THE SYNTHESIS OF THE FIRST NAPHTHANNELATED DIMETHYLDIHYDROPYRENE AND CHEMICAL SHIFT - BOND ORDER CORRELATIONS

by

SANTHANAGOPALAN VENUGOPALAN

B. Sc., University of Madras, India, 1981

M. Sc., University of Madras, India, 1983

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to the required standard

[redacted]
(R. H. Mitchell)

[redacted]
(T. W. Dingle)

[redacted]
(W. W. Kay)

[redacted]
(Y.-H. Lai)

University of Victoria

Supervisor : Professor R. H. Mitchell

ABSTRACT

The synthesis of the title compound, *trans*-14c,14d-dimethyl-14c,14d-dihydrodibenzo[de,qr]naphthacene, **25**, has been achieved in 9 steps from 2,3-dibromonaphthalene in an overall yield of 3.9%. This represents the first synthesis of a naphthannelated DMDHP, with **25** being the more stable isomer compared with the corresponding cyclophanediene **28**.

An improved correlation has been devised for predicting the chemical shift(s) of the internal methyl protons of various DMDHP's based on the change in RE when a delocalized aromatic moiety is fused onto a DMDHP with the change in shielding of the DMDHP's methyl protons. The anisotropy introduced by the mode of annelation can also be taken into account.

The X-ray structural determination of the teraryl **31** clearly demonstrates for the first time the existence of *syn*- and *anti*-conformers in the teraryl series, which had been postulated from solution studies. The barrier to rotation in the teraryls **31** and **43** have been determined by ^{13}C NMR and ^{1}H NMR, respectively, and found to be slightly higher than that for the corresponding benzo-analogues.

Naphtho[e]DMDHP, **25**, is found to be photochromic like its benzo-analogue **15**. Though not overly sensitive to oxygen, **25** undergoes decomposition during prolonged exposure to UV light. The effect that [e]-annelation has on the photochromic behaviour (as opposed to [a]-annelation) has been noted, with implications for use in switch-type devices.

The photoisomerization of **28** to **25** has been studied by UV-VIS spectroscopy and the activation barrier determined to be very similar to that observed in the case of the benzo-analogue **15**.

Examiners:

[redacted]

(R. H. Mitchell)

[redacted]

(T. W. Dingle)

[redacted]

(W. W. Kay)

[redacted]

(Y.-H. Lai)

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BuLi	butyllithium
c.c.	correlation coefficient
DIBAL-H	diisobutylaluminium hydride
DMSO	dimethyl sulphoxide
HCCP	hexachlorocyclopentadiene
IR	infrared
w	weak
m	medium
s	strong
br	broad
LDA	lithium diisopropylamide
MeOH	methanol
m.p.	melting point
MS	mass spectrum
CI	chemical ionization
EI	electron impact
NMP	1-methyl-2-pyrrolidinone
NMR	nuclear magnetic resonance
s	singlet
d	doublet
t	triplet
dd	doublet of doublets
m	multiplet
ppm	parts per million

RE	resonance energy
UV-VIS	ultraviolet-visible
VT	variable temperature

ACKNOWLEDGEMENTS

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

To the

memory of my brother

Srinivasagopalan

" ...... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth."

August Kekule, 1865.

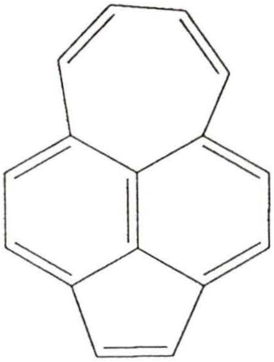
CHAPTER ONE

INTRODUCTION

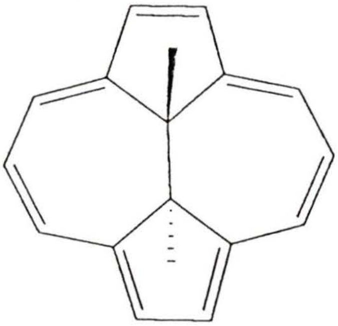
1.1 General Introduction

At the turn of the nineteenth century, the term 'aromatic' was applied to compounds having an aromatic odour, which had been isolated from volatile vegetable oils. Examples included benzaldehyde (from oil of bitter almonds), methyl salicylate (from oil of wintergreen) and anethole (from aniseed) amongst many others. Also included were non-benzenoid compounds, usually terpenoid natural oils. From the mid-1800's till the middle of this century, the term practically became synonymous with the implications of being benzenoid, *i.e.*, derivatives of benzene.[1]

It was the enunciation of Hückel's rule in 1931,[2] which states "amongst fully conjugated, planar, monocyclic polyolefins only those possessing $(4n+2)\pi$-electrons, where n is an integer, would have special stability" that has proved to be an enormous contribution to the growth of organic chemistry. Apart from providing an adequate explanation for the alternation in properties shown by the first three members of the cyclic polyene series (cyclobutadiene, benzene and cyclooctatetraene) and predicting new stable species (Hückel predicted $C_7H_7^+$, which was subsequently prepared and characterized in 1954 [3]), it has inspired and generated an enormous amount of synthetic organic chemistry. Though Hückel's rule strictly applies only to monocyclic systems, the definition has been extended by various workers so that polycyclic systems such as **1** [4] and even those containing no benzene moiety at all, *e.g.*, **2** [5] and **3** [6] now fall under the 'aromatic' category.



1



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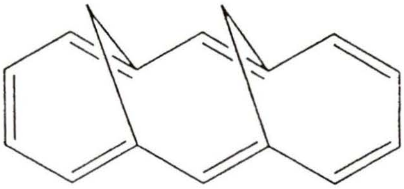

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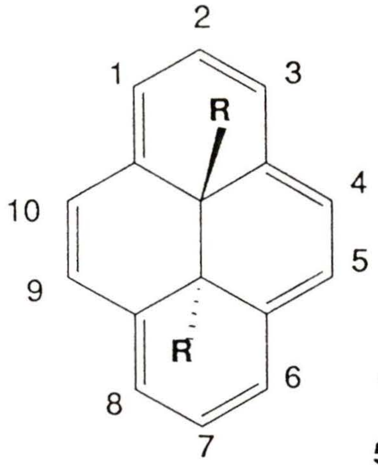
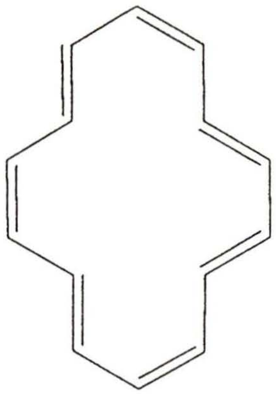
It is only during the last two decades that diatropicity or the ability to sustain an induced ring current has become a criterion of aromaticity.[7,8] Convincing experimental evidence for the ring current effect comes from Sondheimer's NMR studies in the annulene series,[9] where a clear distinction was revealed between the [4N]- and [4N+2]annulenes.[10] Perhaps, more striking as examples are the dihydropyrenes **4** [11] and **5**,[12] routes to which were developed in the 1960's and 1970's by Boekelheide's group.[13] In contrast to Sondheimer's [14]annulene, **6** [14] these compounds have an almost planar periphery in addition to being rigid. However, because the internal hydrogens can readily eliminate and yield pyrene, **4** proves less suitable



4 R = H

5 R = Me



6

than **5**. Indeed, compounds in this series where one of the internal substituents is hydrogen, generally eliminate RH (R = H, Me) to give pyrene.[15] Dimethyldihydropyrene, **5**, however, is found to be stable and has thus been used as a probe molecule and studied extensively. Of the various types of annulenes known, Boekelheide's dimethyldihydropyrenes (DMDHP) are of crucial interest owing to their planarity and to the existence of internal groups which are sensitive probes for the evaluation of ring currents. This is borne out by the fact that the chemical shift(s) of the internal methyl groups does not change significantly upon substitution with a variety of groups at a number of positions. The chemical shifts of the internal methyl groups for a number of derivatives of **5** are presented in Table 1. For the reasons mentioned above, they are also excellent systems for the investigation of benzannelation effects[16] discussed later.

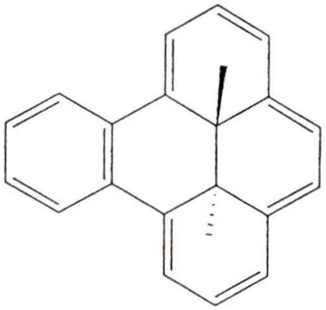
Table 1: δ_{Me} for some derivatives of **5**

Compound	Substituent(s)	Position(s)	δ	Ref.
5	--	-	-4.25	12
7	Br	2	-4.07, -4.08	17
8	NO_2	2	-4.03	18
9	CHO	2	-3.92	18
10	ϕ	2	-4.00, -4.03	19
11	DMDHP	2	-3.68, -3.77	19
12	CHO	2,7	-3.60	20
13	CH_3	2,7	-4.09	20
14	CH_3	1,3,6,8	-4.04	21

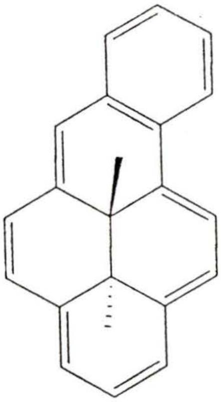
In order to study the effects of bond fixation by annelation of benzene rings onto the parent DMDHP **5**, Mitchell *et al.* have prepared compounds **15** - **18**.[22-25] The observed chemical shifts were used along with π-SCF calculations of bond orders to derive a correlation which could be used to predict chemical shifts of these and other unknown examples.[26] The relevant data for compounds **15** - **18** are presented in Table 2. Rees and co-workers have reported the synthesis of the [10]annulene, 7b-methyl-7b*H*-cyclopent-

Table 2: Experimental and calculated δ_{Me} for compounds **15-18**

Compound	δ_{Me} (calc.)[26]	δ_{Me} (expt.)	Ref.
15	-1.80	-1.85	22
16	-1.86	-1.60	23,24
17	-3.22	-3.58	24,25
18	+0.04	+0.02	24,25



15



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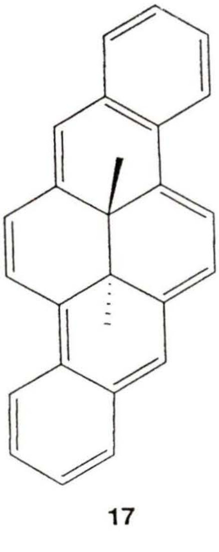

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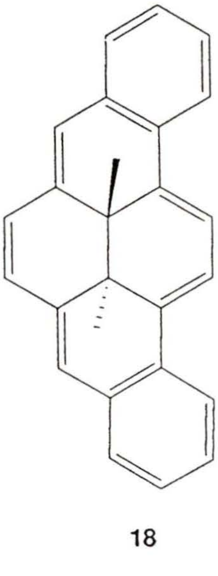
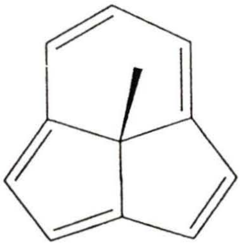


18

[*cd*]indene, **19**[27] and its benzannelated derivative, 9c-methyl-9c*H*-cyclopenta[*jk*]fluorene, **20**.[28] The internal methyl groups of **19** and **20** are observed in the ^1H NMR spectrum at δ -1.67 and -0.79, respectively. The authors, based on an analysis of the coupling constants of **16** and **20**, suggest that a similar degree of bond fixation is present in these molecules.[28] This is surprising, since the 10π-system is expected to be less affected by benzannelation when compared with the 14π-system **5**, as the resonance energy (RE) of a 10π-system is greater than that of a 14π-system.[29] This loss of resonance energy in **19** has been rationalized on the basis of torsional strain in the periphery.[28] In accordance with the above, **19** sustains a slightly larger ring current on benzannelation (67%)[28] compared to 49% in the case of **5**[23] on benzo[a]annelation.



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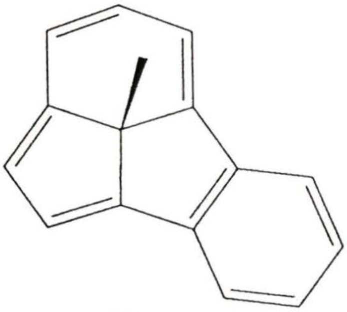
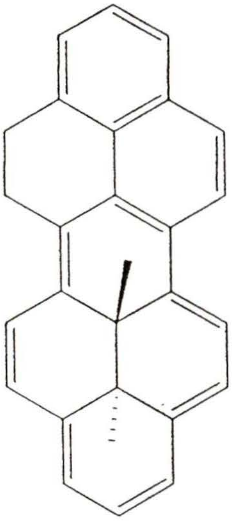


20

Several predictions of chemical shifts were also made for the compounds **21** - **24**.[26] The predicted and observed chemical shifts for the internal methyl protons are compiled in Table 3. As can be seen from Table 3, there is an excellent agreement between the theoretical predictions and experimental values obtained. In order to extend the



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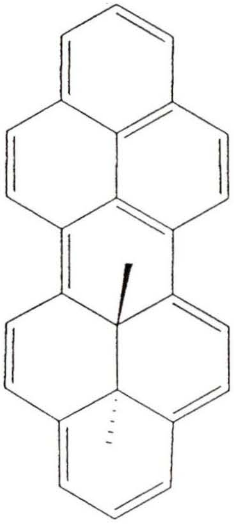

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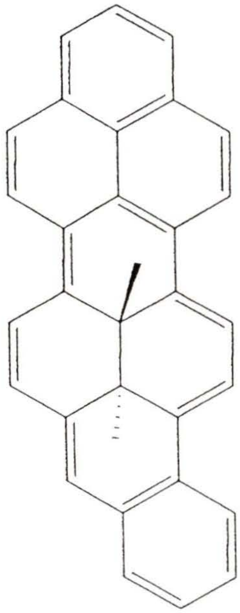

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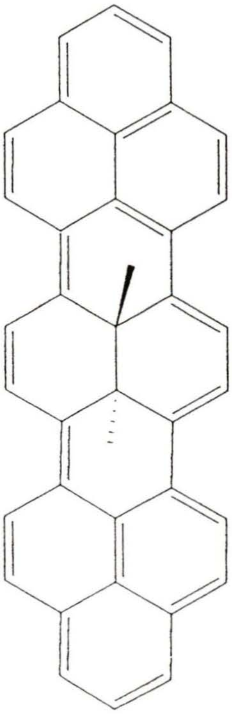

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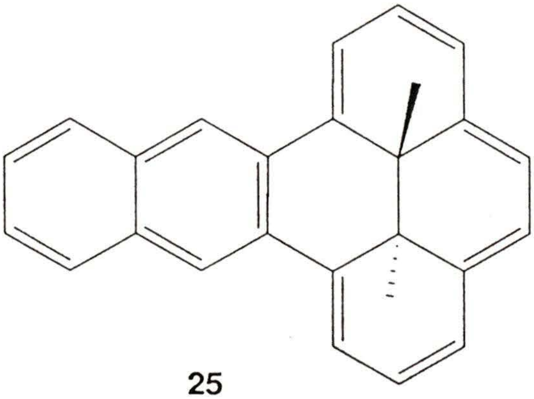
Table 3: Calculated[26] and experimental δ_{Me} for **21** - **24**

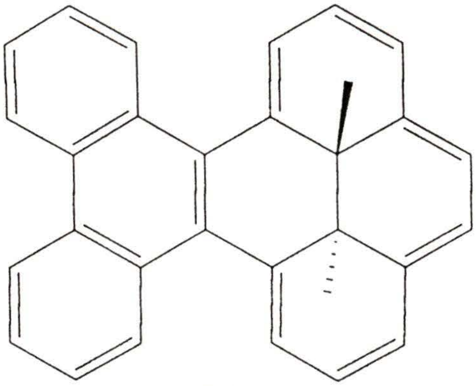
Compound	δ_{Me} (calc.)	δ_{Me} (expt.)
21	-2.75	-2.78
22	-3.97	-4.19 -4.28
23	-1.73	-1.35 -1.41
24	-2.99	-3.20

applicability of their correlation, Mitchell *et al.* have calculated the internal methyl proton shifts for a series of 15 unknown annelated derivatives of **5**,[26] one of which is **25**. Compound **25** was of particular interest to us since **17** was the only anth-fused[30] annulene known and found to have special properties.[25] However, no anth-fused example was known where the DMDHP moiety was at the end of the molecule as in **25**. The aim of this project was thus to prepare and study the properties of the naphthannelated derivative **25**. The predicted chemical shift for the internal methyl protons of **25** was δ -1.25.[26] The synthesis of **25** would serve as the first test of the chemical shifts predicted by the empirical relationship based on π-SCF calculations.[26] It would also have been the first annelated DMDHP to be reported since

