 MHz) δ_{Me} - 0.52 and - 0.86 for one isomer; - 0. 56 and - 0.89 for the other isomer.

5.4 Photochemical Reactions and Low Temperature NMR and UV Spectra

For NMR: An NMR tube containing the solution of the cyclophane (2.9 mg in 0.5 mL d_8-THF) **82** or **95** (in d_8-THF) was first cooled to about - 80 °C in a cooling bath of pentane, which was cooled by liquid nitrogen outside. Then the NMR tube in a small pentane cooling bath was transferred immediately into a photochemical reactor and irradiated with light of 300 nm for ~ 1 min. A very heavy frost formed very quickly on the cooling bath and on the NMR tube and this probably blocked further photons from entering the solution for the photocyclization. The frost was removed ny methanol on a tissue and then the NMR tube was transferred into the NMR instrument which was already set at the desired temperature and the NMR spectrum was immediately recorded at the desired temperature.

For UV: A solution of cyclophane **82a** (1.1 mg in 200 mL THF) was cooled to about - 50 °C in a UV cell directly and then was irradiated with the light of wavelength 300 nm for

about 15 sec, and then the cell was transferred into the UV-Vis instrument and the scanning started immediately.

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Appendix I The NMR Spectra of Compound 82a and its Closed Isomer 82b

Figure 1.

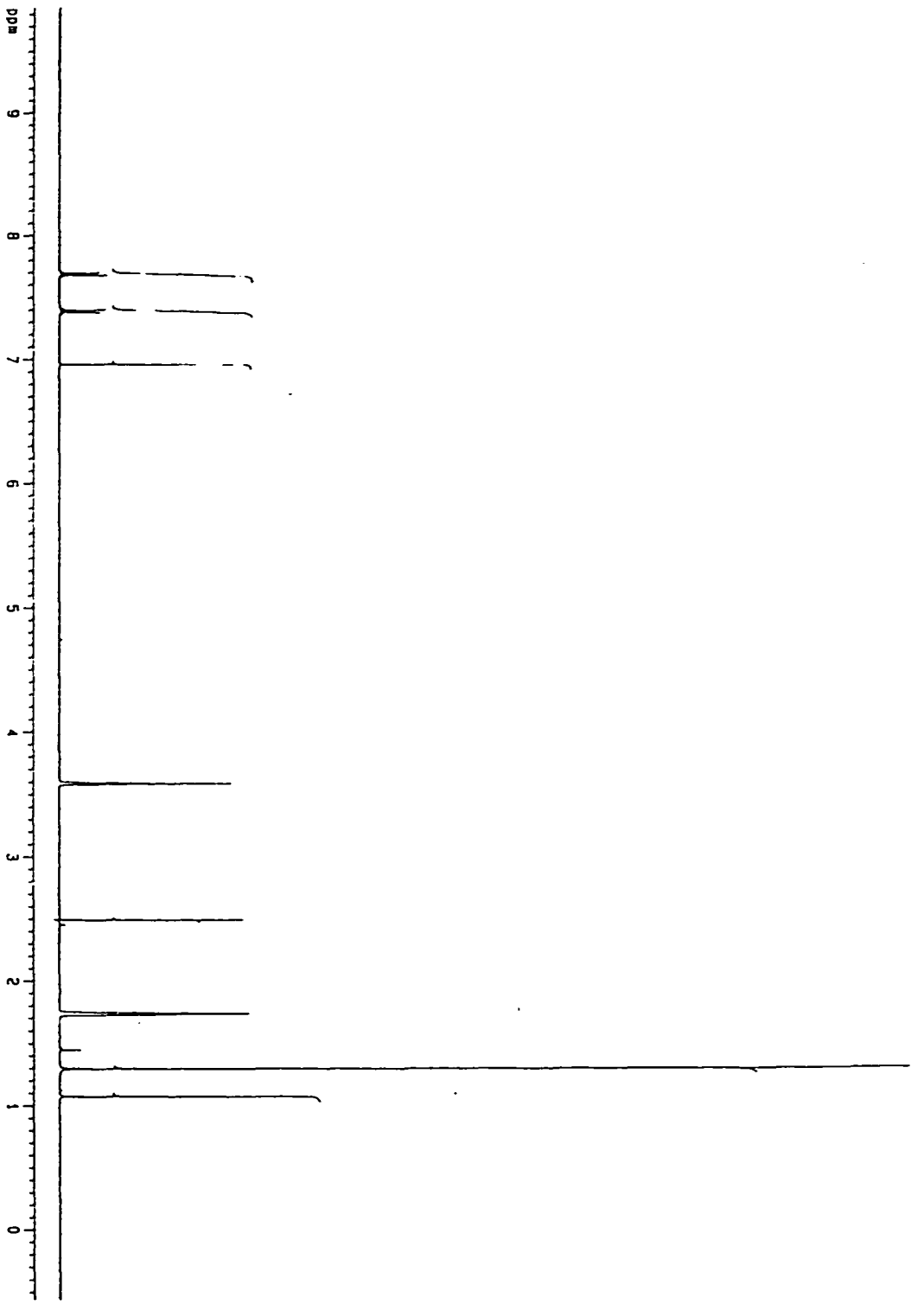


Figure 2.