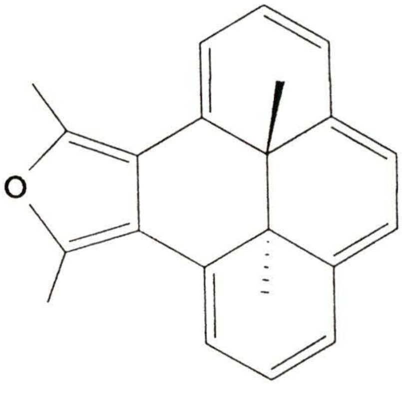


25

Mitchell's predictions[26] were published. However, Lai has reported the synthesis of **26** during the course of this work.[31] The internal methyl protons of **26** are observed at δ -3.32 in the ^{1}H NMR spectrum, in excellent agreement with a value of δ -3.41 as calculated from π-SCF bond orders.[32] However, since benzo[e]DMDHP, **15** and phenanthro[e]DMDHP, **26** are already known, the synthesis of **25** now fills a gap in this series. Recently, Lai has also reported the synthesis of the furanoDMDHP **27**, the first heterocyclic-annelated DMDHP.[33]



26



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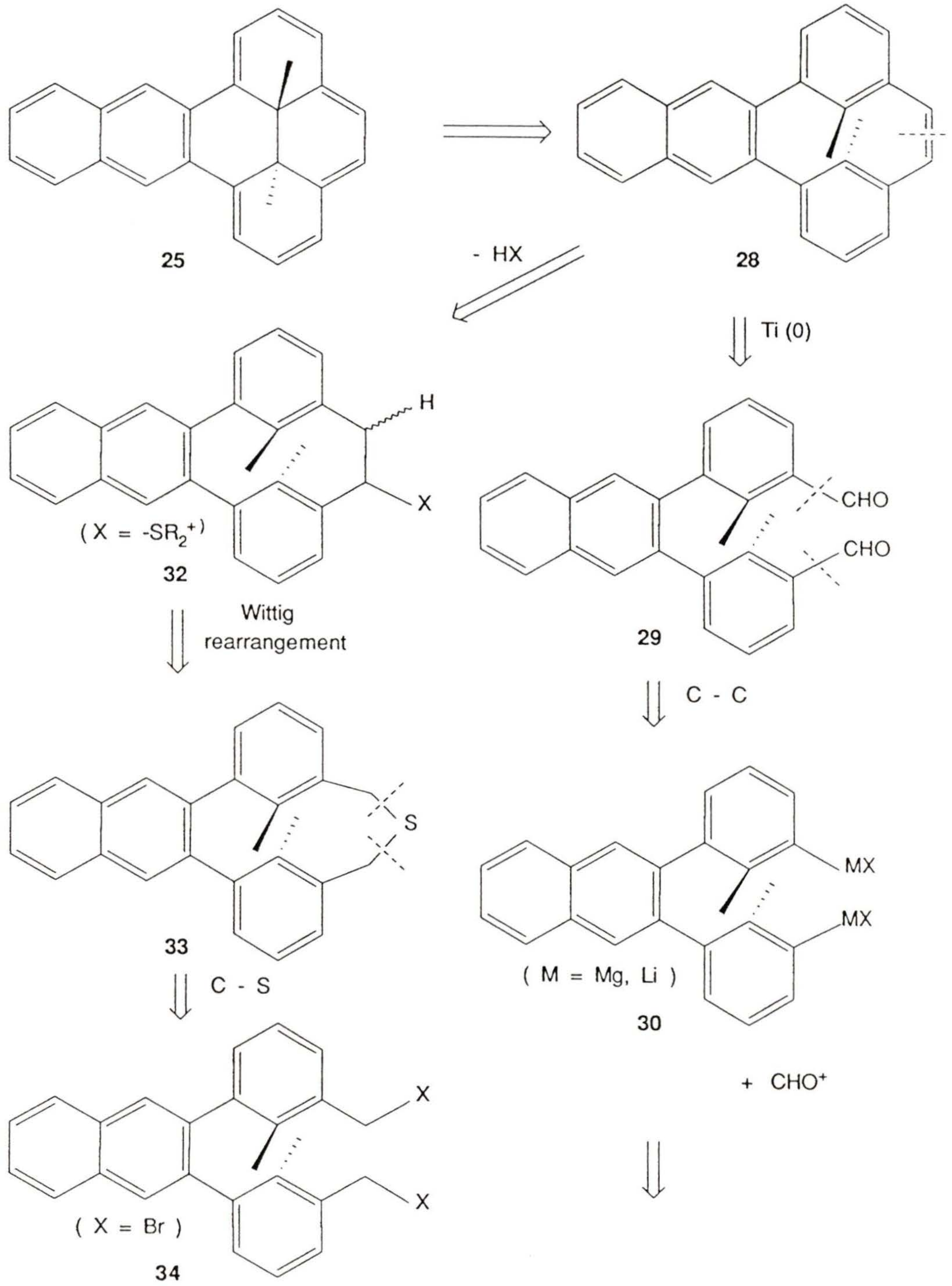
1.2 Retrosynthetic Analysis

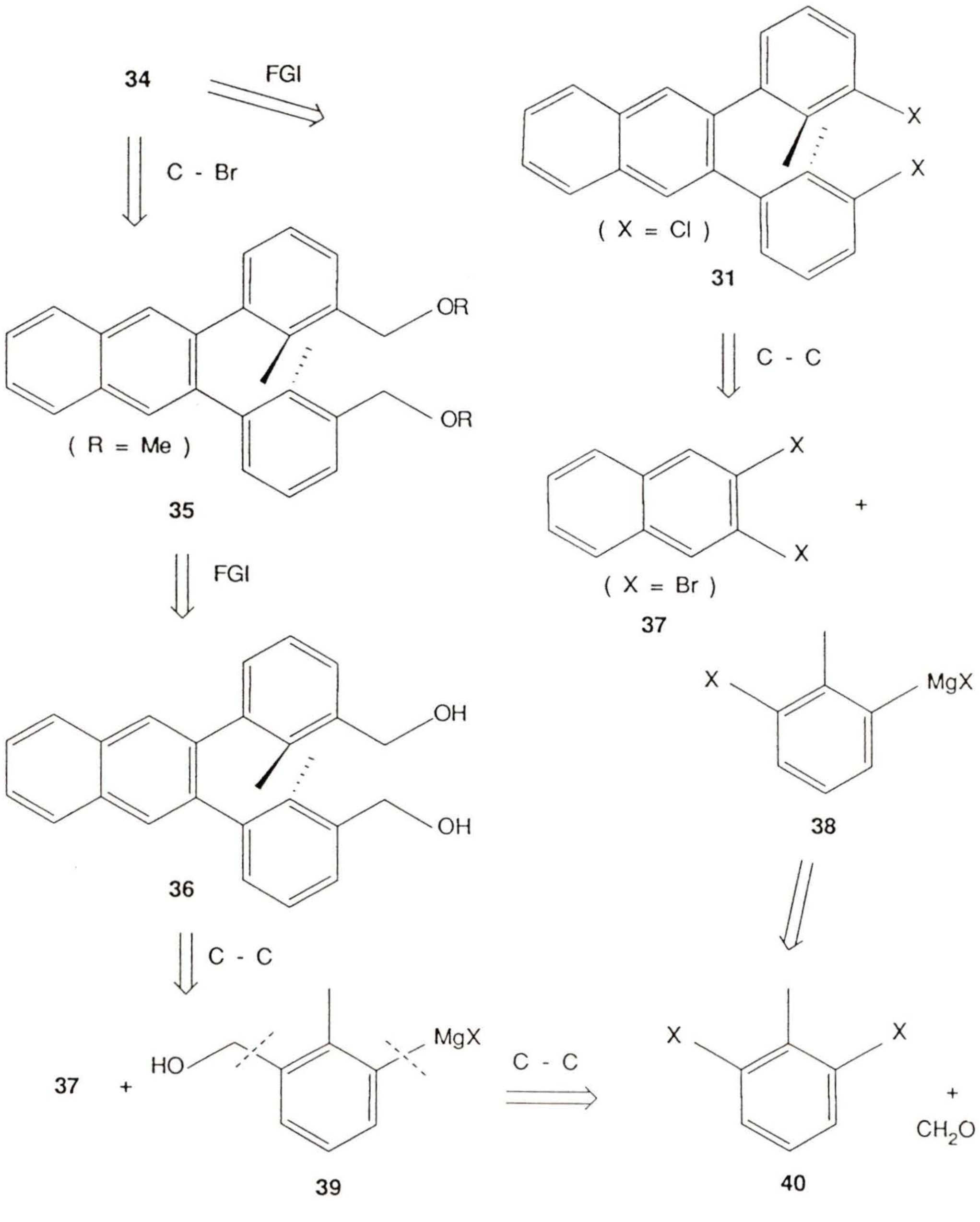
A retrosynthetic analysis for the title compound **25** is shown in Scheme 1. Synthetically, between **25** and **28**, the latter is more approachable, and hence, is the intermediate of choice for further analysis.

An examination of the double bond of the cyclophanediene **28** suggests a disconnection to two carbonyl groups, *i.e.*, the dialdehyde **29**. Compound **29** could, in turn, be obtained by reaction of an organometallic derivative, **30** (obtainable from the corresponding organic halide, *i.e.*, **31**) with an appropriate carbonyl compound. This represents the most convergent synthesis of **28**, and hence, **25**.

Compound **28** can also be obtained by a Hofmann elimination of a molecule of HX ($X = -SR_2$) from **32**, which in turn, is obtainable by a Wittig rearrangement of the thiacyclophane **33**. The symmetry of **33** demands a precursor of the type of **34**. Access to compound **34** can be achieved *via* two routes: a) by a series of functional group interconversions (FGI) leading to a dihalide of the type of **31** and b) from the bis(ether) **35**, which in turn, can be obtained from the diol **36**. Both **31** and **36**, can be made from the same starting materials, *viz.*, **37** and **40**.


25
28
- HX
Ti (0)
H
X
(X = -SR₂⁺)
32
Wittig rearrangement
CHO
CHO
29
C - C
S
33
C - S
MX
MX
(M = Mg, Li)
30
+ CHO⁺
X
X
(X = Br)
34

Scheme 1



Scheme 1 (contd.)