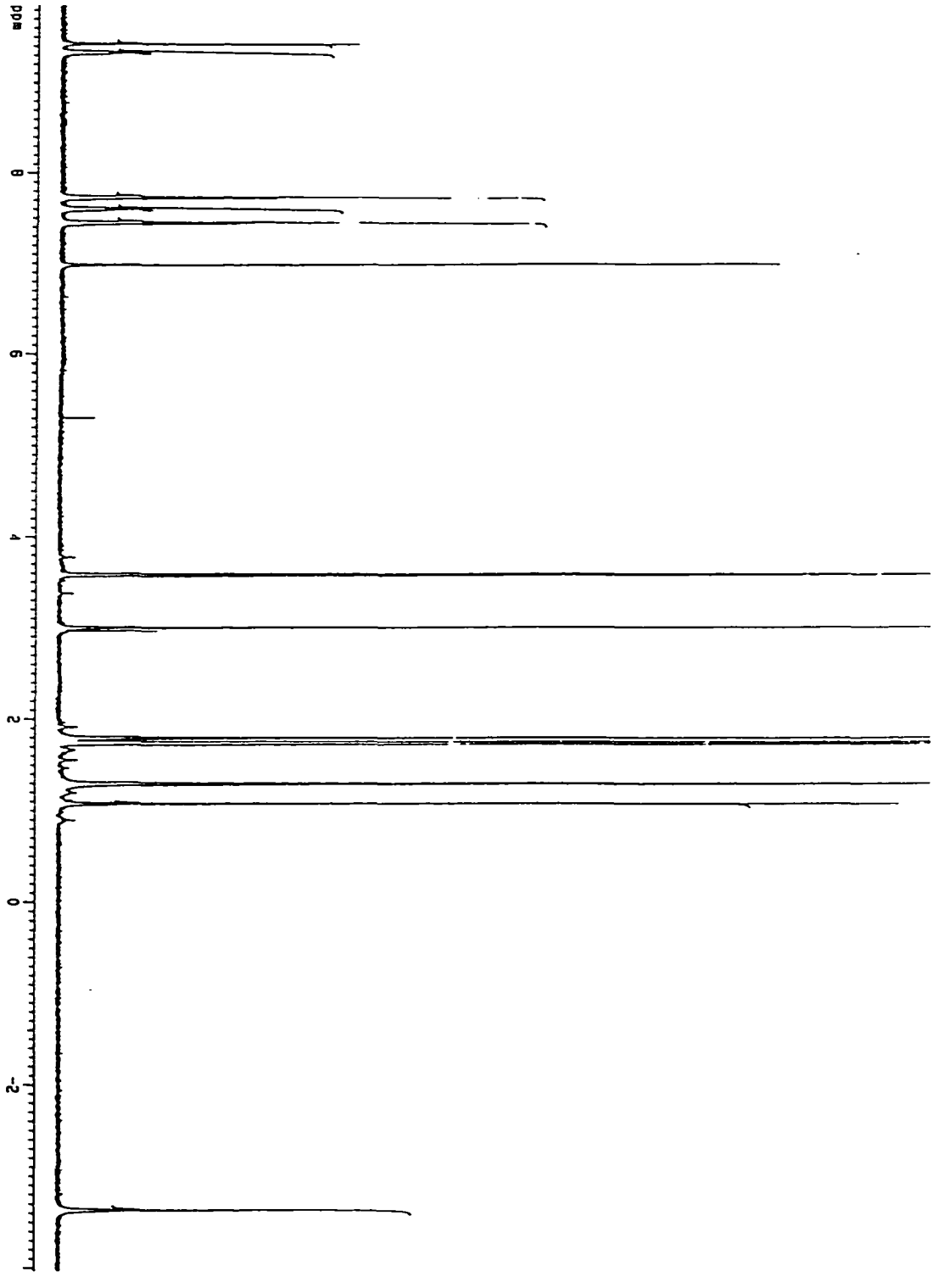
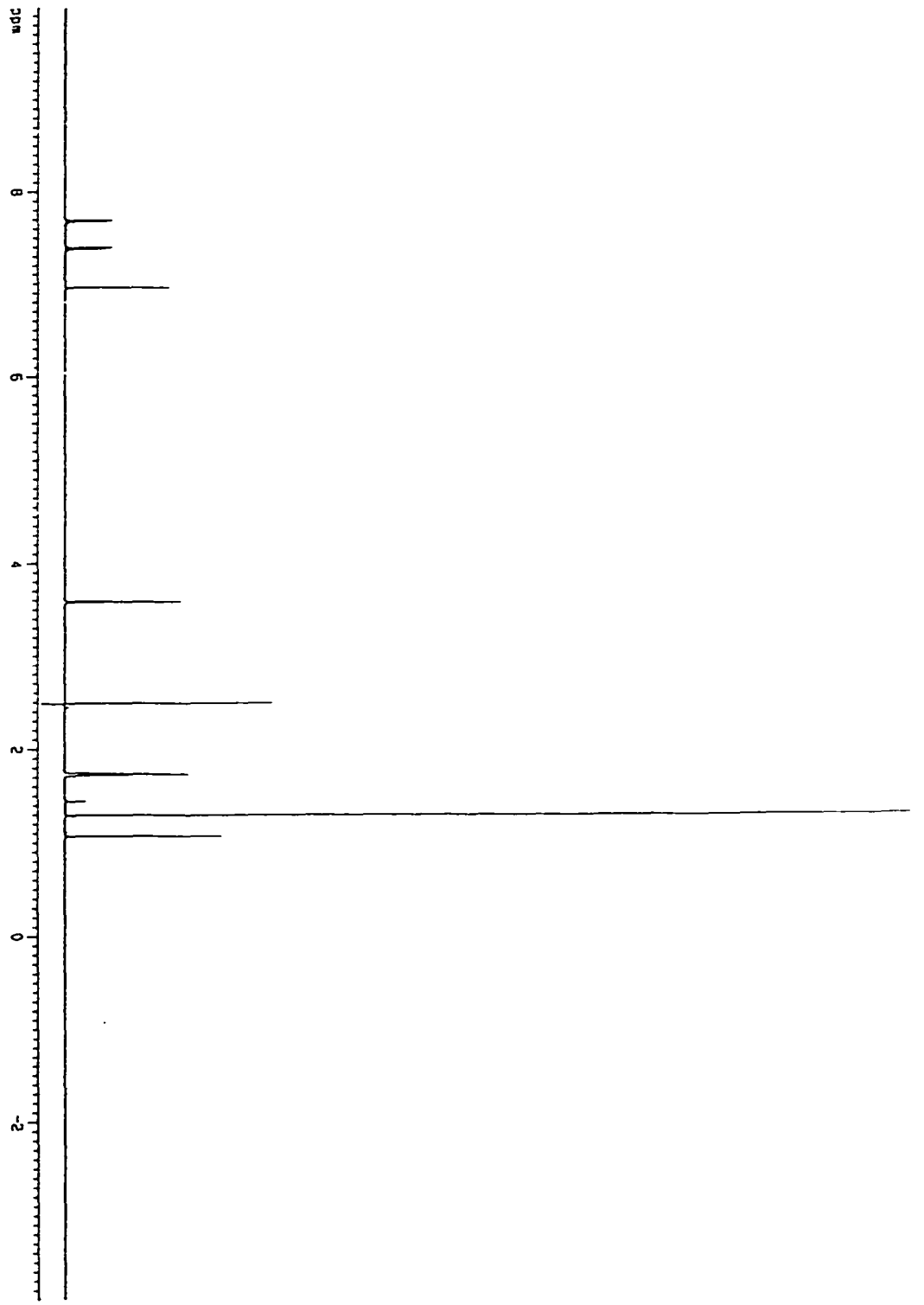
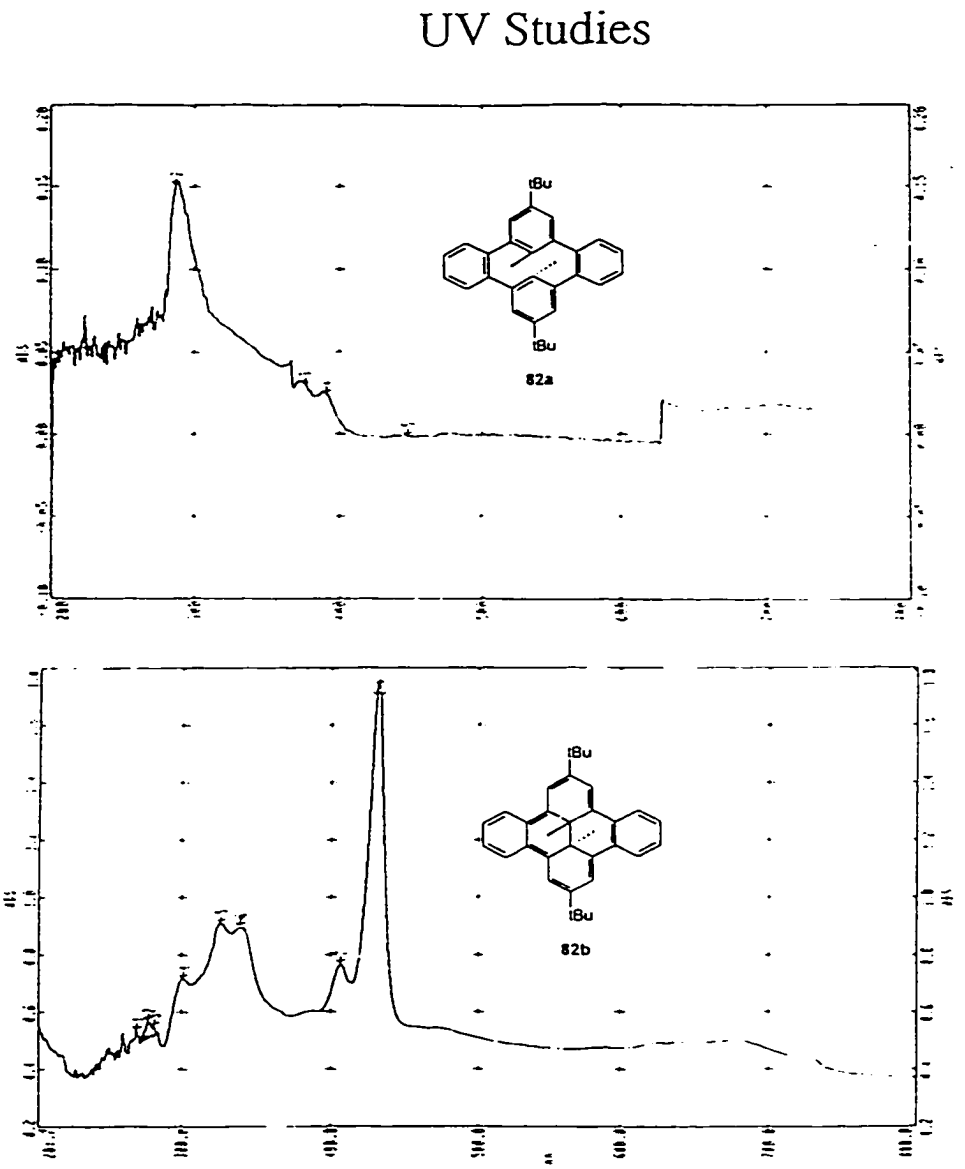


Figure 3.



Appendix II The UV Spectra of Compounds 82a and 82b



Cyclophane 82a: λ_{max} **(THF) = 295 nm**
ϵ_{max} **(THF) = 11,000**

Pyrene 82b: λ_{max} **(THF) = 431 nm**
ϵ_{max} **(THF) = 150,000**

Appendix III The VT-NMR Spectra of 82b and the Plots for the Calculation of E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$

For the first order reaction:

$$-\ln C = kt + \text{Constant} \qquad (1)$$

C = the concentration of the reactant, k = rate constant

For the thermal return reaction from **82b** to **82a**, if

the ratio (**r**) = [**82b**]/[**82a**], and the initial concentration of **82b** = C_0

$$\text{then } C = C_0 [r/(1+r)], \text{ so}$$

the rate equation (1) can be rewritten as (2)

$$-\ln r/(1+r) = k\,t + \text{constant} \qquad (2)$$

The ratio **r** can be obtained from each NMR spectrum directly. Then plotting - ln r/(1+r) vs time (t) gives the rate constant **k** at each temperature.

The rate constants at 233K, 243K, 253K and 263 K have been measured. Then plotting -lnk vs 1/T (temperature) gave the activation energy E_a. Plotting -ln (k/T) vs 1/T (The Eyring Equation (4)) gave values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

$$-\ln (k/T) = (1/T)(\Delta H^{\neq}/R) - (\Delta S^{\neq}/R) - \ln (K/h) \qquad (4)$$

or $-\ln (k/T) = (1/T)(\Delta H^{\neq}/8.314) - (\Delta S^{\neq}/8.314) - \ln (1.381 \times 10^{-23}/6{,}626 \times 10^{-34})$

The error values were obtained directly from the plots as the standard derivation. Such errors were generally larger than the errors from the NMR ratios (5 % normally), and were thus used.

The thermodynamic data for the thermal reaction from **95b** to **95a** were measured in the same way.

Some of the plots are attached below. The error bars (± 0.05 for -ln r/(1+r)) in the plots of - ln r/(1+r) vs **t** are transfered from the possible error (± 5%) of the NMR ratio **r** to that of ln r/(1+r).

List of attached spectra and plots.

Figure 1. The ^{1}H NMR spectra of **82a/82b** at 0 min, 2 min, 4 min, 10 min and 20 min after the irradiation of compound **82a** at - 20 ^{0}C.

Figure 2. The aromatic part of the ^{1}H NMR spectrum of **82a/82b** after the irradiation of **82a** at -20 ^{0}C.

Figure 3. The expanded ^{1}H NMR spectra for internal methyl protons from Figure 1.

Figure 4. The expanded ^{1}H NMR spectra for aromatic protons from Figure 1.

Figure 5. The plot - ln r/(1+r) vs Time at 263 K for the thermal return reaction of **82b** to **82a**.

Figure 6. The plot - ln r/(1+r) vs Time at 253 K for the thermal return reaction of **82b** to **82a**.

Figure 1.

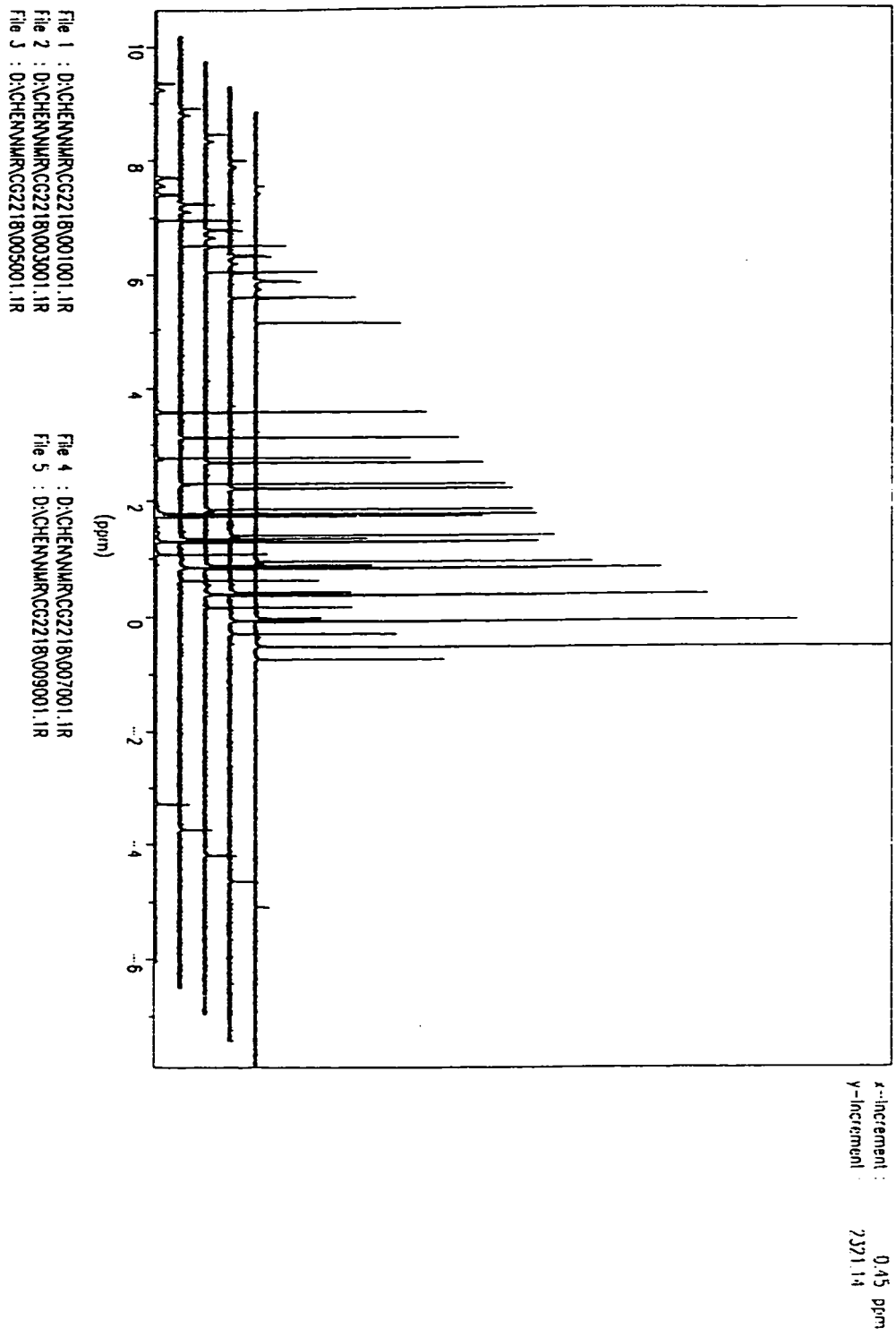
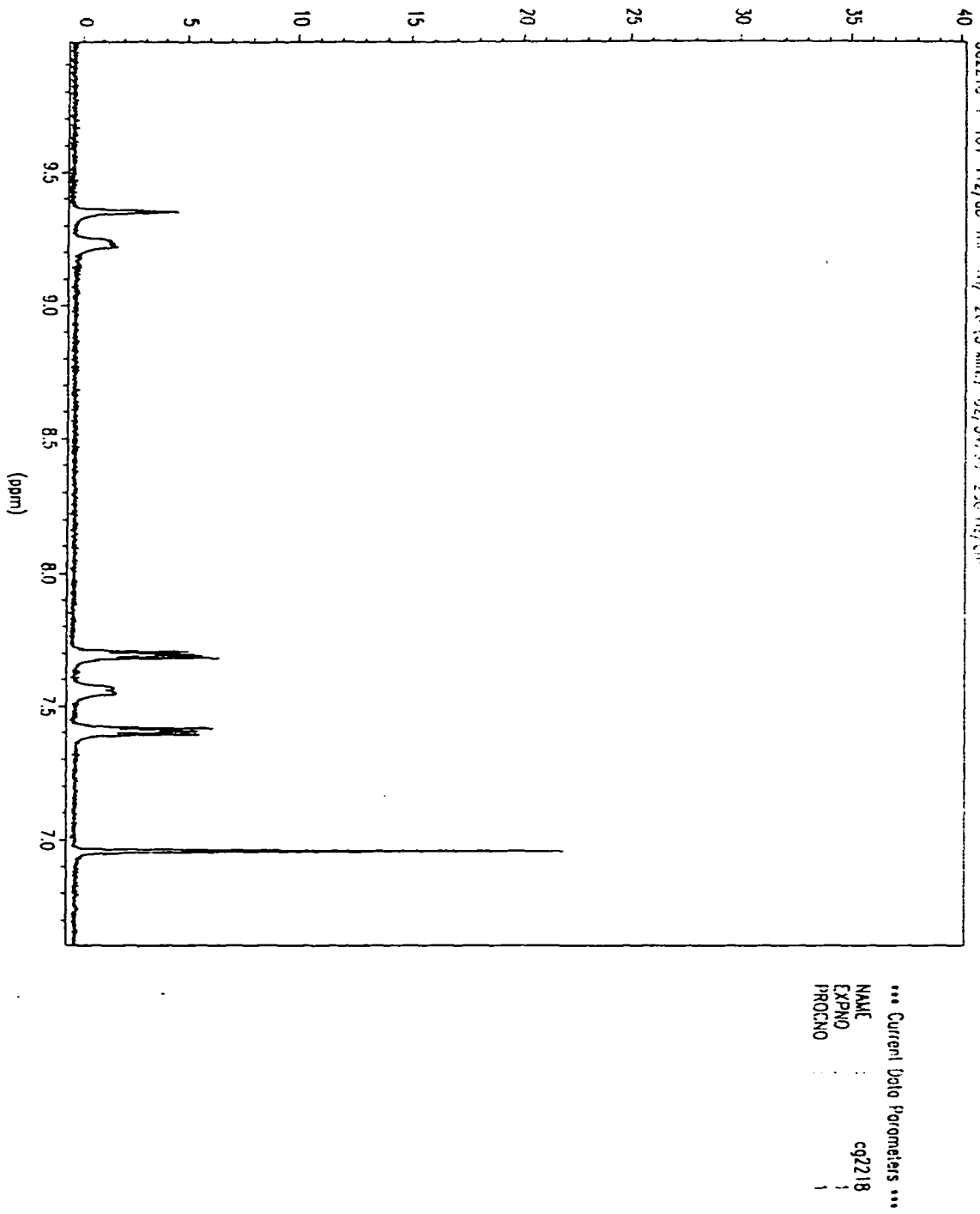

Stack Plot
x-increment : 0.45 ppm
y-increment : 7371.14
10
8
6
4
2
0
-2
-4
-6
(ppm)
File 1 : D:\CHEN\NMR\CG2218\001001.1R
File 2 : D:\CHEN\NMR\CG2218\003001.1R
File 3 : D:\CHEN\NMR\CG2218\005001.1R
File 4 : D:\CHEN\NMR\CG2218\007001.1R
File 5 : D:\CHEN\NMR\CG2218\009001.1R

Figure 2.