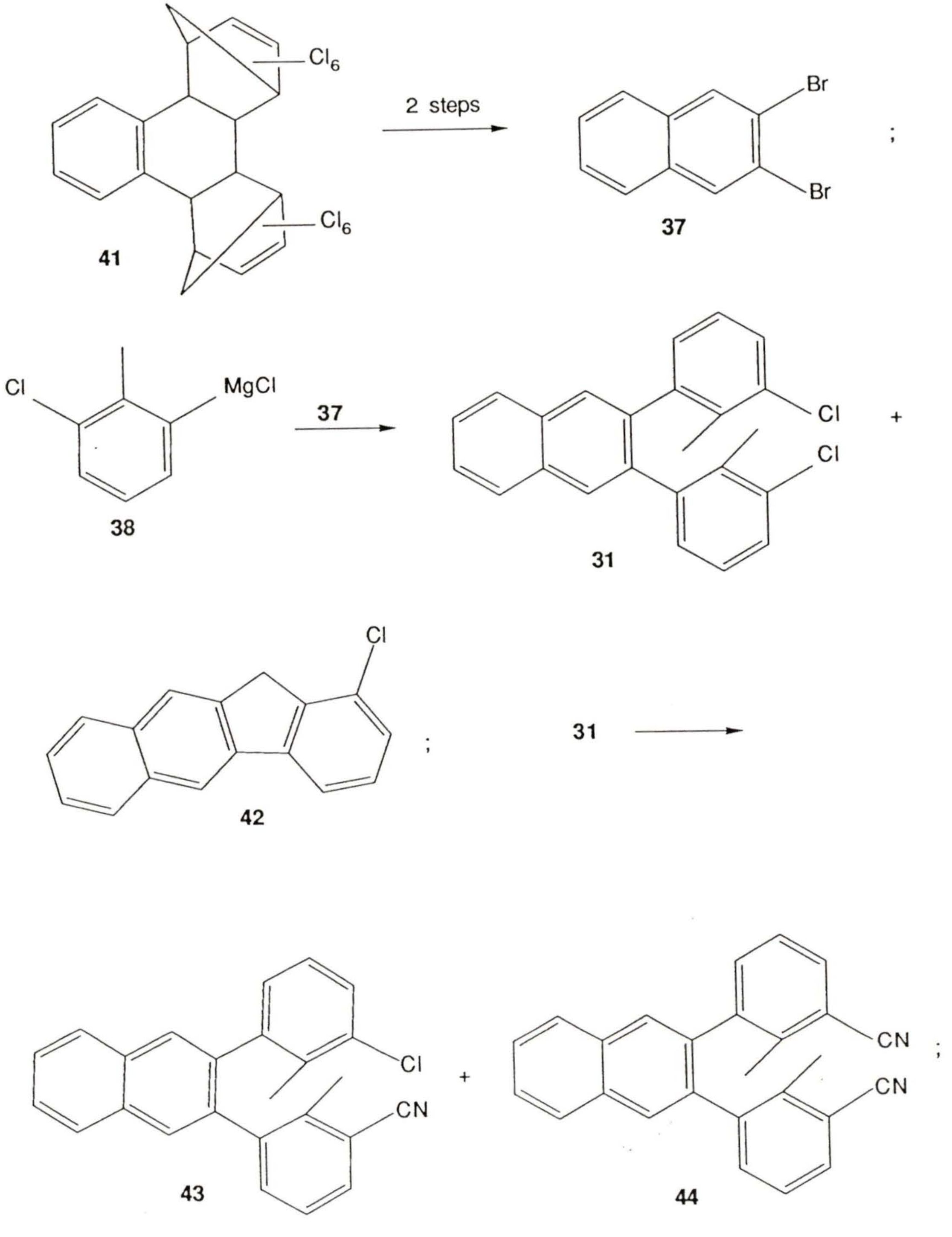
CHAPTER TWO

RESULTS AND DISCUSSION

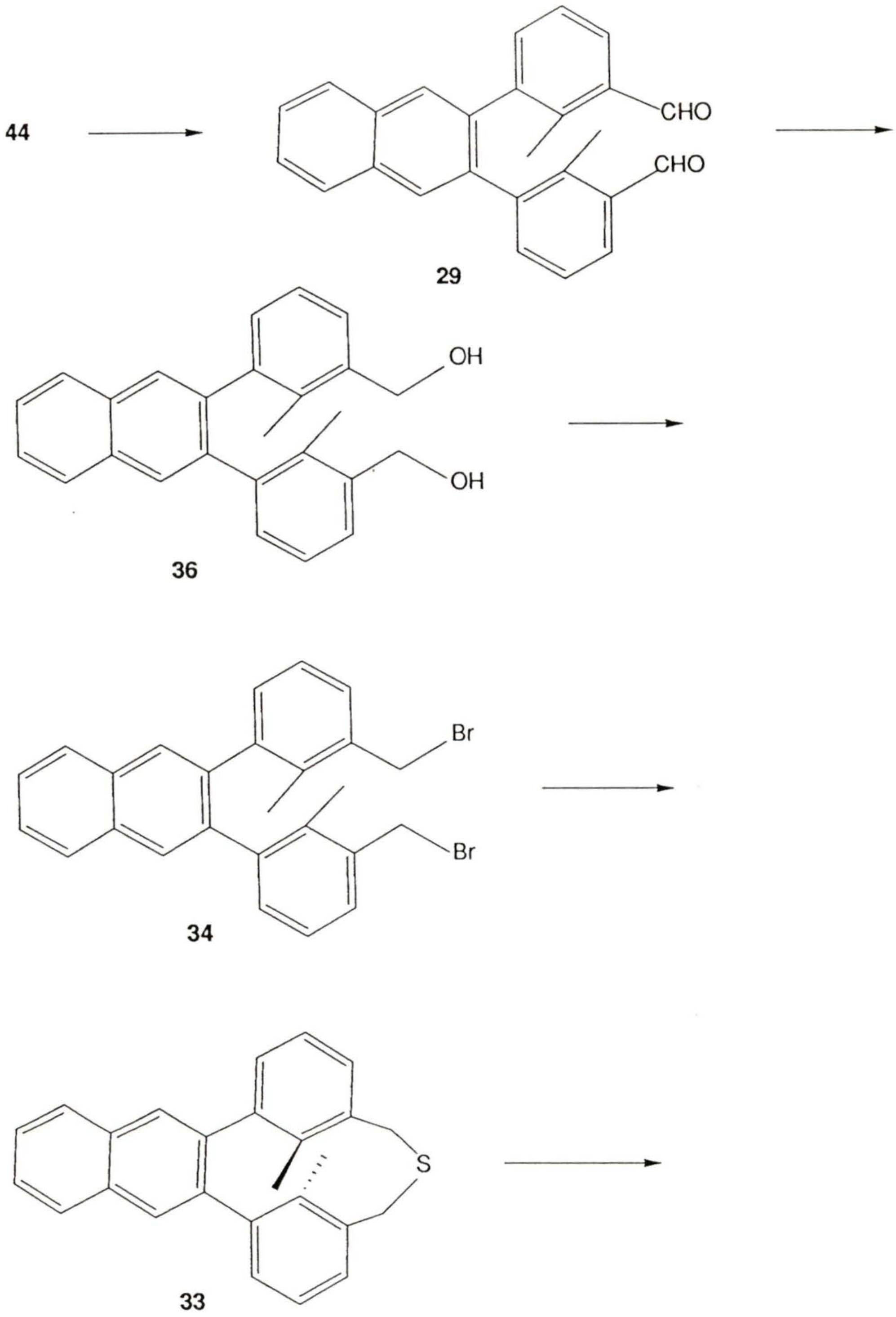
2.1 Synthesis of *trans*-14c,14d-dimethyl-14c,14d-dihydrodibenzo[de,qr]naphthacene, 25

The synthetic route utilized for the preparation of **25** is outlined in Scheme 2. The route is similar to that used by Mitchell and co-workers for the synthesis of the benzo-analogue, *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]-pyrene, **15**.[22,34]

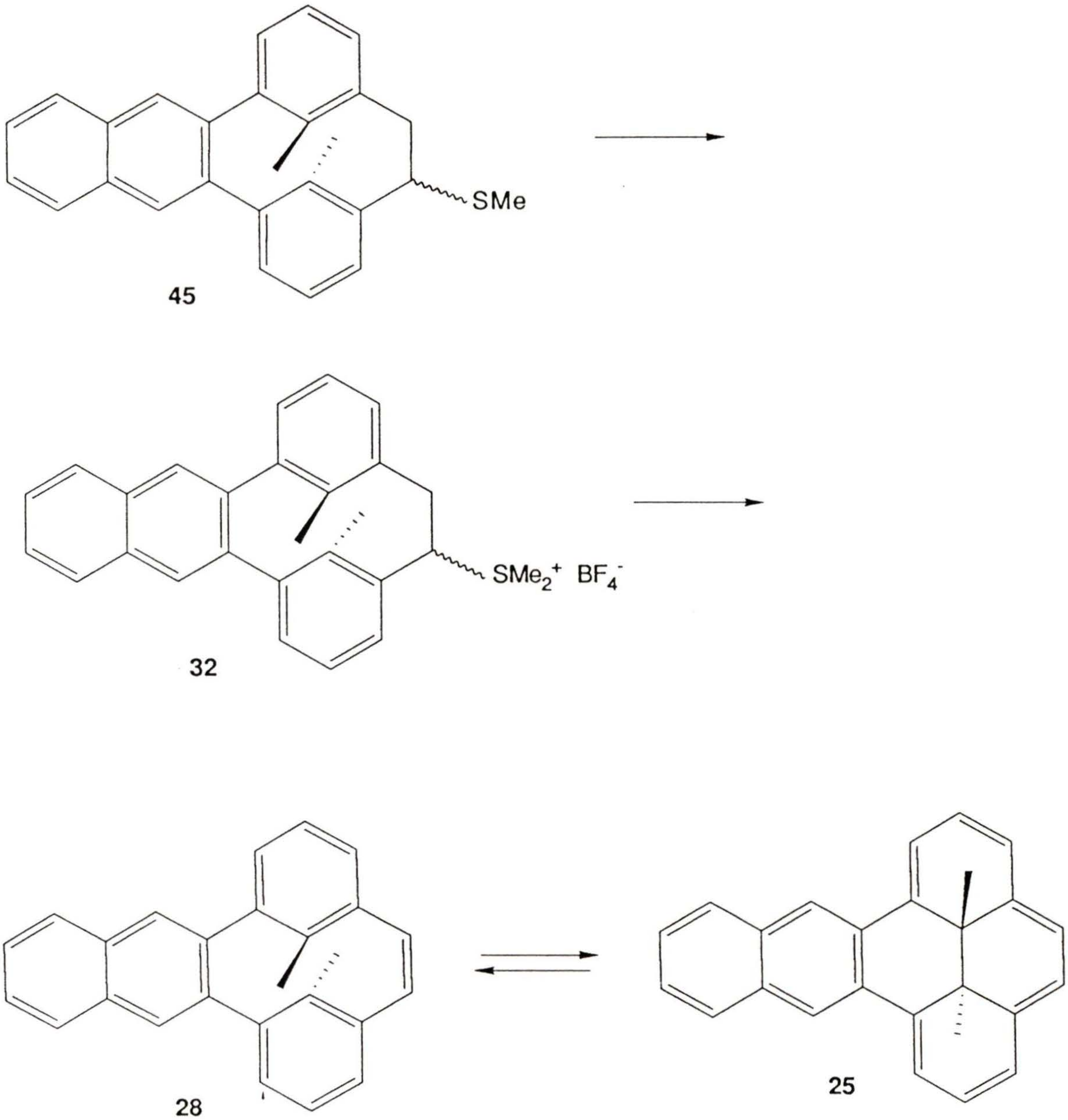
The starting material, 2,3-dibromonaphthalene, **37** was prepared by the method of Danish and co-workers,[35] which involves bromination of the naphthalene-bis(hexachlorocyclopentadiene) adduct **41** and then a reverse Diels-Alder reaction to give **37** and hexachlorocyclopentadiene (HCCP). It was purified by using the procedure of Prill,[36] which removes the unwanted HCCP by a Diels-Alder reaction with maleic anhydride, followed by chromatography over basic alumina using petroleum ether as eluant to yield 85% of **37** (Scheme 3). IR and ^{1}H NMR data were in agreement with those reported in the literature[37] and further supported by mass spectral data which exhibited the correct isotopic pattern for the two bromine atoms and satisfactory elemental analysis. Furthermore, the ^{13}C NMR chemical shifts measured were found to be in excellent agreement (± 0.1 ppm) with those reported by Seita and co-workers.[38] Reaction of the mono-Grignard of 2,6-dichlorotoluene **38**, with 2,3-dibromo-


Cl6
Cl6
41
2 steps
Br
Br
37
;
Cl
MgCl
38
37
Cl
Cl
31
+
Cl
42
;
31
Cl
CN
43
+
CN
CN
44
;

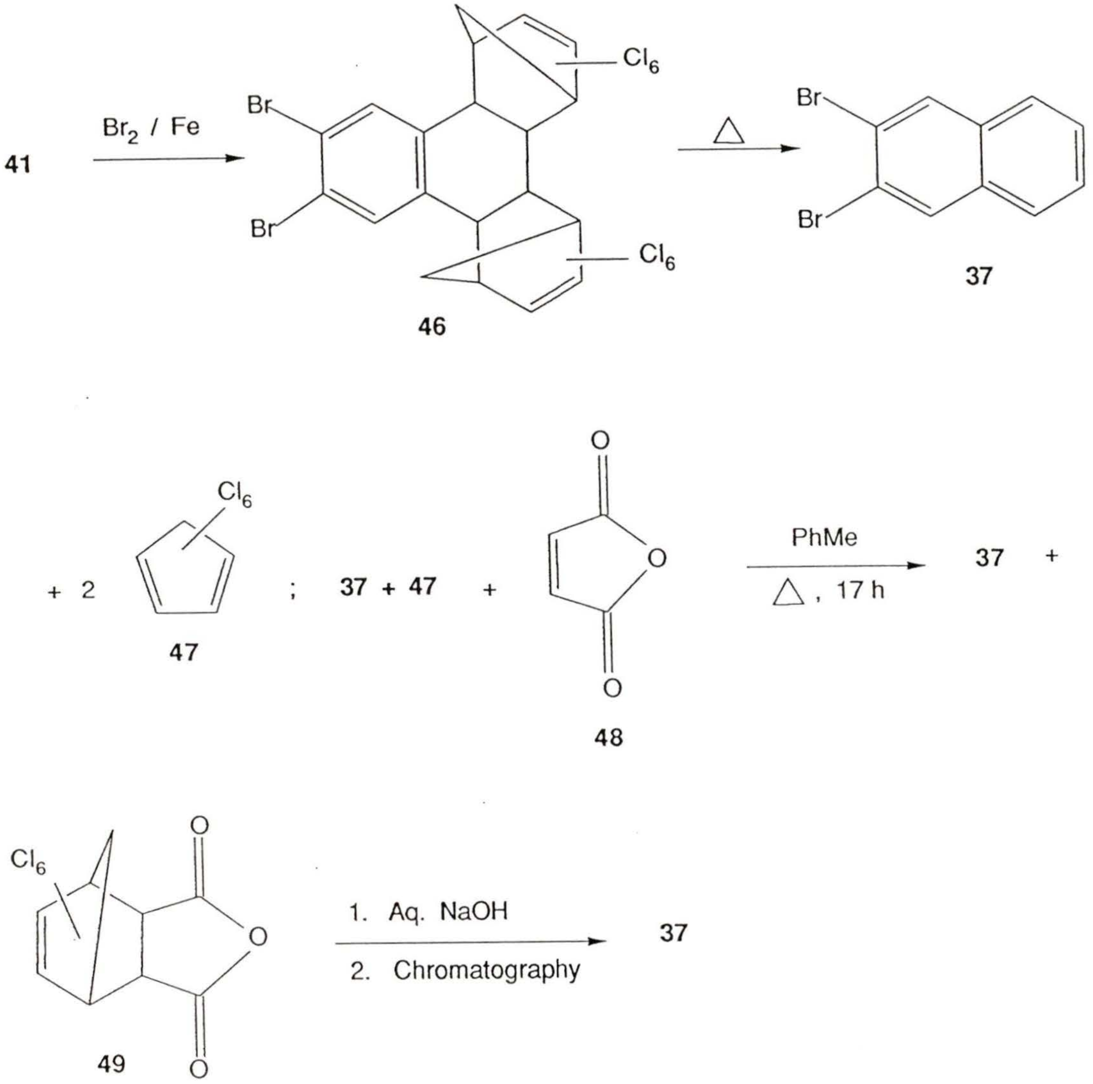
Scheme 2



Scheme 2(contd.)