0
5
10
15
20
25
30
35
40
9.5
9.0
8.5
8.0
7.5
7.0
(ppm)
*** Current Data Parameters ***
NAME cg2218
EXPNO 1
PROCNO 1

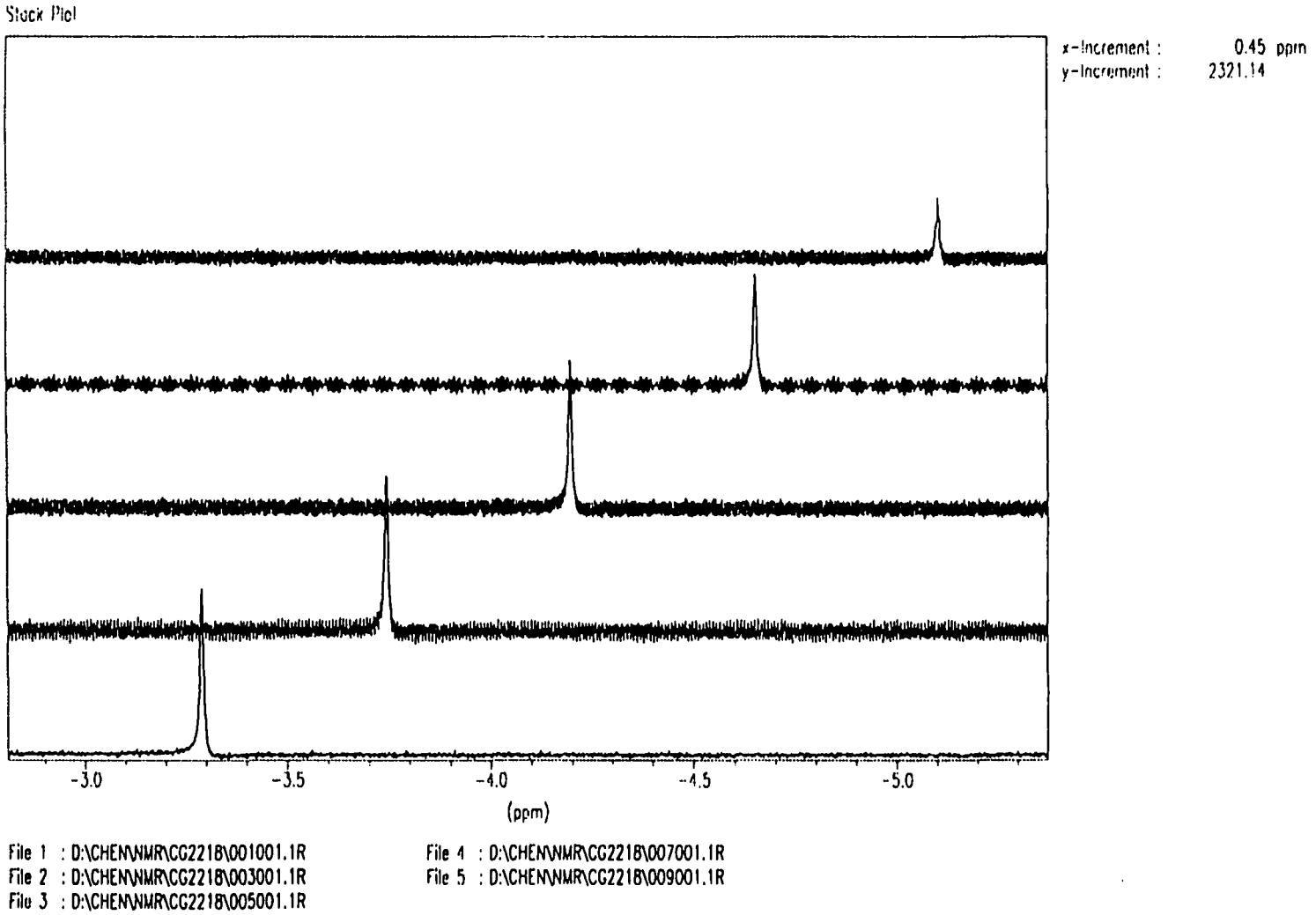

Stack Plot
x-Increment : 0.45 ppm
y-Increment : 2321.14
-3.0
-3.5
-4.0
-4.5
-5.0
(ppm)
File 1 : D:\CHEM\NMR\CG2218\001001.1R
File 2 : D:\CHEM\NMR\CG2218\003001.1R
File 3 : D:\CHEM\NMR\CG2218\005001.1R
File 4 : D:\CHEM\NMR\CG2218\007001.1R
File 5 : D:\CHEM\NMR\CG2218\009001.1R

Figure 3.

Figure 4.

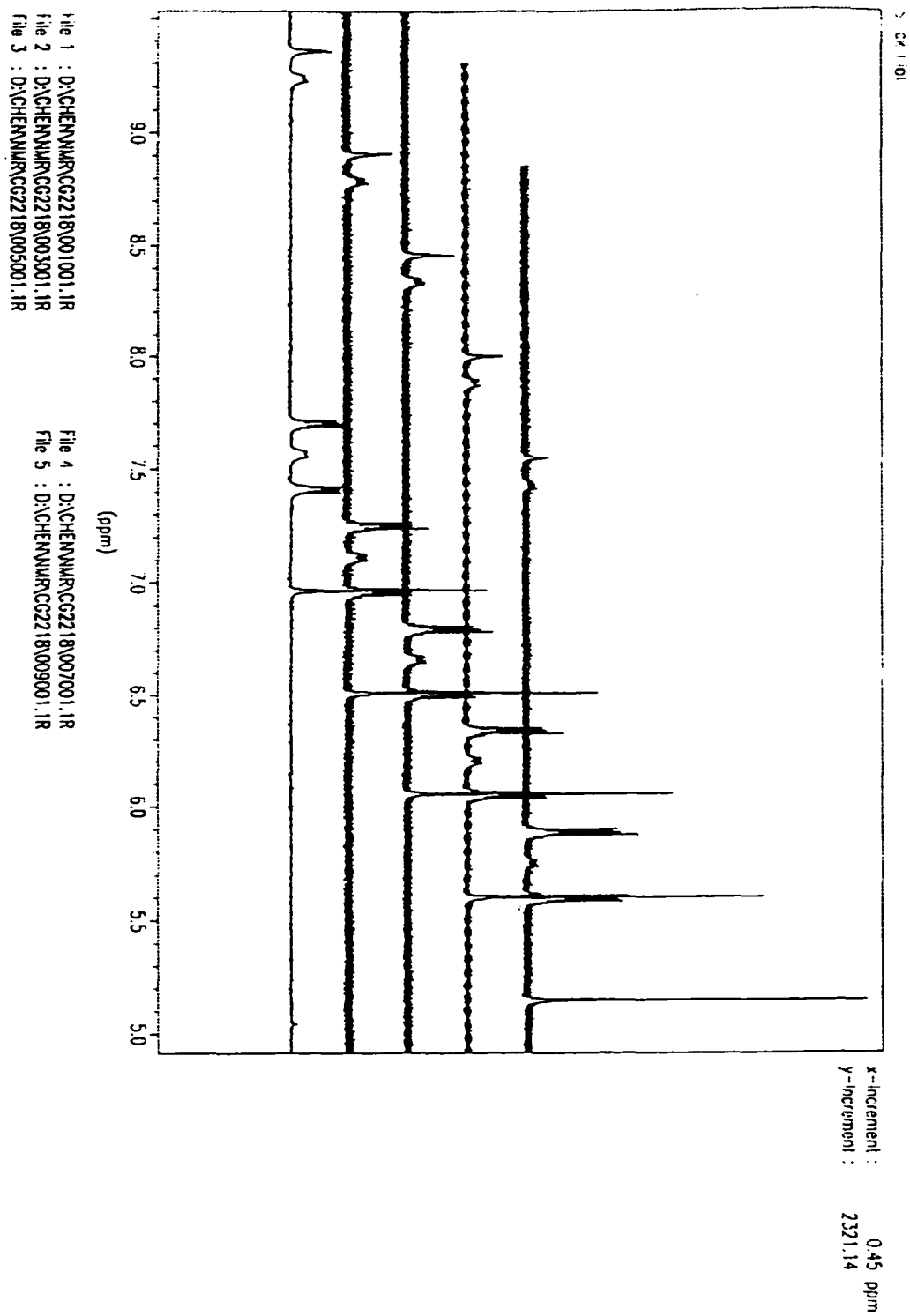

File 1 : D:\CHEN\WMR\CG2218\001001.1R
File 2 : D:\CHEN\WMR\CG2218\003001.1R
File 3 : D:\CHEN\WMR\CG2218\005001.1R
File 4 : D:\CHEN\WMR\CG2218\007001.1R
File 5 : D:\CHEN\WMR\CG2218\009001.1R
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
(ppm)
x-increment : 0.45 ppm
y-increment : 2321.14

Figure 5.

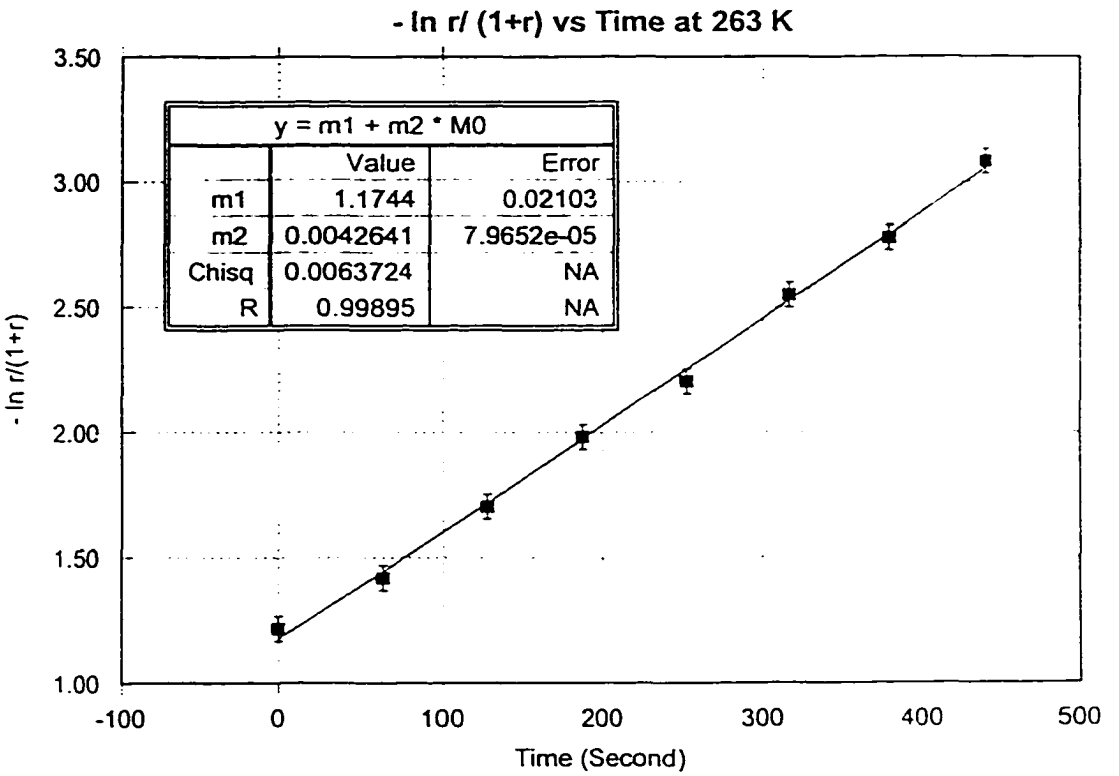

- ln r/ (1+r) vs Time at 263 K
y = m1 + m2 * M0
Value
Error
m1
1.1744
0.02103
m2
0.0042641
7.9652e-05
Chisq
0.0063724
NA
R
0.99895
NA
- ln r/(1+r)
3.50
3.00
2.50
2.00
1.50
1.00
-100
0
100
200
300
400
500
Time (Second)

Figure 6.

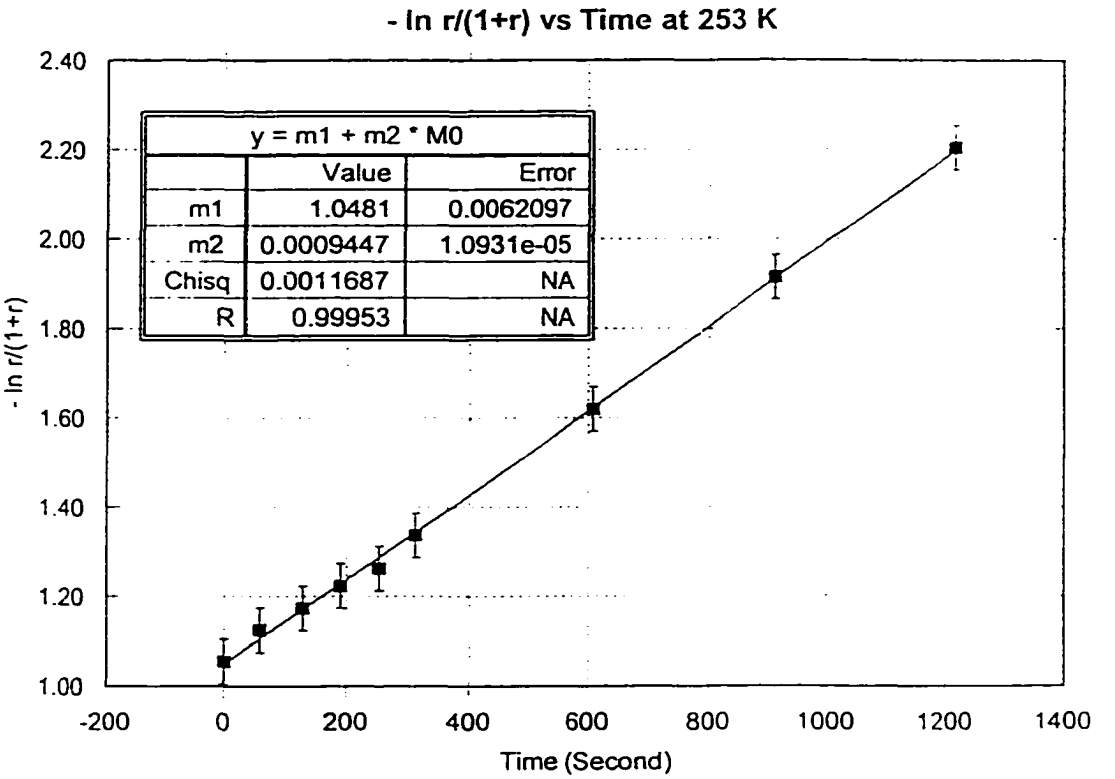

- ln r/(1+r) vs Time at 253 K
y = m1 + m2 * M0
Value
Error
m1
1.0481
0.0062097
m2
0.0009447
1.0931e-05
Chisq
0.0011687
NA
R
0.99953
NA
- ln r/(1+r)
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
-200
0
200
400
600
800
1000
1200
1400
Time (Second)

Figure 7.

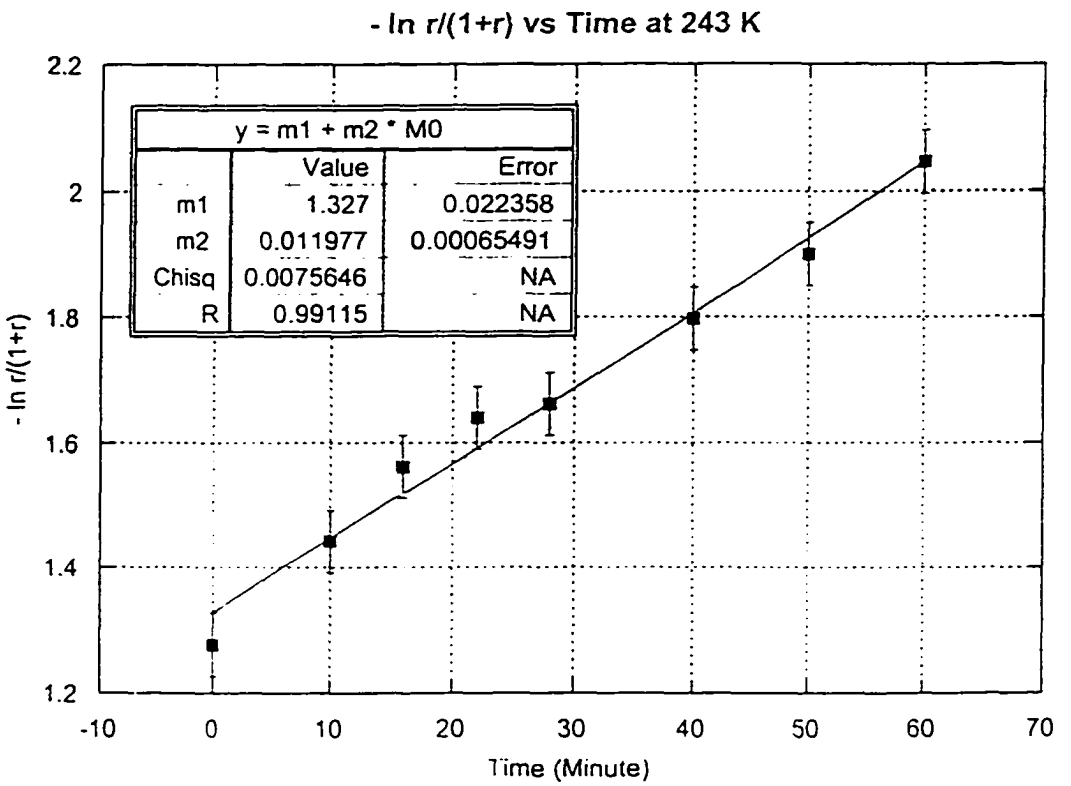

- ln r/(1+r) vs Time at 243 K
y = m1 + m2 * M0
Value
Error
m1
1.327
0.022358
m2
0.011977
0.00065491
Chisq
0.0075646
NA
R
0.99115
NA
- ln r/(1+r)
Time (Minute)
2.2
2
1.8
1.6
1.4
1.2
-10
0
10
20
30
40
50
60
70

Figure 8.

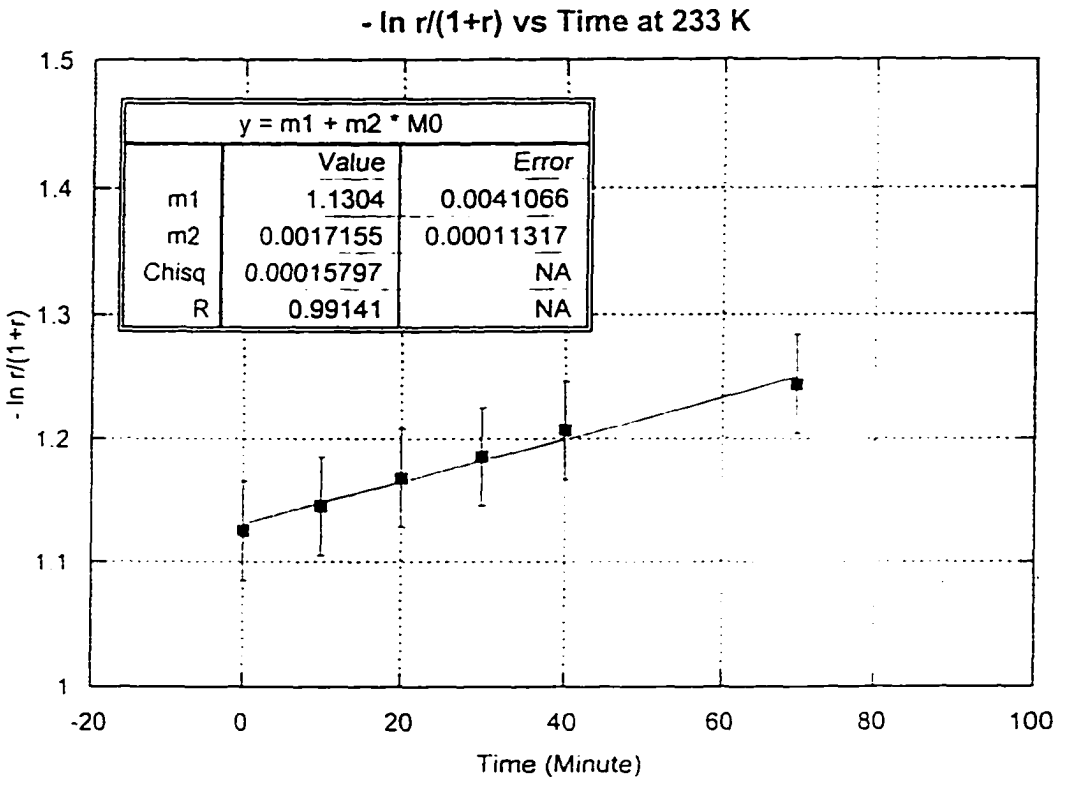

- ln r/(1+r) vs Time at 233 K
y = m1 + m2 * M0
Value
Error
m1
1.1304
0.0041066
m2
0.0017155
0.00011317
Chisq
0.00015797
NA
R
0.99141
NA
- ln r/(1+r)
Time (Minute)
1.5
1.4
1.3
1.2
1.1
1
-20
0
20
40
60
80
100

Figure 9.