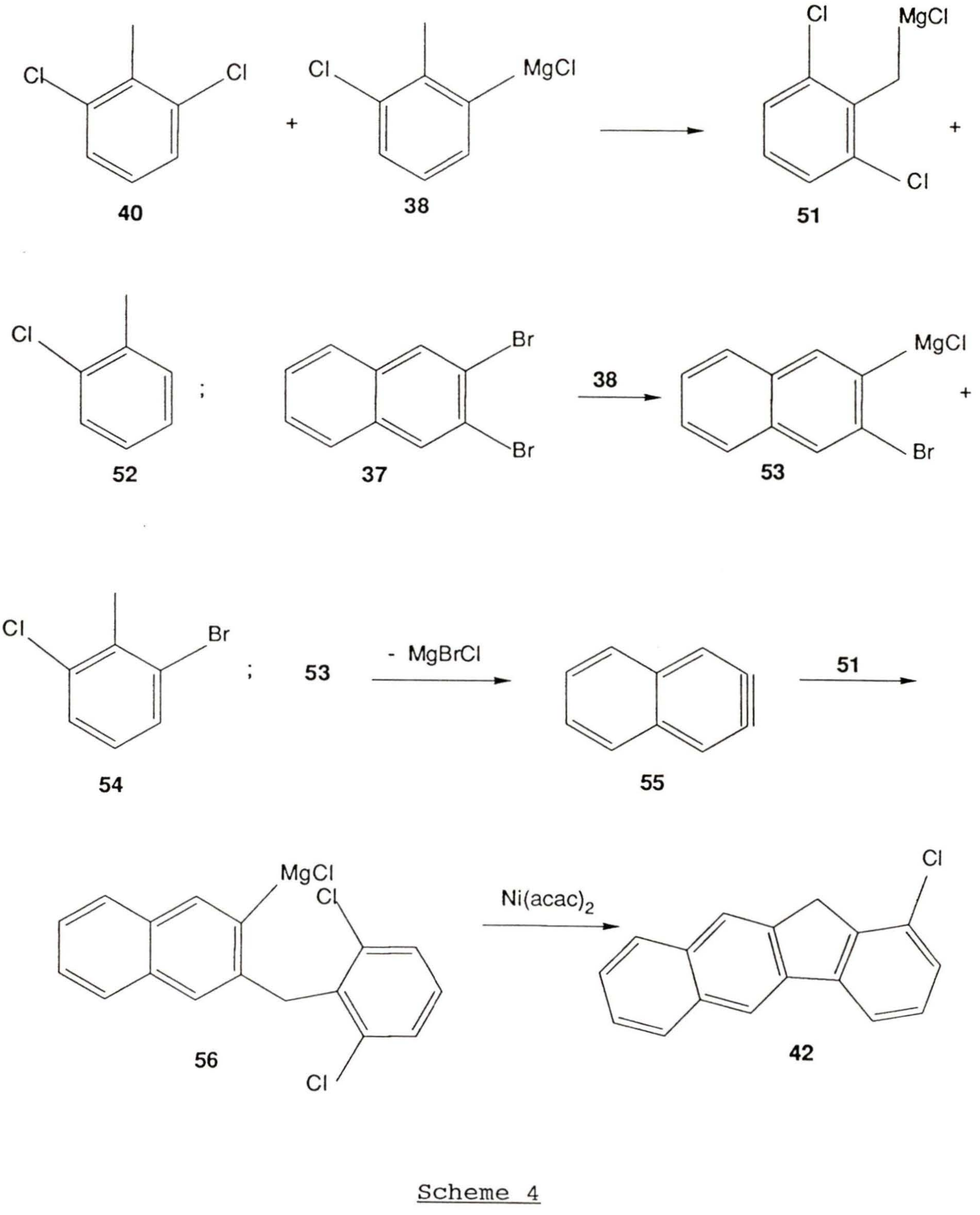


Scheme 2

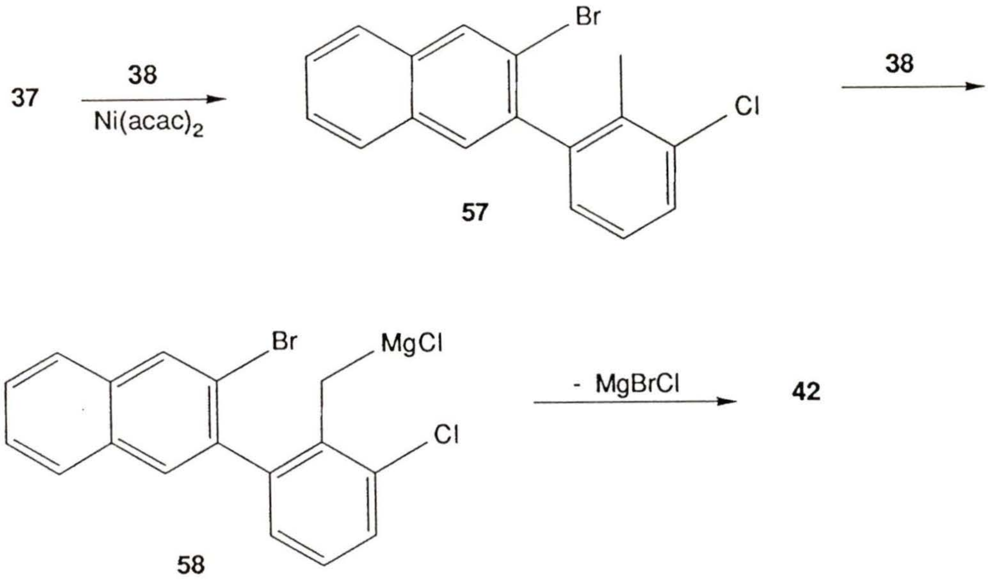


Scheme 3

naphthalene in the presence of Ni(acac)$_2$ yielded the teraryl **31**, m.p. 155-156°C, in 27% yield. The structure of **31** was supported by a mass spectrum with an $M^{+\cdot}$ peak at *m/e* 376, with the correct isotopic pattern for two chlorine atoms. Although in the ^1H NMR spectrum, the internal methyl protons appear as a singlet at δ 2.15, in the ^{13}C NMR spectrum at ambient temperatures, the internal methyl groups appear as two signals in addition to the aromatic region exhibiting more than the 11 lines expected on the basis of symmetry. At higher temperatures the appropriate number of lines is seen. The variable temperature properties are discussed in Section 3.2. Also isolated in 1% yield was the hitherto unreported 1-chloro-11*H*-benzo[b]fluorene, **42**, m.p. 198-200°C. It gave an $M^{\ddagger}$ peak at *m/e* 250 with the correct isotopic pattern for the single chlorine atom in its mass spectrum. The structure was assigned on the basis of its ^{13}C NMR spectrum which had the expected 17 lines and matched quite closely the spectrum reported for the parent compound,[39] 11*H*-benzo[b]fluorene, **50** and also on the basis of its ^{1}H NMR spectrum which showed a 2H singlet at δ 4.07. It also gave a satisfactory elemental analysis for C and H. Two plausible mechanisms for the formation of **42** are given in Schemes 4 and 5. The mechanism proposed in Scheme 4 is analogous to that proposed by Du, Hart and Ng[40] inasmuch as an aryne is generated from an *o*-disubstituted arene, followed by attack by a Grignard reagent. The next step in building the carbon skeleton was achieved in 86% yield by treating the teraryl **31** with CuCN in refluxing NMP for 24 h. A -C≡N stretch at 2211 cm^{-1} in the IR spectrum and an $M^{\ddagger}$ peak in the mass spectrum at *m/e* 358 were consistent with the structure assigned for **44**. Also isolated in 4% yield was the mononitrile **43**, m.p. 161-163°C, which had $M^{\ddagger}$ peaks


Cl
Cl
40
+
Cl
MgCl
38
Cl
MgCl
Cl
51
+
Cl
52
;
Br
Br
37
38
MgCl
Br
53
+
Cl
Br
54
;
53
- MgBrCl
55
51
MgCl
Cl
Cl
56
Ni(acac)$_2$
Cl
42

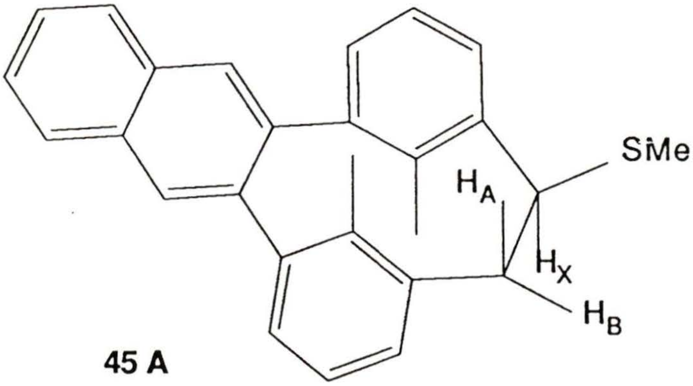
Scheme 4



Scheme 5

at *m/e* 367 and 369 (correct isotopic pattern for the single chlorine atom). The structure was further supported by the presence of a -C≡N stretch at 2211 cm^{-1} in the IR spectrum. The bis(nitrile) **44**, was reduced to the corresponding dialdehyde **29**, using DIBAL-H in 90% yield. The aldehyde protons appeared at δ 10.2 in the ^1H NMR spectrum. A carbonyl stretch at 1663 cm^{-1} in the IR spectrum and an $M^{+\cdot}$ peak at *m/e* 364 lend further support to the structure assigned to **29**. Sodium borohydride reduction of the dialdehyde **29** gave the hydroxymethyl derivative **36**, m.p. 155-157°C in practically quantitative yield. The structure was assigned on the basis of the methylene protons at δ 4.57, the -OH protons at δ 1.56 (which exchange with D_2O), the $M^{+\cdot}$

peak at *m/e* 368 in the mass spectrum and the -OH stretch at 3351 cm^{-1} coupled with the loss of the carbonyl stretch in the IR spectrum. The precursor to the thiacyclophane, the bromomethyl compound **34**, m.p. 148-149°C, was obtained in 92% yield from **36** by reaction with a mixture of 48% HBr and a small amount of conc. H_2SO_4 at room temperature. The structure of **34** was supported by a mass spectrum in which the $M^{+\cdot}$ peaks exhibit the 1:2:1 intensity ratio consistent with the presence of two bromine atoms. The key intermediate, the thiacyclophane **33**, m.p. 198-200°C, was obtained in 27% yield from the coupling reaction between **34** and $Na_2S.9H_2O$ in ethanol/benzene. The ^1H NMR spectrum showed an AB quartet for the $-CH_2-$ protons. As expected, the internal methyl protons were shielded from those of **31** by 1.2 ppm, appearing at δ 0.95, confirming that it is the *anti*-isomer. The Wittig rearrangement, which results in ring contraction, was performed with *n*-BuLi and the reaction quenched with MeI to give **45** in 94% yield. The gross structure was indicated by a $M^{+\cdot}$ peak at *m/e* 380. A single isomer was obtained, which on the basis of its ^1H NMR was assigned structure **45A**, since a single -SMe peak at δ 2.16, together with a single methyl peak at δ 0.69, indicated it to be a pseudoequatorial substituent, where neither internal methyl group is deshielded from the other, as would be the case if the -SMe were pseudoaxial.[22] In the case of the



45 A

H_X: δ 3.83, dd, J_{XB} = 11 Hz ; J_{XA} = 3 Hz.
H_A: δ 3.22, dd, J_{AB} = 12 Hz ; J_{AX} = 3 Hz.
H_B: δ 2.53, t, J_{BA} = 12 Hz ; J_{BX} = 11 Hz.

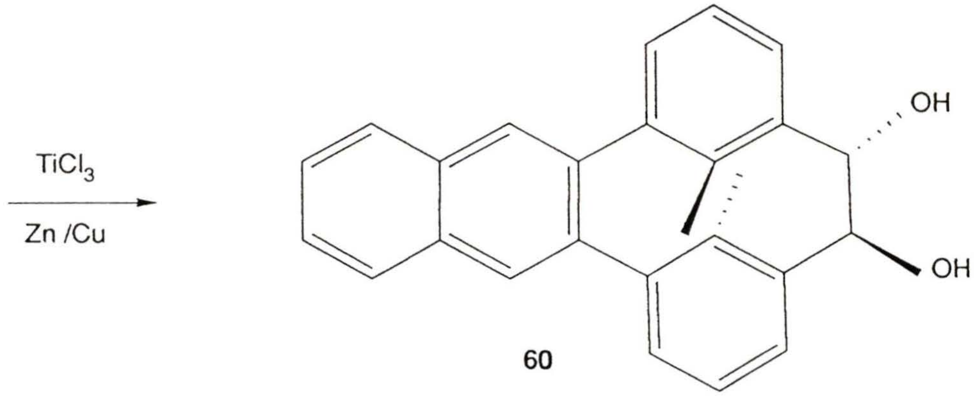
benzo-analogue **59,** also a single isomer is formed.[22] This has been rationalized in terms of an unfavourable interaction between an axial $-S^-$ and the aromatic methyl group.[41]

Conversion of **45** to **32** was achieved with Borch's reagent,[42] $(MeO)_2CHBF_4$, in 90% yield. Treatment of **32** in THF with potassium *t*-butoxide at room temperature yielded the desired dihydropyrene **25** in 90% yield. The characteristic internal methyl protons of **25** appear at δ -0.49 in C_6D_6 and at δ -0.74, -0.75 and -0.77 in $CDCl_3$, THF-d_8 and $(CD_3)_2CO$, respectively. The ^{13}C NMR exhibits the expected 13 lines consistent with a C_2 level of symmetry. The structure is further supported by an $M^{+\cdot}$ peak at *m/e* 332 and peaks at *m/e* 317 and 302, corresponding to the loss of one and two methyl groups, respectively, in the mass spectrum. Thus, the synthesis of the title compound **25**, was achieved in an overall yield of 3.9% in 9 steps from **37**. Compound **25** represents the first synthesis of a naphthannelated DMDHP (**21** has an extra saturated two-carbon bridge).

2.2 Other synthetic routes

As suggested by the retrosynthetic scheme, though low-valent titanium coupling might be expected to yield the desired dihydropyrene **25** directly from the dialdehyde **29**, earlier work by Weerawarna[43] in our laboratories yielded only the diol **60**. Hence, we decided to explore other possibilities.

29



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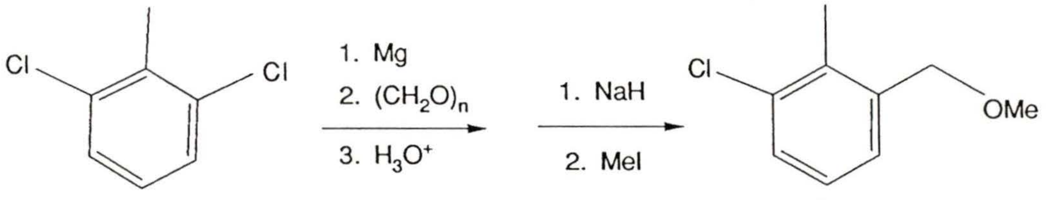
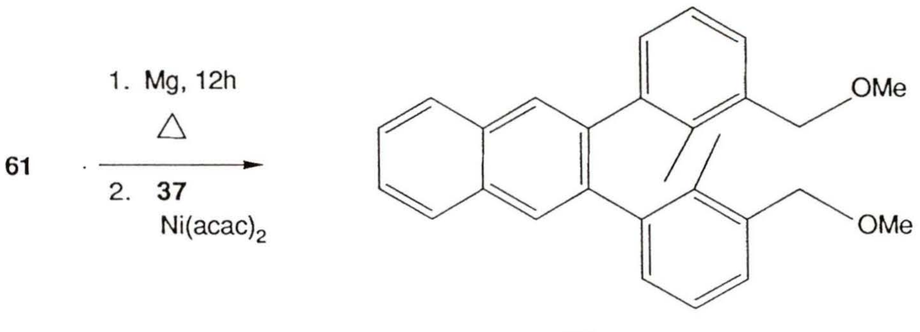
In order to shorten the route outlined in Scheme 2, and hence, to improve the overall yield, two approaches, both based on the concept of convergency were attempted. The first, started with the Grignard reagent of the ether **61**, prepared from 2,6-dichlorotoluene, **40** in two steps by the method of Mitchell and Lai.[44] This strategy would result in shortening of the scheme by three steps, bypassing the intermediates **44**, **29** and **36**. However, the formation of the Grignard reagent of **61** was very sluggish and the yields of **35** were consistently below 10%. Therefore, this approach was abandoned.

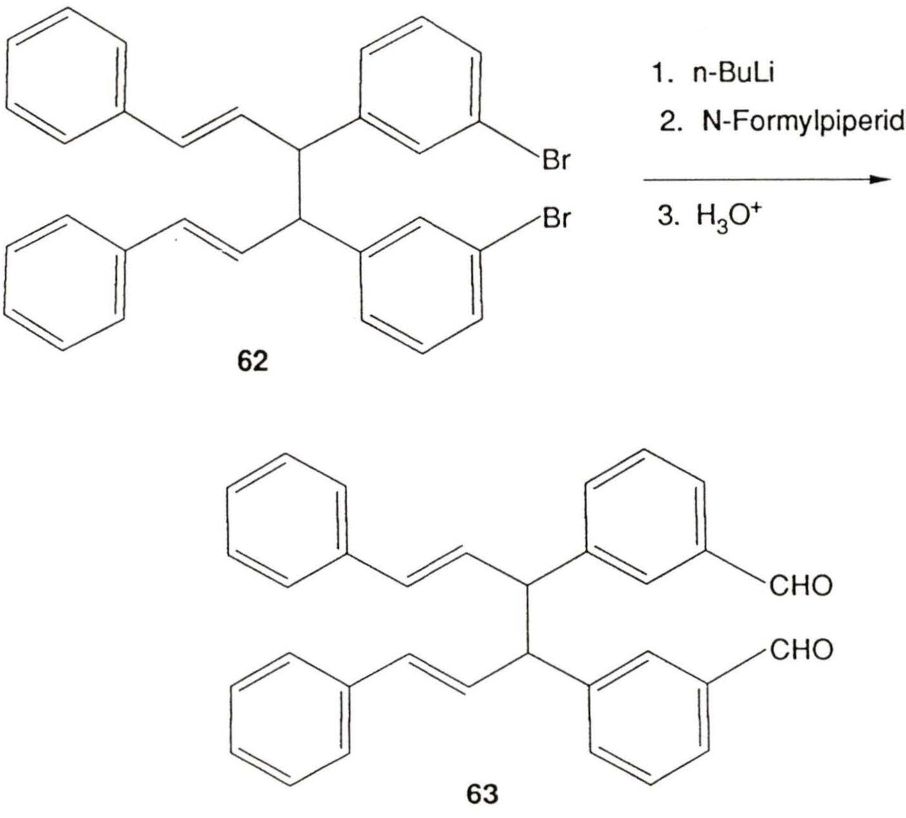


40 **61**



35

Since aryl halides are known to undergo metallation reactions with alkyllithiums, metallation was attempted on the bis(chloride) **31**. Reaction of **31** with *n*-BuLi and quenching with paraformaldehyde returned the starting material quantitatively. Earlier, Eisen and Vögtle had reported a similar reaction on a tetraaryl-substituted biallyl compound, **62**.[45] In this case however, despite the presence of the more reactive Br and the sterically less demanding internal hydrogens as opposed to Cl and internal methyls in **31**, the yield was only 32%. Thus, with hindsight, it is perhaps not surprising that **31** did not undergo the metallation reaction.



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63

2.3 Chemical shift - bond order correlations

In the ^{1}H NMR of the dihydropyrene **25**, the internal methyl protons are observed at δ -0.74 in $CDCl_3$ solution. Earlier Mitchell and co-workers[26] had predicted a chemical shift of δ -1.25 based on π-SCF calculations. While this difference of 0.5 ppm is not large, it is larger than that for any other annelated DMDHP thus far prepared, and we felt that it needed an explanation. Since the predicted chemical shift is calculated from π-SCF bond orders, we decided first to evaluate bond orders in **25** from the ^{1}H NMR spectrum.

The ^{1}H NMR spectrum of **25** in THF-d_8 (aromatic region only) is shown in Figure 1. The protons were assigned on the following basis: H-9,14 (see page 30) appear, as expected, as a singlet at δ 9.21 and are the most deshielded protons. The bay protons of **25**, H-1,8 and H-10,13 (which form part of an AA'XX' multiplet) appear overlapped at δ 8.11. The other part of the AA'XX' multiplet, corresponding to H-11,12 is observed at δ 7.54. The signal corresponding to H-3,6 is expected to be and is seen as a doublet at δ 7.15, J = 8.96 Hz (coupled to H-2,7, respectively), with the *meta* coupling to H-1,8, respectively, too small to be observed. The doublet of doublets which would be expected for H-2,7 is observed at δ 6.91 and the singlet due to H-4,5 appears overlapped with the most upfield peak of the doublet

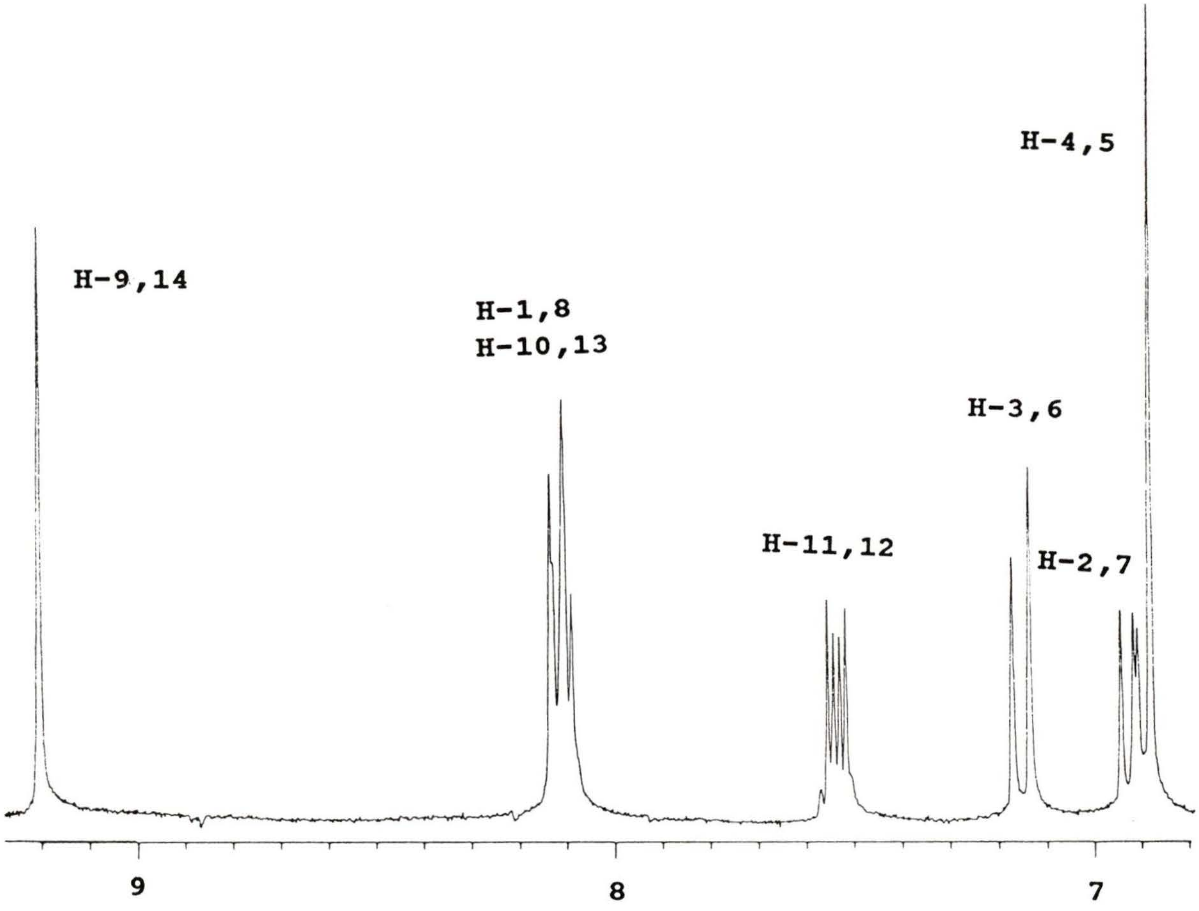
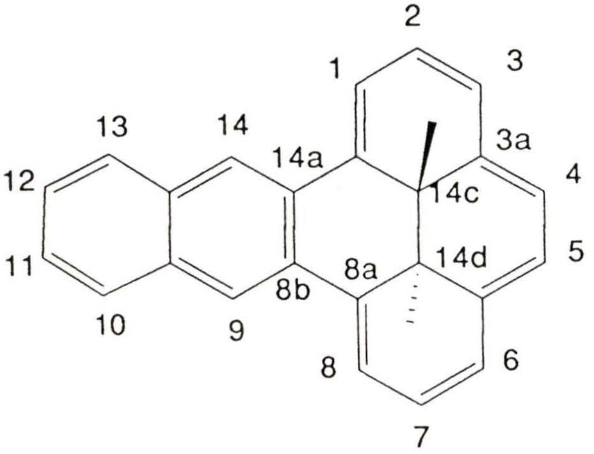


Figure 1 : ^{1}H NMR Spectrum (250 MHz) of **25** in THF-d_8 (aromatic region only).

of doublets at δ 6.88.

The spectrum for the non-singlet protons (H-1, 2, 3, 10, 11, 12 and 13) of **25** have been simulated (Figure 2). The spectrum was treated as two sub-spectra -- ABC and AA'XX'. The AA'XX' sub-spectrum was analyzed following the treatment of Günther.[46] The coupling constants obtained after refinement are given below:



$J_{11,12}$ = 6.81 Hz

$J_{12,13}$ = 8.41 Hz

$J_{10,12}$ = 1.23 Hz

$J_{10,13}$ = 0.00 Hz

$J_{1,2}$ = 6.51 Hz

$J_{1,3}$ = 0.00 Hz

$J_{2,3}$ = 8.82 Hz

Error of input data point = 0.02 Hz

Since, the bond order, $P_{\delta,\epsilon}$, and the vicinal coupling constant, ${}^3J_{\delta,\epsilon}$, for benzenoid hydrocarbons are related by the expression[47]

$$P_{\delta,\epsilon} = 0.104({}^3J_{\delta,\epsilon}) - 0.120 \quad \ldots\ldots\ldots \quad (1)$$

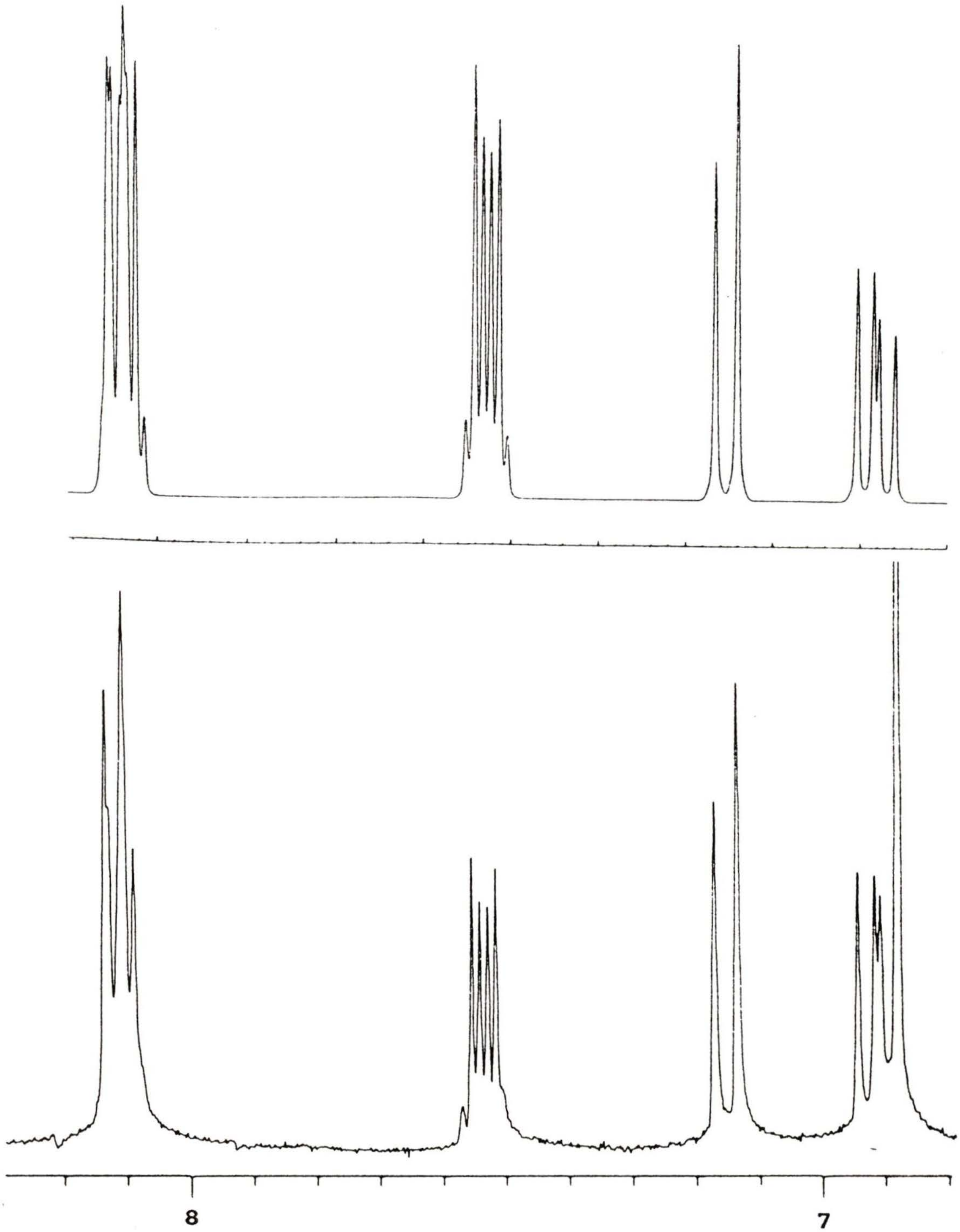


Fig. 2 : a) Simulated and b) observed ^1H NMR (250 MHz) spectrum of **25** in THF-d_8.

the four coupling constants for **25**, yielded four estimated bond orders (labelled a to d), given below in Table 4. As can be seen, there is good general agreement between the two sets of bond orders, with the exception of bond d. A steric compression correction of 0.08 Hz and 0.30 Hz, respectively, has been applied (Figure 3) to 1,8-naphthalene- and 4,5-phenanthrene-type interactions.[48] Only the bond orders of significance for the calculation of the chemical shift are given in Table 5. Due to the symmetry of the molecule all the bonds with the exception of bond 4-5 appear twice in the calculation. Though four bond orders were calculated from the NMR data, only two, *viz.*, those for bonds 1-2 and 2-3 are of use here. The rest of the values are obtained from π-SCF calculations.[26] Table 5 presents the bond orders (P_{μ} x 10^3), for the molecule **25.** The sum of the moduli of the deviations (ΔP_{μ}) of bond order from the "ideal" or perfectly delocalized Hückel bond order value for a [14]annulene[47] of 0.642 is given for the macroring of **25** excluding only the naphthannelating ring-fused bond, i.e., 8b-14a. The exclusion of the bond common to both the 10π- and 14π-rings has been justified on the basis that both the annelating and annelated ring systems may have opposing ring currents, and may also introduce structural effects.[26] Thus, $\Delta P_{\mu} = \Sigma_m |(P_{\mu} - 642)|$, where m is the difference between the number of bonds in the perimeter of the macroring and the number

Table 4: Comparison of experimental and calculated bond orders

	Experimental			Theoretical[26]
Bond[A]	^3J (Hz)	$^3J_{corr.}$ (Hz)	$P_\mu \times 10^3$	$P_\mu \times 10^3$
a	6.81	6.81	588	577
b	8.41	8.33[B]	746	747
c	6.51	6.21[C]	526	528
d	8.82	8.74[B]	789	747

A: see page 38

B: naphthalene-type correction

C: phenanthrene-type correction

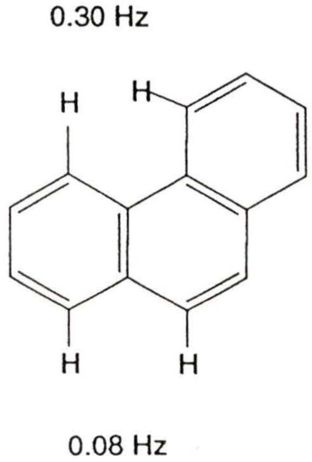


Figure 3: Phenanthrene- and naphthalene-type interactions and corrections[48] (to be subtracted from experimental coupling constants).

Table 5: Calculation of the chemical shift[26] incorporating bond orders derived from NMR data

Bond	$P_\mu \times 10^3$		
	π-SCF[26]	NMR	π-SCF/NMR
14a-14b	454	---	454
14b-1	767	---	767
1-2	528	526	526
2-3	747	789	789
3-3a	531	---	531
3a-4	734	---	734
4-5	546	---	546
$\Delta P_\mu = \Sigma_m \lvert P_\mu - 642 \rvert$	1566	526	1654
m	13	4	13
$\Delta P_\mu/m = \Delta r$	120.46	131.50	127.23
$\Delta\delta_{calc}$	2.22	1.91	2.03
$\delta_{calc} = 0.97 - \Delta\delta_{calc}$	-1.25	-0.94	-1.06

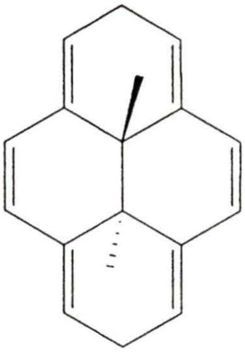
of annelating ring-fused bonds. The average deviation of bond order, Δr, is then calculated as the mean value of ΔP_μ, *i.e.*,

$$\Delta r = \Delta P_\mu/m \quad \ldots\ldots\ldots\ldots \quad (2)$$

This deviation, Δr, was plotted against $\Delta\delta$, where

$$\Delta\delta = \delta_{CH_3}(\mathbf{64}) - \delta_{CH_3}(\text{annulene}) = 0.97 - \delta \quad \ldots\ldots \quad (3)$$

i.e., $\Delta\delta$ is the shielding of the internal methyl protons of the annulene from those of the bis-triene **64**.[12]



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A least squares fit gave[26]

$$\Delta\delta_{calc} = 5.533 - 0.02752 \ \Delta r \quad \ldots\ldots\ldots \quad (4)$$

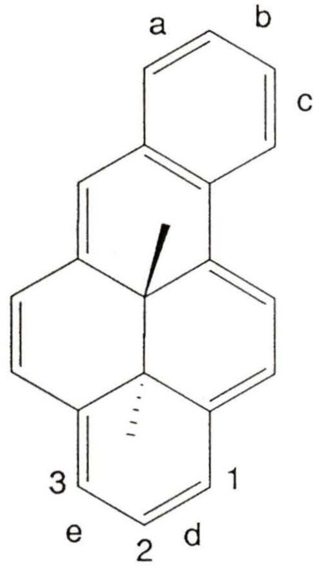
The chemical shifts obtained using either experimental, *i.e.*, bond orders derived from NMR alone or a combination of π-SCF and experimental bond orders give values which are quite comparable to that obtained from π-SCF calculations alone. However, it should be noted that both of these modified approaches do shift the calculated chemical shift in the direction of the experimental value of δ -0.74 in $CDCl_3$. Thus, an analysis of the coupling constants, and hence, bond orders, does not by itself provide us with an explanation of the difference observed between the two chemical shifts.