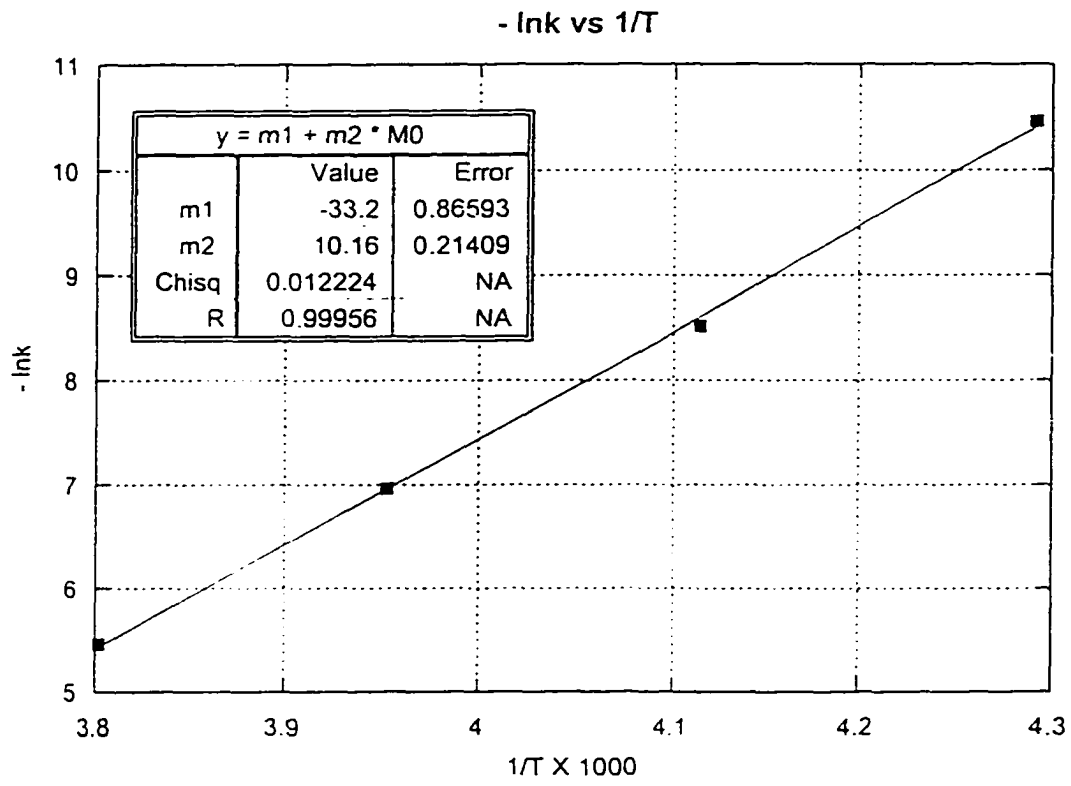
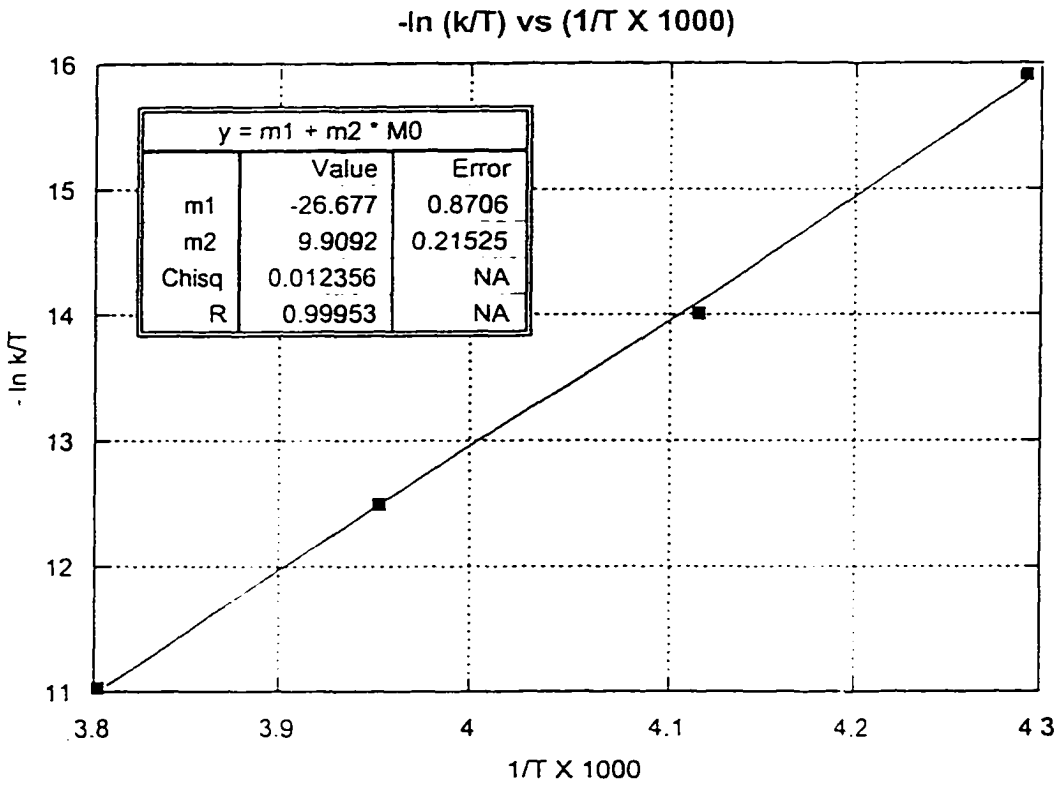

- lnk vs 1/T
y = m1 + m2 * M0
Value Error
m1 -33.2 0.86593
m2 10.16 0.21409
Chisq 0.012224 NA
R 0.99956 NA
- lnk
11
10
9
8
7
6
5
3.8
3.9
4
4.1
4.2
4.3
1/T X 1000

Figure 10.


-ln (k/T) vs (1/T X 1000)
y = m1 + m2 * M0
Value Error
m1 -26.677 0.8706
m2 9.9092 0.21525
Chisq 0.012356 NA
R 0.99953 NA
- ln k/T
16
15
14
13
12
11
3.8
3.9
4
4.1
4.2
4 3
1/T X 1000

Appendix IV The Calculation of Through Space Anisotropic Effect of Organometallic Species on Methyl Protons in the Metal Complex 125a.

The experimental data from Tables 4 and 5 indicate that the through space anisotropy effect of the organometallic moieties in the metal complexes such as compound **125a** are rather small. This can also be proved by calculation using McGlinchey's equation.[77]

McGlinchey has made use of the McConnell equation together with a composite geometric term for the organometallic moiety to determine magnetic susceptibility χ values for several organometallic groups. We can thus use his χ value for organometallic fragments to determine the through space (de)shielding of these groups on any of the protons in our compounds containing the organometallic moieties. Application to compound **125a** is shown in Figure 1 as an example.

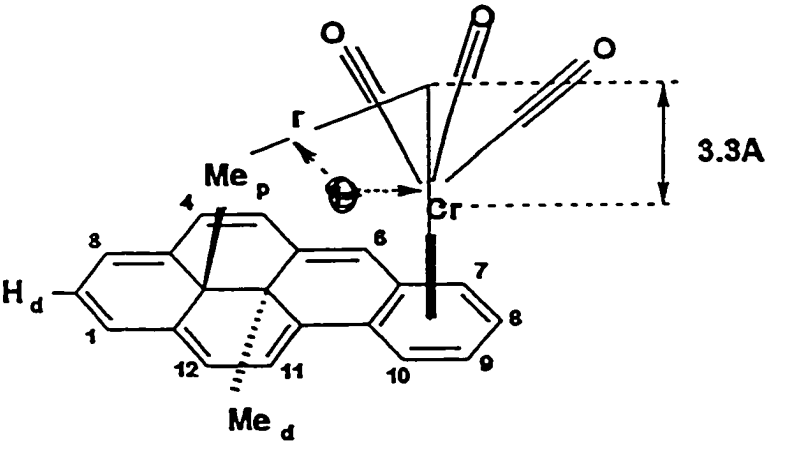


Figure 1: Diagram to show parameters r and θ used in equation (1).

The general McGlinchey's equation is (1):

$$\sigma = -\chi_{ai} \times 10^{36} (3\cos^2\theta - 1)/12\pi r^3 \qquad (1)$$

σ: the expected anisotropic effect from the organometallic moiety (positive for shielding and negative deshielding);

χ_{ai}: diamagnetic anisotropy values of the organometallic moiety;

r: the distance from the centre of the organometallic moiety group to the proton under consideration;

θ: the angle made by r with the central axis of the moiety (e.g for $Cr(CO)_3$ group, it is the angle made by r and the C_3 axis as shown of $Cr(CO)_3$ in Figure 1);

For -$Cr(CO)_3$, the three carbonyl groups are considered as a "super-carbonyl" along the C_3 axis. The centre of the super-carbonyl is found 3.3 Å from Cr atom. Using McGlinchey's values $\chi_{ai} = -2124 \times 10^{-36}$ m^3/mol, the McGlinchey's equation (2) for moiety $Cr(CO)_3$ is then

$$\sigma = 56.34 (3\cos^2\theta - 1)/r^3 \qquad (2)$$

where σ is the shielding (ppm) expected for proton caused by anisotropic effect of the $Cr(CO)_3$.

The parameters **r** and θ were obtained from PCMODEL minimized structures, which

in our experience[34] gives rather good geometries in both the dihydropyrenes and cyclophanes, agreeing well with X-ray data where available.

Whereas the values of **r** and θ for the ring hydrogens are unambiguous, those for the methyl groups, which can rotate out, are not. The most consistent results for the methyl protons are calculated by considering the methyl protons to be at a point at the centre of the circle that they sweep out on rotation. Thus for the methyl groups of compound **125a**, values of σ for the *proximal* methyl group were found to be -0.104 ppm, and for the *distal* methyl group +0.118 ppm respectively (the proximal methyl group, Me_p is on the same side as the $Cr(CO)_3$, and the distal methyl group, Me_d, is on the opposite side).

Using equation (3):

$$\delta_{calc} = \delta_{exp} + \sigma \qquad (3)$$

the calculated chemical shifts for the two internal methyl protons of **125a** after removal of the (de)shielding due to the $Cr(CO)_3$ anisotropy are -0.975 (Me_p) and -0.859 (Me_d).The average chemical shift of the two methyl groups of **125a** in the absence of the $Cr(CO)_3$ anisotropy is thus -0.92 (±.06) ppm, and this is the value we will use in the relative bond fixing ability calculation in the thesis. Clearly the $Cr(CO)_3$ group does not have a large through space (anisotropic) effect on the methyl protons. Even for the isolated proton adjacent to the complexed ring, (H-6), σ is only calculated to be +0.25 ppm!. Thus the change in the chemical shift on complexation, δ (**125a**) - δ(**110**) of about 0.7 ppm is not a through space anisotropy effect of the $Cr(CO)_3$ group.

McGlinchey reported[77] the value of χ_{SI} for the $Cr(CO)_3$ "supercarbonyl" moiety to be

-2124 x 10^{-36} m^3/molecule. Using his technique, this can be determined experimentally from the difference in the chemical shift $\Delta\delta$(Me) of the *same* methyl group in two isomers of **125a**, and the difference in the factors Δf, where $f = (3\cos^2\theta-1)/r^3$ using equation (4):

$$\chi_{SI} = -12\pi \times 10^{-36}\, \Delta\delta(Me)/\, \Delta f \qquad (4)$$

Thus for **125a**, using Me_d of **125a** and Me_p of **125b**, $\Delta\delta = \delta(Me_d\text{-}Me_p) = -0.170$ ppm, and $\Delta f = f_d\text{-}f_p = 0.0026342$ giving $\chi = -2432 \times 10^{-36}$ m^3/molecules, in good agreement with McGlinchey's values. This method relies on the assumption that the geometry of the molecule does not change between isomers. This is not completely true, because PCMODEL calculations indicate a slight changing of the skeleton.

In a similar fashion, the χ_{SI} (- 836 x 10^{-36} m^3/molecule) of -Ru^{2+}(HMB) was determined by using the internal methyl chemical shifts of the two isomers of compounds **105**. Note the centre of anisotropy was taken as the Ru atom. With this χ_{SI} (-836 x 10^{-36} m^3/molecule) of -Ru^{2+}(HMB) value, similarly the through space anisotropy effect of -Ru^{2+}(HMB) in compound **105a** and the anisotropy free average chemical shifts of the internal methyl protons, δ_{calc}, were calculated using McGlinchey's equation as - 0.72 ppm. This was used to calculate the relative bond fixing ability of this organometallic moiety.

Appendix V NMR Spectra of Compounds **48**, **81** and **125**

Figure 1.

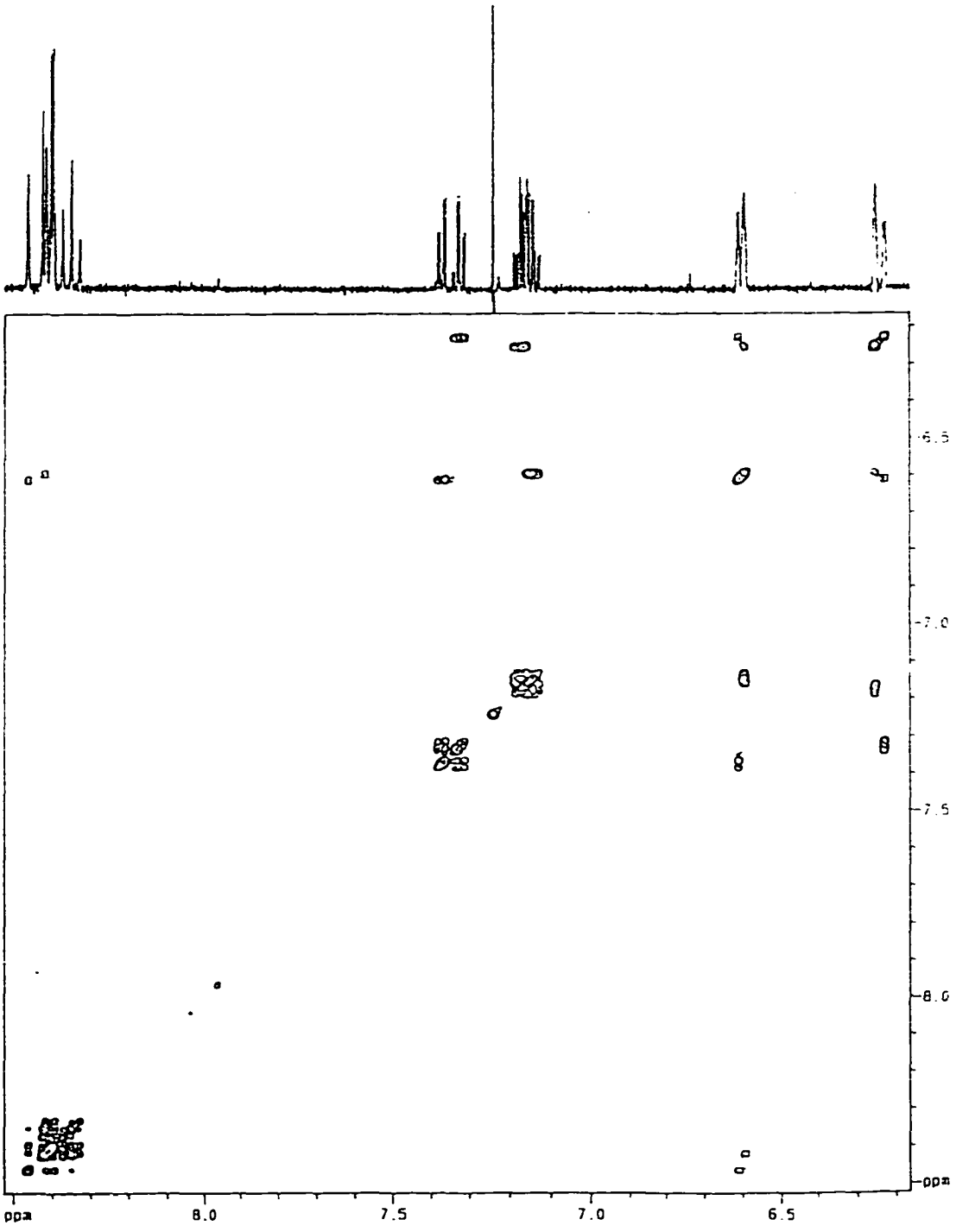


Figure 2.