Earlier, a similar analysis of coupling constants and bond orders was carried out on benzo[e]DMDHP, **15** and benzo[a]DMDHP, **16**.[22,23] The results along with those for the title compound **25** and the parent **5** (for comparison) are given in Table 6. As can be seen, it is clear that even for the parent **5**, deviations of approximately 0.3 Hz between the calculated and experimental coupling constants are to be expected. Further, in all the three annelated cases, the worst correlation is found for bond d. This might be indicative of an unusual steric effect for H-1 in **16** and H-3 in **15** and **25** (see page 38), respectively. An examination of the dihedral angles obtained from molecular mechanics calculations[49] does indicate a difference between the parent and annelated examples. The results are given in Table 7. From the experimental data, *i.e.*, coupling constants obtained, one would expect the dihedral angles corresponding to the deviant protons, i.e., bond d (H-29, H-36 and H-41 in **15**, **16** and **25**, respectively, see page 40) to be significantly non-planar. However, molecular mechanics calculations indicate H-31, H-39 and H-38 in **15**, **25** and **16**, respectively (corresponding to bond c in **15** and **25**, and bond e in **16**) are found to deviate much more from planarity than anticipated. We are not at present able to explain the

Table 6: Calculated and experimental coupling constants

Bond Compound	a	b	c	d	e
16 (Benzo[a]DMDHP)[23]					
$^3J_{calcd.}$ (corr., Hz)	8.09	7.04	8.29	8.13	6.74
$^3J_{exptl.}$ (Hz)	7.96	6.75	8.21	8.86	6.54
ΔJ (Hz)	0.13	0.29	0.08	0.73	0.20
15 (Benzo[e]DMDHP)[22]					
$^3J_{calcd.}$ (corr., Hz)	7.09	8.25	6.74	8.24	--
$^3J_{exptl.}$ (Hz)	6.93	8.26	6.84	8.97	--
ΔJ (Hz)	0.16	0.01	0.10	0.73	--
25 (Naphtho[e]DMDHP)					
$^3J_{calcd.}$ (corr., Hz)	6.70	8.42	6.53	8.42	--
$^3J_{exptl.}$ (Hz)	6.81	8.41	6.51	8.82	--
ΔJ (Hz)	0.11	0.01	0.02	0.40	--
5 (DMDHP)					
$^3J_{calcd.}$ (corr., Hz)	--	--	7.46	7.38	--
$^3J_{exptl.}$ (Hz)	--	--	7.73	7.65	--
ΔJ (Hz)	--	--	0.27	0.27	--

Labelling Scheme



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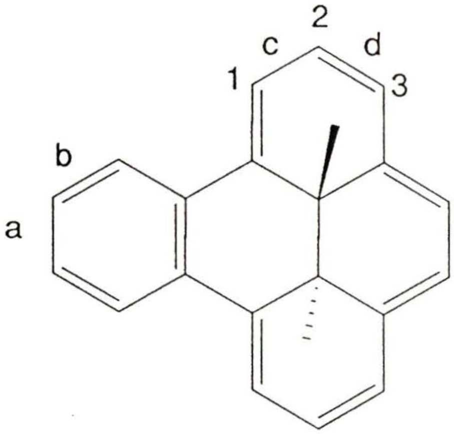

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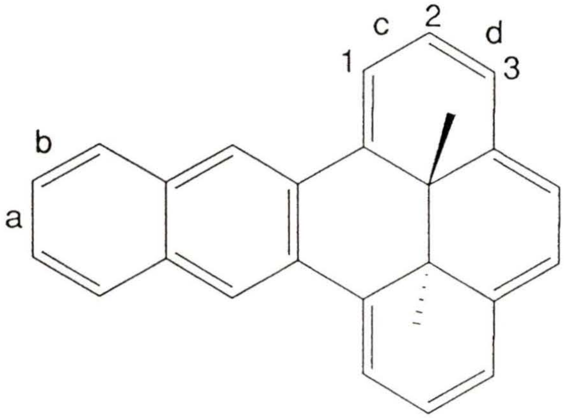

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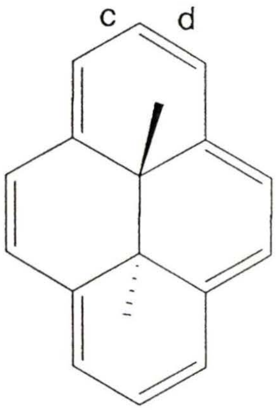

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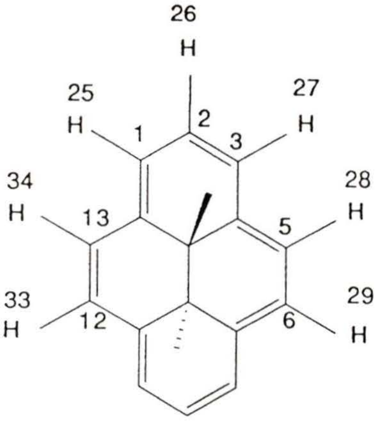
Table 7: Selected dihedral angles for **5, 15, 16** and **25**

Compound	Dihedral	Angle (deg.)
5	26,2,1,25	3.815
	26,2,3,27	-3.375
	3,4,5,28	5.000
	28,5,6,29	9.228
	34,13,12,33	-9.387
15	30,2,3,31	-7.952
	30,2,1,29	0.066
	1,18,17,40	-4.054
	4,5,6,32	8.736
	40,17,16,39	-13.825
	6,5,10,9	-14.010
16	37,13,14 38	6.511
	37,13,12,36	-1.831
	10,11,12,36	-10.475
	3,2,1,29	9.282
	3,2,7,6	-10.901
	34,9,10,35	12.796
	39,16,17,40	-4.505

25	40,13,12,39	7.315
	40,13,14,41	-1.024
	14,15,16,42	2.247
	11,1,2,33	-2.533
	42,16,17,43	14.025
	2,1,6,5	6.463

Labelling Scheme



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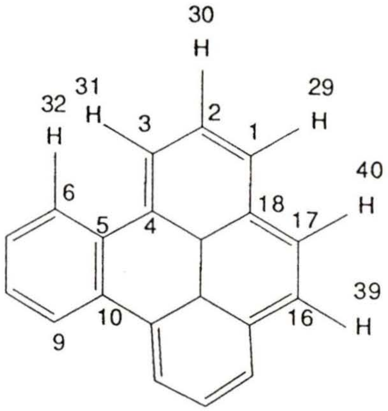

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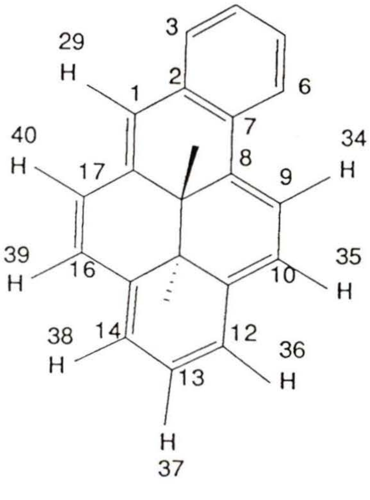

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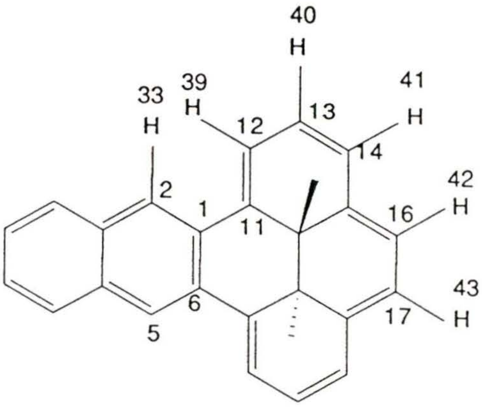

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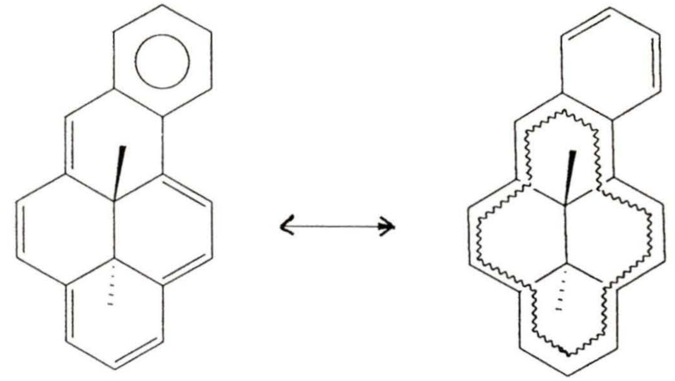
difference in the angles and their relation to chemical shift. In order to further study this effect, an X-ray crystallographic investigation will be undertaken shortly. In this direction, the crystal structure of the parent dihydropyrene **5** has been recently obtained.[50]

An attempt was made to predict the chemical shift of the internal methyl protons of **25** by correlating the change in resonance energies (RE) when a delocalized aromatic moiety is fused onto a dihydropyrene (DHP) with the change in shielding of the DHP's methyl protons. For the 14π-system to fully delocalize in **16** (or **15**), the delocalization of the benzene must be interrupted, leaving only a *cis*-butadiene residual. The loss of RE is approximately that of a benzene. By analogy, for the dibenzannelated analogue **18**, the loss of RE is twice that of **16**. For the naphth-fused example **21**, a styrene is left when the 14π-system delocalizes. Here, the loss of RE approximates to the difference between those of naphthalene and styrene, *i.e.*, 0.47 eV. The RE's of the various residuals are given in Table 8.[51] The change in shielding, Δ, is defined as the difference in the chemical shift of the methyl protons of the reference compounds and the parent dihydropyrene **5**. The change in shielding of the model compounds, Δ, and the difference in RE between the annelating moiety and the residual fragment when the annelating bond participates



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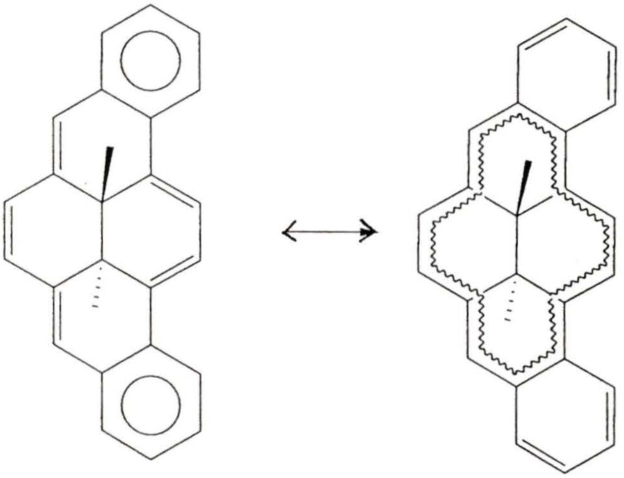

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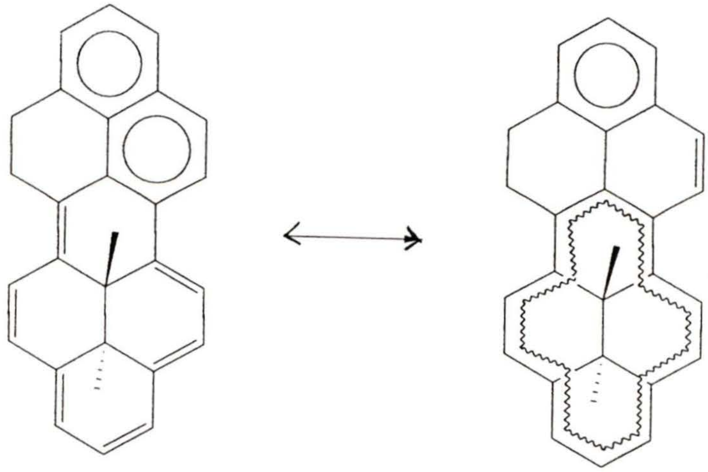

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Table 8: Resonance energies of various residuals[51]

Residual	RE (eV)
Benzene	0.869
Naphthalene	1.323
Phenanthrene	1.933
Styrene	0.858
s-*cis*-butadiene	0.034
$CH_2{=}C(CH{=}CH_2)_2$	-0.025

fully in the 14π-system, RE*, are presented in Table 9. A plot of the RE*'s of **5**, **15**, **18** and **21** *versus* the change in shielding, Δ, (Figure 4) yields a straight line of the form

$$\Delta = 2.5212\ \mathrm{RE}^* + 0.1630 \quad (\mathrm{c.c.} = 0.9962) \quad \ldots\ldots \ (5)$$

For compound **25**, the whole resonance energy of naphthalene is lost (leaving behind an *o*-quinodimethane residual) when the 14π-system delocalizes, and hence, RE* = 1.32 eV. This interpolates to a Δ value of 3.49, which translates to δ - 0.76 for the internal methyl protons of **25**, which is in excellent agreement with the experimental value of δ -0.74.

When **16** is used instead of **15**, a slightly different relationship is obtained:

Table 9: RE*'s and the change in shielding of the model compounds

Compound	RE* (eV)	$\Delta = \lvert -4.25 - \delta \rvert$
5	0.000	0.00
15	0.835	2.40
18	1.670	4.27
21	0.465	1.47
16	0.835	2.65
17	0.000	0.67
25	1.323	3.51
65	1.323	3.81

$$\Delta = 2.5366\ \mathrm{RE}^* + 0.2141 \quad (\mathrm{c.c.} = 0.9905) \quad \ldots\ldots (6)$$

This yields a value of δ -0.68 for the internal methyl protons. The fact that the internal methyl protons of **15** and **16** appear 0.25 ppm apart with **15** being more shielded, should have its origin in anisotropy, since both are expected to experience the same ring current effect. By analogy, the latter value, *i.e.*, δ -0.68, should correspond to the chemical shift of the internal methyl protons of naphtho[a]DMDHP, **65**, which has been synthesized after the

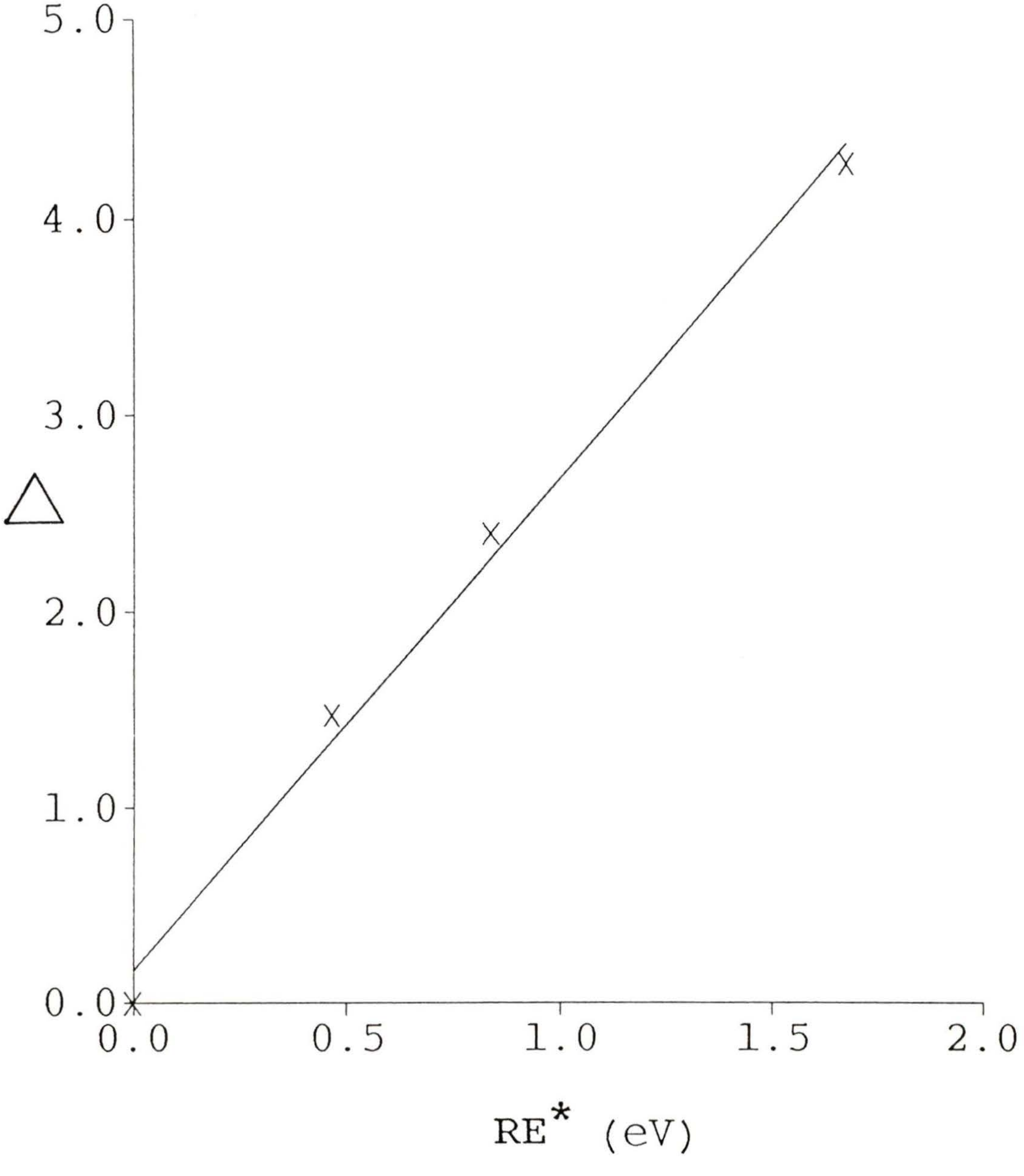
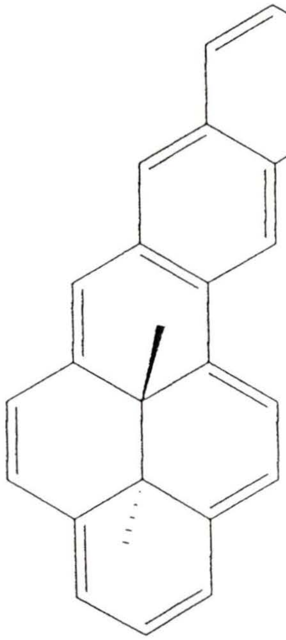


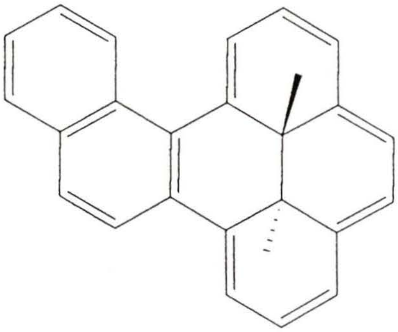
Figure 4 : Plot of RE* *versus* change in shielding, Δ

completion of this work by Zhou and Mitchell *via* an aryne route.[52] The internal methyl protons of **65** appear at δ -0.44, in good agreement with that predicted by equation (6). It is worth noting that the predictions for both **25** and **65** from these correlations have been shifted downfield by



65

approximately 0.5 to 0.6 ppm from the π-SCF predictions[26] of δ -1.25 and δ -1.28, respectively. The two other remaining mononaphthannelated isomers are **66** and **67**, of which the former is being synthesized by Peck and Lai.[53] The synthesis of **67** can be achieved in two steps from 2-formylDMDHP, **9**,[18] *via* a Wittig reaction,[54] followed by photocyclization.[55] Both **66** and **67** are similar to **21**, inasmuch as RE* = 0.47 eV, the difference in RE's between naphthalene and styrene. For **66** and **67**, equations (5) and (6) predict the chemical shifts of the internal methyl protons at δ -2.90 and δ -2.84, respectively, compared with δ -2.71 predicted by π-SCF calculations[26] for **66**. The presently available experimental data[22,23,52] for comparable sets of compounds, *e.g.*, the monobenzoDMDHP's **15** and **16**, and the mononaphthoDMDHP's **25** and **65** (both annelated along the 2,3-bond) indicate that of the two isomers, the one [e]-annelated is more diatropic and the chemical shifts differ by approximately 0.25 - 0.30 ppm. Though small, this effect can be explained as due in part to the higher symmetry of the [e]-isomer. Based on the above observations, between **66** and **67** (both annelated along the 1,2-bond), one would expect **66** to be the more diatropic. The chemical shifts of the internal methyl protons predicted by equations (5) and (6) are in agreement with this, though as noted above a slightly larger difference in the chemical shifts of the two isomers



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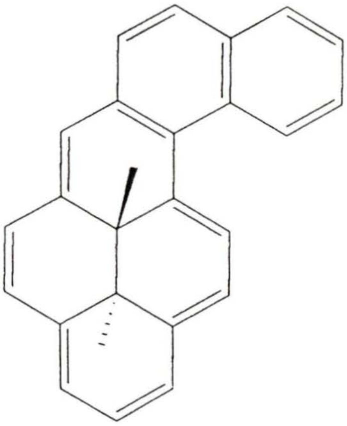
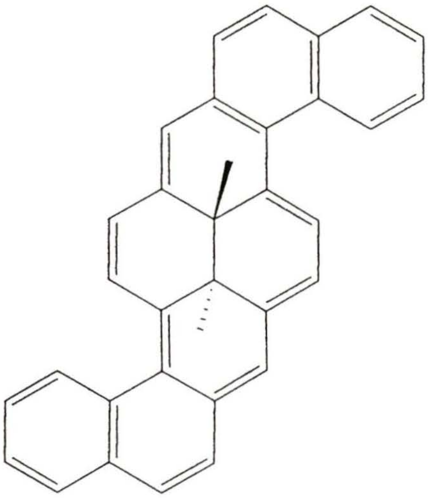


67

may be anticipated.

Starting from 2,7-diformylDMDHP,[20] **12**, the same synthetic sequence can be used for the synthesis of **68** and **69**, the naphtho-analogues of **17** and **18**. In the case of **69**, RE* = 0.93 eV, since two naphthalene moieties are lost when



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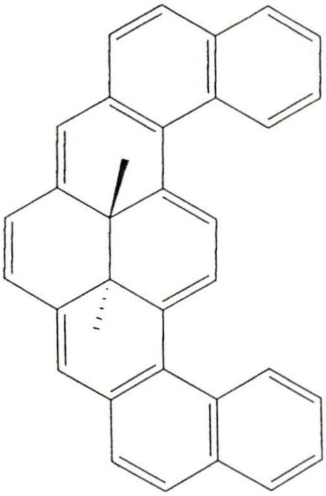
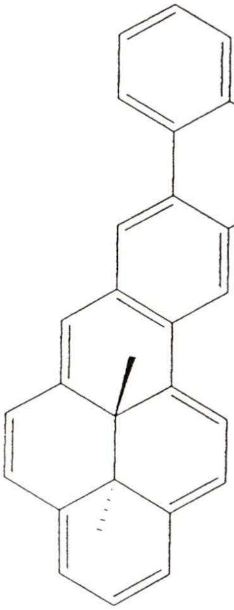


69

the 14π-system is preserved, with the generation of two styrene moieties. However, in the case of **68**, in either of the two possible resonance structures, one of the two naphthalene moieties is always intact, and hence, RE* = 0.47 eV. Using equation (6) which is more appropriate for [a]-annelation (as well as [b]-, [h]- and [i]-annelation), yields Δ values of 1.34 and 2.47, which translate to δ -2.91 and δ -1.78, respectively, for the internal methyl protons of **68** and **69**. This compares favourably with values of δ -3.64 and δ -1.17, respectively, for **68** and **69**, predicted from π-SCF calculations.[26] The synthesis of compounds **66 - 69** should serve to verify the above predictions.

Finally, Zhou[52] has very recently synthesized one of two possible isomeric (out of a possible seven) phenanthro[a]DMDHP's, **70** or **71**, *via* an aryne route. In the case of both **70** and **71**, RE^* = 1.09 eV, being the difference in RE's between phenanthrene and the two residuals -- benzene and $CH_2=C(CH=CH_2)_2$. This leads to a prediction for the internal methyl protons of δ -1.27 using equation (6). This compares favourably with the experimentally observed shift of δ -0.88.



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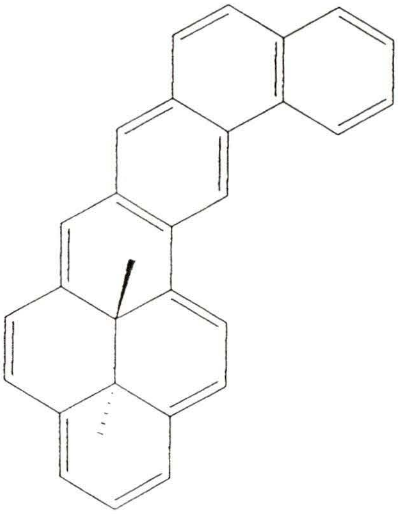

71

In conclusion, this approach seems to give us the best theoretical prediction for **25**, as well as giving reasonably good predictions for **65** and **70/71**. Using the experimental data available for **5**, **15**, **16**, **17**, **18**, **21**, **25** and **65**, we have derived a general correlation for future use:

$$\Delta = 2.4355\ \mathrm{RE}^{*} + 0.3835 \quad (\mathrm{c.c.} = 0.9887) \quad \ldots\ldots \quad (7)$$

What makes this method particularly attractive, is its apparent simplicity as a pencil-and-paper method.

2.4 ^{1}H NMR Spectrum of 25

The ^{1}H NMR spectrum of **25** has been predicted by Vogler by means of semiempirical quantum chemical procedures.[56] The predicted chemical shifts of the external protons and those observed in $CDCl_3$, THF-d_8 and C_6D_6 are presented in Table 10. As can be seen, the same general trend is observed in all three solvents. However, due to the overlap of signals from H-2,7 and H-4,5 in all three solvents and H-1,8 and H-10,13 in the case of THF-d_8 alone, some of the predicted orders appear reversed due to the approximations involved. The only deviation from Vogler's predictions (in terms of the order in which the protons appear downfield from TMS) involves the protons H-4,5. Whereas, H-2,7 are predicted to be the most shielded protons, H-4,5 are observed to be the most shielded. As can be seen from Table

7, H-4,5 deviate from the mean molecular plane to the extent of 14°, which is the largest observed for the protons affected by the inclusion of the bridge carbons. Earlier, Bartle *et al.*[57] have attributed a similar upfield shift of 0.4 ppm of a proton experiencing a phenanthrene-type interaction from a methyl group in 9,10-dimethyl-1,2-benzanthracene, **72**, to a deviation from planarity, which diminishes the ring current, which in turn, makes the protons concerned less deshielded. It is worth noting that the order predicted by Vogler[56] for the benzo[e]-analogue **15** is identical to that predicted for the title compound **25**. However, in the the case of **15**, the order of the signals for H-3,6 and H-4,5 appear reversed, with the latter being more shielded.

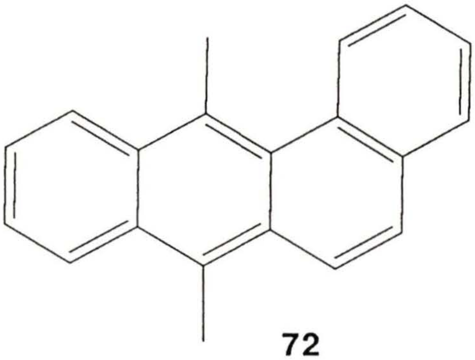

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Table 10: Predicted and observed chemical shifts of **25** in various solvents

Protons[a]	Predicted shifts (δ)[56]	Chemical shifts (δ) in CDCl$_3$	THF-d_8	C_6D_6
2,7	7.06	6.89[b]	6.91[b]	6.71[b]
3,6	7.09	7.13	7.15	7.03
4,5	7.19	6.85	6.88	6.72
11,12	7.54	7.54	7.55	7.41
1,8	7.72	8.02	8.12[c]	7.72
10,13	7.86	8.07	8.11	7.94
9,14	9.02	9.09	9.21	8.94

[a] See page 30

[b] Signals overlapped with those from H-4,5

[c] Signals overlapped with those from H-10,13

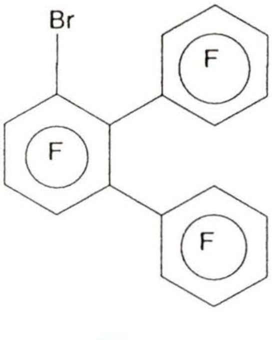
CHAPTER THREE

PROPERTIES OF THE TERARYLS

3.1 X-ray structure of the teraryl 31

As mentioned in Section 2.1, the ^{13}C NMR spectrum of the teraryl **31** exhibits more than the 11 lines expected on the basis of symmetry in the aromatic region. Also, **31** was inert towards efforts at metallation with *n*-BuLi (Section 2.2). The above observations along with the fact that there has been no direct structural evidence hitherto, for the presence of *syn*- and *anti*-conformers in such systems prompted us to undertake an X-ray structural determination of **31**.

A survey of the literature revealed that only three compounds which were either an *o*-terphenyl or an *o*-teraryl derivative had been characterized by X-ray structural determination: 1-bromo-4,5,6-trifluoro-2,3-bis(pentafluorophenyl)benzene,[58] **73**, perchloro-1,2,3-triphenylnaphthalene,[59] **74**, and perchloro-*o*-terphenyl,[60] **75**. However, in all three cases, since, the substituents on the



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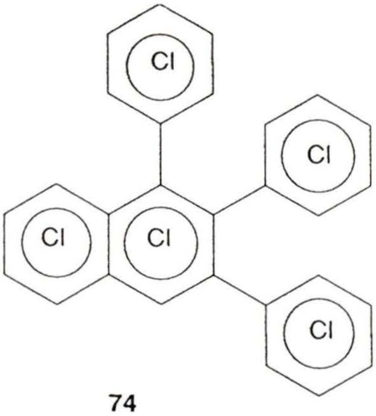

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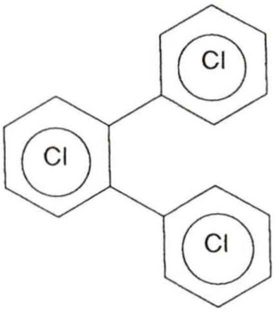
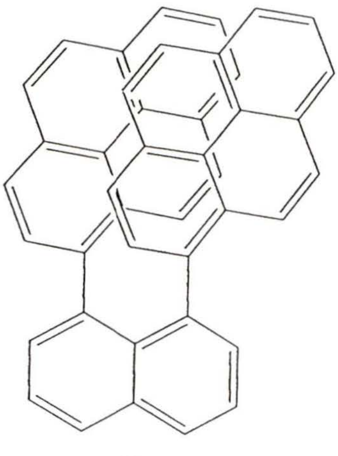


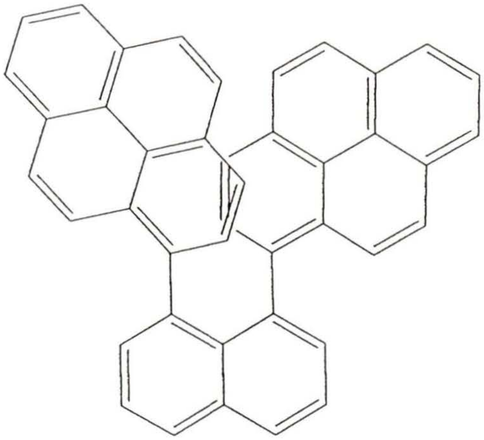
75

phenyl rings are the same, there is no possibility of the existence of *syn*- and *anti*-forms.

The closest related system for which the X-ray structure had been determined was *peri*-dipyrenylnaphthalene, **76.**[61] In the case of 1,8-di(1-pyrenyl)naphthalene, two stereoisomers with different extents of overlap of the pyrene units, corresponding to the *syn*- and *anti*-conformers, were studied. In the *syn*-conformer, one of the pyrene rings



76a



76b

is perpendicular to the naphthalene rings, while the other is nearly so (85°), whereas, in the *anti*-conformer, both the rings are at 75° to the plane of the naphthalene ring.

In agreement with the observations in solution that more than one conformer was present, the X-ray structure of the teraryl **31** shows that in the solid state, both the *syn*- and *anti*-conformers are present (Figures 5 and 6). However, the disorder in the crystal is such that the structure could not be refined beyond 9.8%, and hence, reliable bond angles and distances are not available. The crystal data is collected in Table 11. In the case of *syn*-**31**, the tolyl rings are at 87° and 106°, respectively, to the plane of the naphthalene ring, while those for *anti*-**31** are 88° and 98°, respectively. Thus, in both the conformers of **31**, one of the rings is almost perpendicular to the naphthalene ring, while the other deviates from orthogonality by approximately 8° and 16°, respectively, in the case of *anti*- and *syn*-**31**.