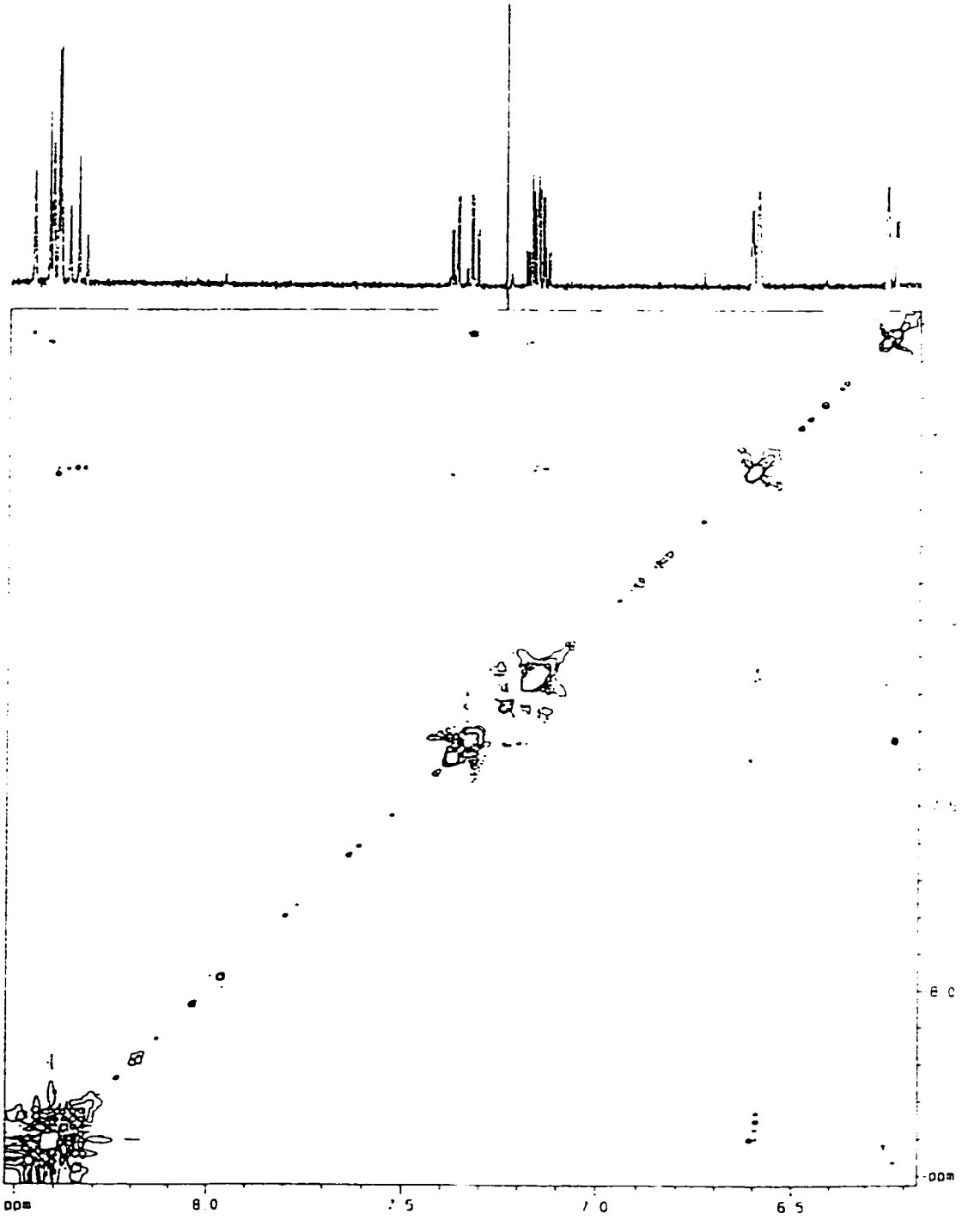


Figure 3.

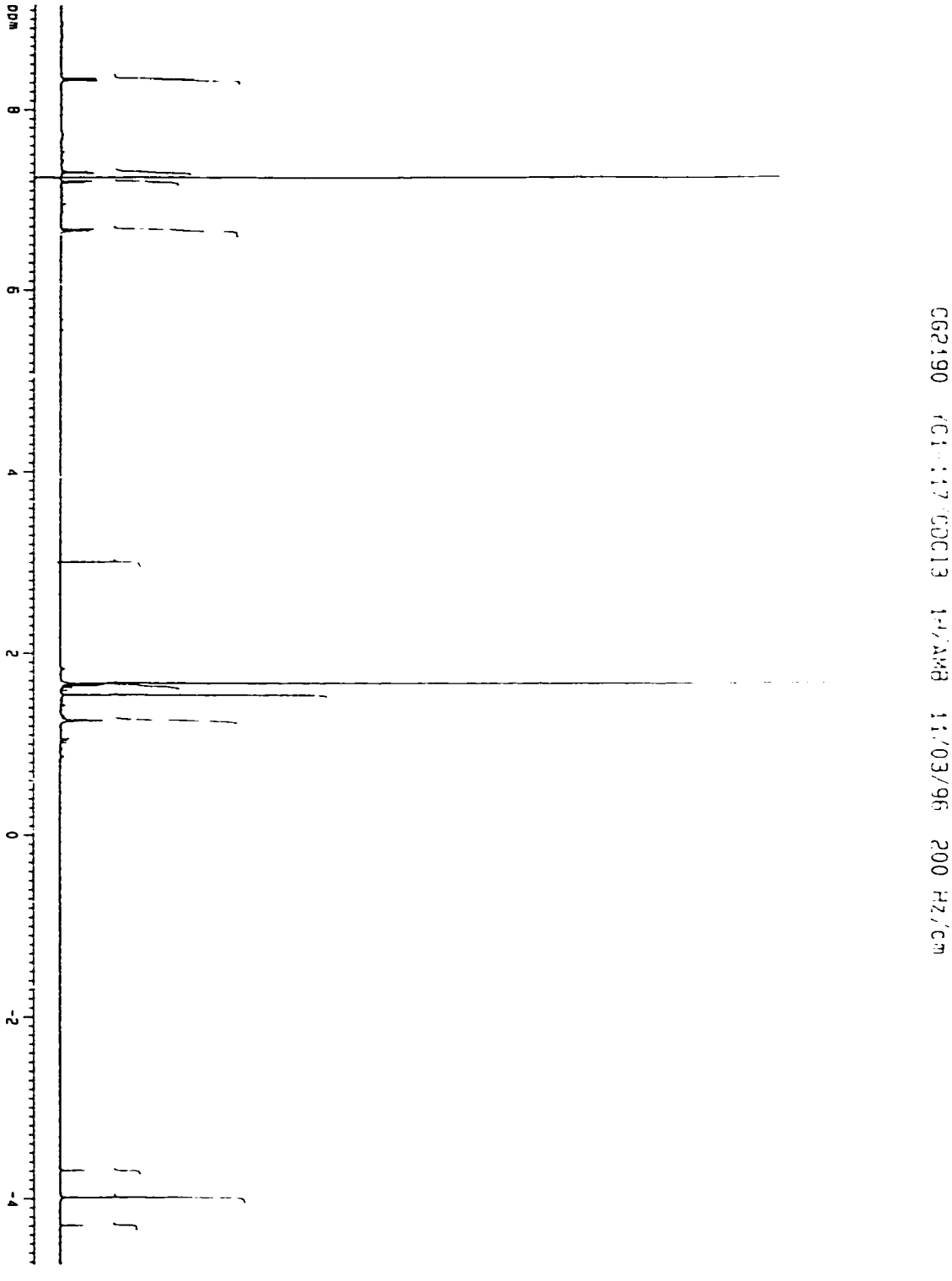


Figure 4.

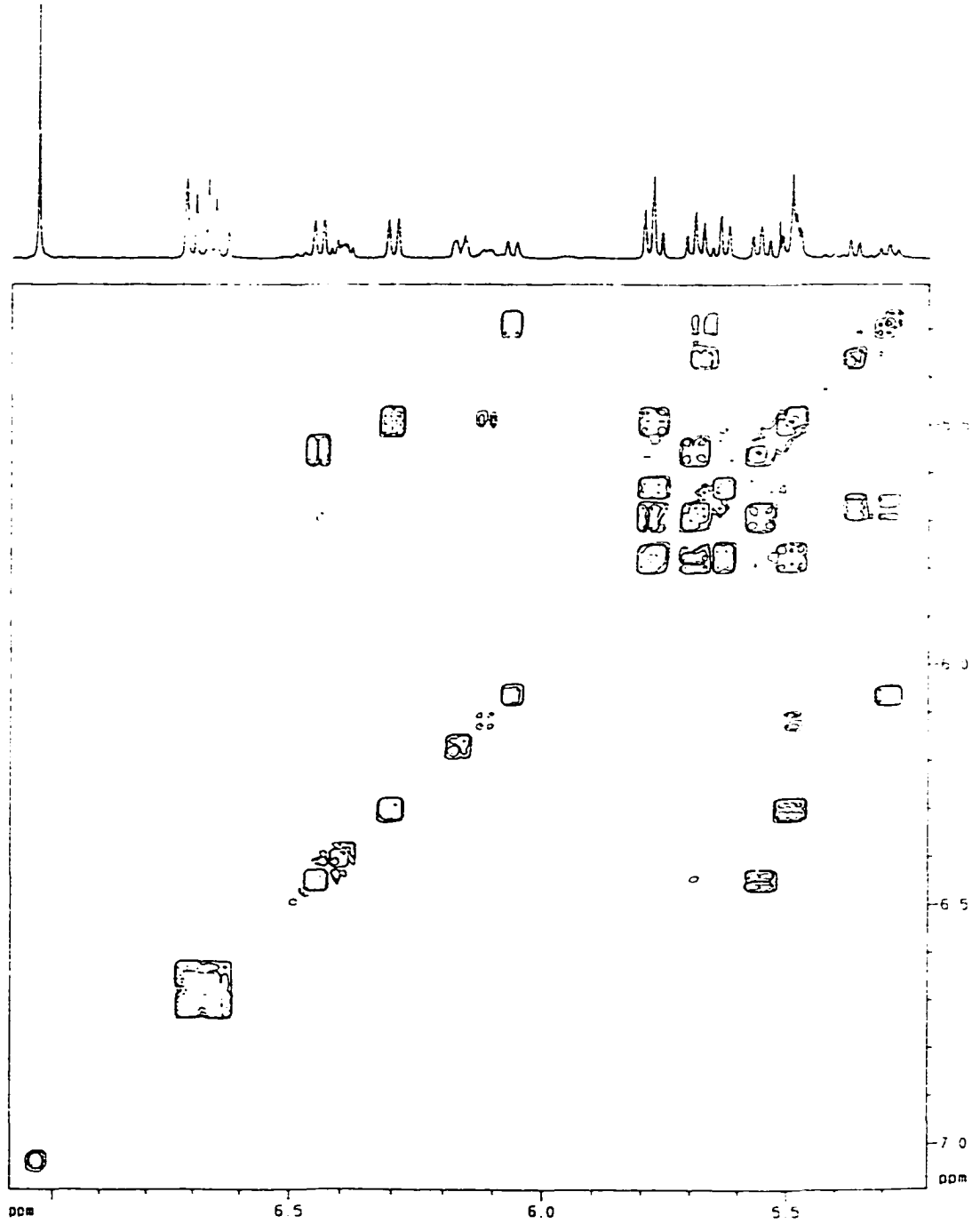


Figure 5.