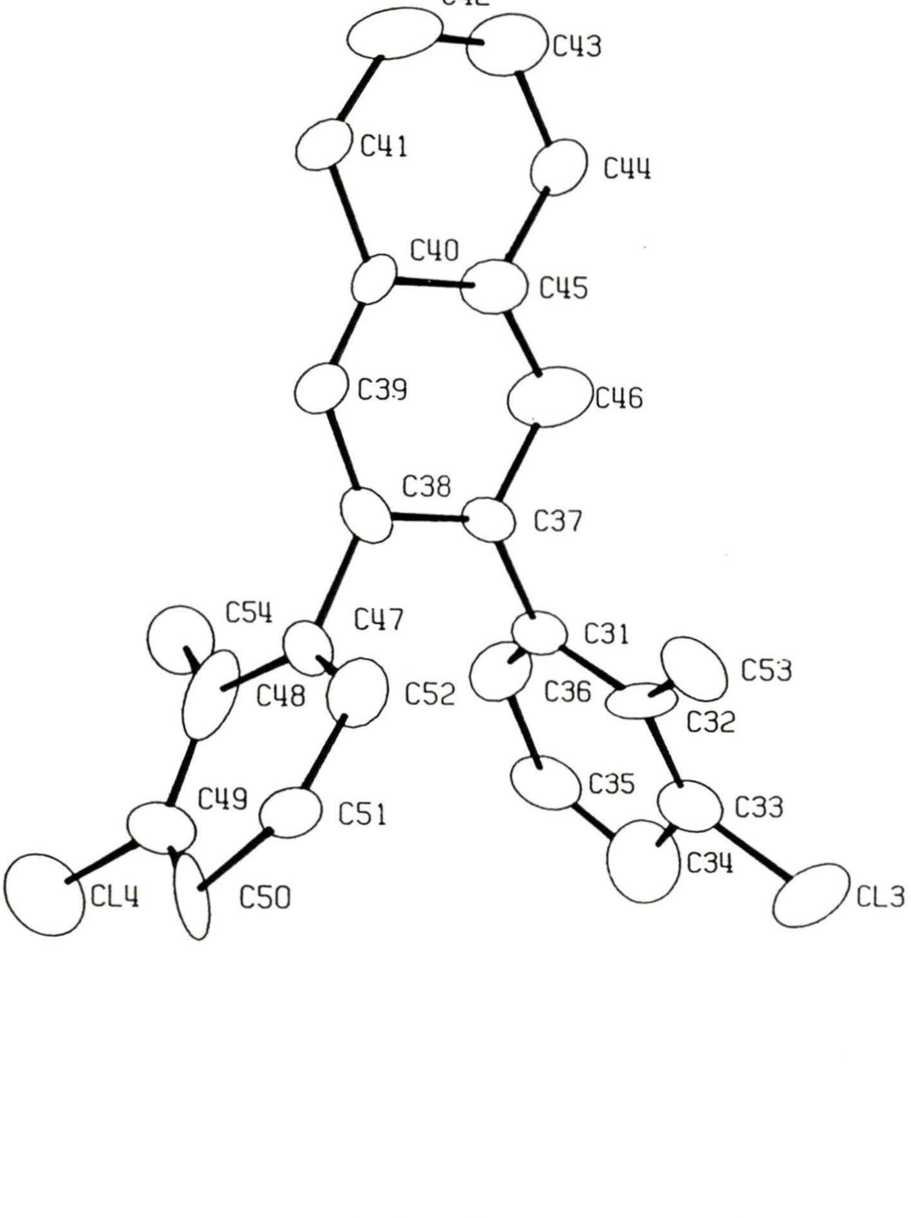


Figure 5: ORTEP diagram of *anti*-**31**

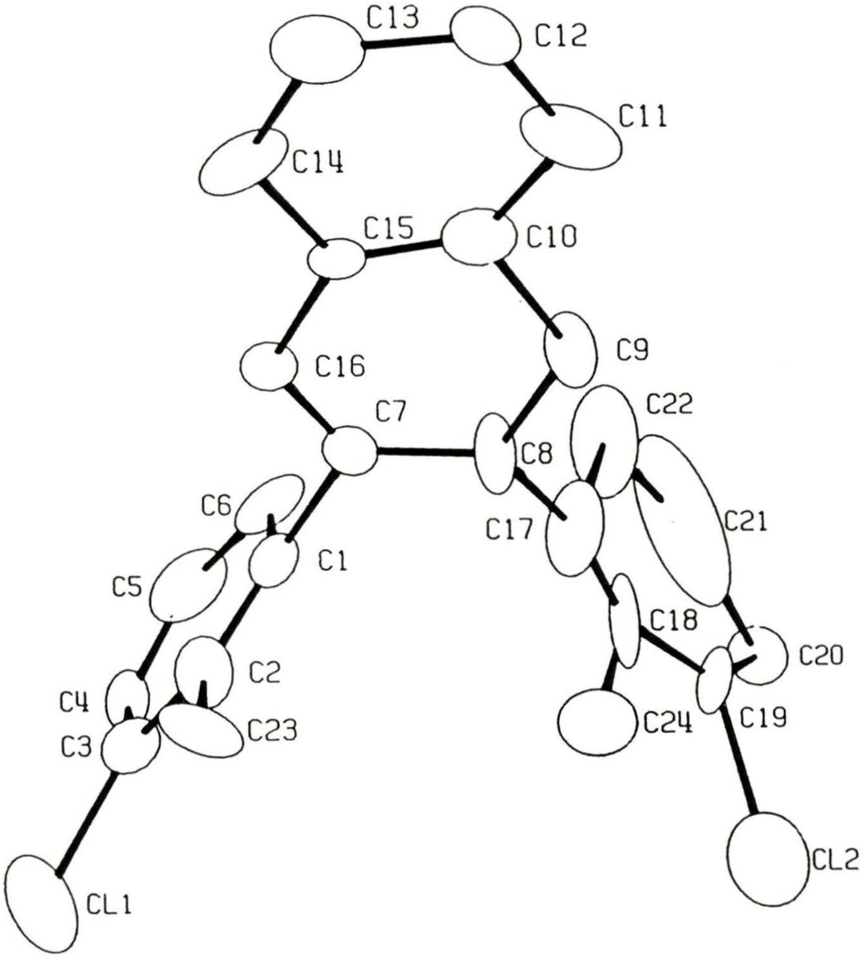


Figure 6: ORTEP diagram of *syn*-**31**

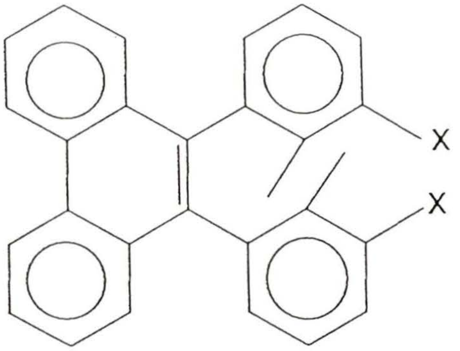
Table 11: Crystal data for **31**

2,3-bis(3-chloro-2-methylphenyl)naphthalene	$C_{24}H_{18}Cl_2$
Monoclinic, non-centrosymmetric	Mol. wt. 377.3
Space group *Pc*	$Z = 4$
$a = 10.152(2)$ Å	$\rho_{meas.} = 1.295$ g cm^{-3}
$b = 24.873(6)$ Å	$\rho_{calc.} = 1.305$ g cm^{-3}
$c = 7.603(1)$ Å	$R = 0.098$ (1741 data points, not converged due to disorder)
$\beta = 90.99(2)°$	

3.2 The barrier to rotation in the dichloride 31 and the monochloride mononitrile 43 -- variable temperature ^{13}C and ^{1}H NMR studies

Recent interest in studying restricted rotation in strained systems such as polyarylbenzenes[62] and *peri*-disubstituted naphthalenes[63] has been largely due to the advances in instrumentation, especially NMR, coupled with the increasing number of compounds amenable to such study. In 1980, Mitchell and Yan[34] reported the barrier to rotation for a series of 2,2"-dimethyl-*o*-terphenyl derivatives to be in the range 69-75 kJ mol^{-1}. More recently, gas chromatographic work by Lai and co-workers on 9,10-di-*o*-tolylphenanthrene,[64] **77**, and 9,10-bis(2,3-dimethylphenyl)-

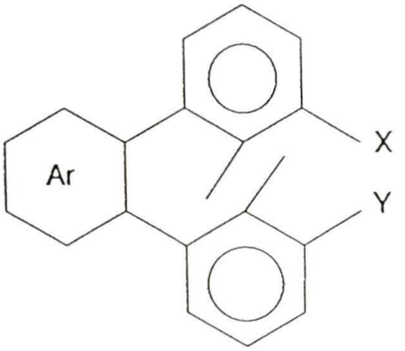
phenanthrene[65] **78**, have estimated the rotational barrier in these systems to lie in the range 115-158 kJ mol^{-1}.



77 X = H

78 X = Me

Since we had access to the teraryls **31** and **43** during the course of the synthesis of the title compound **25**, which are very closely related to the *o*-terphenyls **79** and **80**,[34] we



Compound	Arene	X	Y
31	Naphthalene	Cl	Cl
43	"	Cl	CN
79	Benzene	Cl	Cl
80	"	Cl	CN

decided to study their interconversion barriers. In the ^1H NMR spectrum of **31**, the internal methyl protons appear as a singlet. However, the methyl groups appear as two signals in the ^{13}C NMR spectrum. Hence, we decided to follow the rotational process by means of a ^{13}C NMR variable temperature (VT) experiment. In the case of **43**, it should be possible to get two estimates for the same process.

The data for **31** and **43**, along with that for the benzo-analogues **79** and **80** are collected in Table 12. In both cases, T_c was determined in DMSO-d_6 solutions and the low temperature separation, $\Delta\nu$, determined in $CDCl_3$ for **31** and in $CDCl_3$-CD_2Cl_2 (1:1 v/v) for **43**. As can be seen, the values of $\Delta G_c^\ddagger$ for **31** and **43** are higher by approximately 2 to 7 kJ mol^{-1}, compared to those for **79** and **80**. This can be explained, in part, as due to the increased interaction between the proton on the naphthalene ring suffering *peri*-interaction, *i.e.*, H-3'(8') and the methyl group protons, and consequently, a higher barrier. However, the two estimates for **43** vary by about 6 kJ mol^{-1}, and probably the higher value is more reliable due to a clearer T_c process. Also,

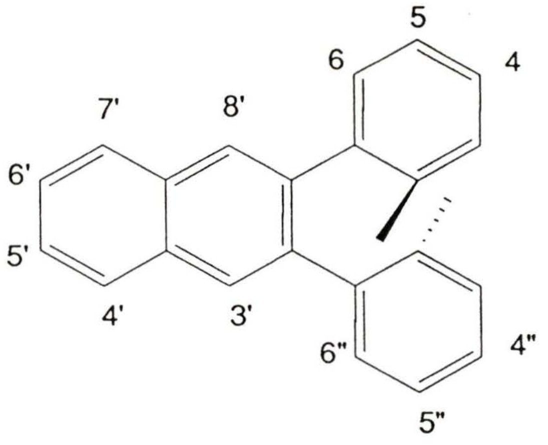


Table 12: Thermodynamic data for the barrier to rotation in **31**, **43**, **79** and **80**

Compound	X	Y	$\Delta\nu$ (Hz)	T_c (°C)	$\Delta G_c^{\ddagger}$ (kJ mol^{-1})
31	Cl	Cl	29 ± 2.5	86 ± 2	76.0 ± 0.7
79 [34]	Cl	Cl	7.1	58	73.7
43	Cl		3.8 ± 0.2	62 ± 2	76.4 ± 0.7
		CN	3.4 ± 0.3	36 ± 2	70.6 ± 0.8
80 [34]	Cl		8.0	42	69.7
		CN	7.1	38	69.1

this value is more closely in agreement with that obtained for the dichloride **31**. Thus, as would be expected, the naphthalene compounds **31** and **43**, have energy barriers similar to their benzo-analogues **79** and **80**, whereas, the phenanthrene derivatives seem to be much more strained in the rotational transition state as evidenced by the relatively very high barriers of upto 160 kJ mol^{-1}. This can be rationalized by considering the distances between the protons on the aromatic ring and the methyl group protons assuming ideal geometry, *i.e.*, sp^2 hybridization. It is evident from molecular models that in all three cases, the protons in question are closest in the planar conformation. In the case of the benzene and naphthalene compounds, the distance between the proton on the aromatic ring and the protons of the methyl group is approximately 0.9 Å, whereas for the phenanthrene system, this distance is less than the sum of the atomic radii, supporting our observations.

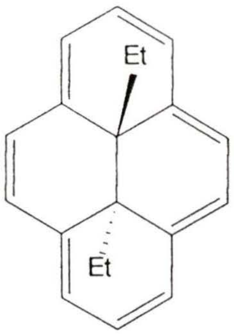
CHAPTER FOUR

PHOTOCHROMISM

4.1 Photochromism

Photochromism is the property of organic compounds to interconvert from a colourless form to a coloured one, or *vice versa*. The interconversion is induced in at least one direction by the action of electromagnetic radiation. If the change in one direction is thermally induced, it is usually spontaneous. The process has been well studied, especially over the last three decades. An example is the photochromism of *cis*-stilbenes to 4a,4b-dihydrophenanthrenes,[55,66] the latter being light yellow in colour.[67]

Earlier, Blattmann *et al.* have studied the photochromic interconversion of the parent DMDHP **5** with the cyclophanediene **88** and found it to be completely reversible and to follow first-order, temperature-dependent kinetics.[68] Subsequently, Blattmann and Schmidt investigated a series of substituted DMDHP's and found that all the derivatives investigated exhibited photochromism.[69] An exception in the dialkyl series is diethyldihydropyrene, **81**,[70] which on heating isomerizes to the corresponding diene **82**, but does not thermally revert back to the closed-form, *i.e.*, **81**. This change in energy relationships between the two isomers **81** and **82**, has been rationalized on the basis of the larger size of the ethyl group (compared to the methyl group in **5**), with the consequently greater steric interaction with the



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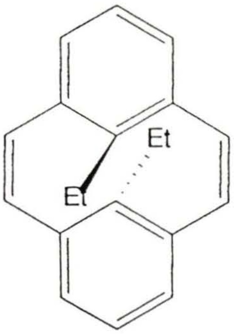
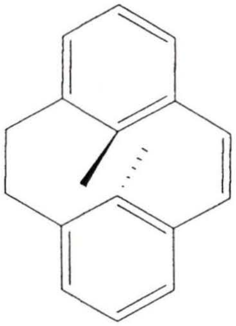


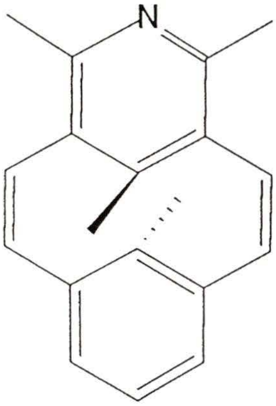
82

aromatic π-cloud being unfavourable.[70] Subsequently, Blattmann and Schmidt reported the photochemical conversion of **82** to **81.**[69] Thus, it seems that the diene **82** is more strained than any of the substituted dimethyl compounds. In 1970, Boekelheide and co-workers synthesized 8,16-dimethyl-[2.2]metacyclophane-1-ene, **83** as a precursor to **5.**[71] Like **5**, **83** was found to be photochromic.[72] The reversible photochemistry of **83** to the corresponding 4,5,15,16-tetrahydropyrene has also been studied by Naef and Fischer.[73] The above examples differ from simple stilbenes, since these contain rigidly constrained *cis*-stilbene moieties. The



83

photochromic behaviour of the azadihydropyrene system is interesting, since although the rate of closure of **84** by a dark reaction (conversion of diene to the respective dihydropyrene) is comparable to the corresponding hydrocarbons, the hydrochloride of **84** closes extremely rapidly at room temperature.[74] Closely related to **83**, and reported recently, are the syntheses[75] of **85 - 87**. Compounds **85 - 87** were found to be photochromic, with the rate of the thermal decolourization increasing by about a thousand-fold on increasing the number of methylene units in the saturated bridge by one. This has been attributed by the authors to increased molecular strain in the coloured species (closed-form) with resultant twist of the π-conjugated bonds.[76]



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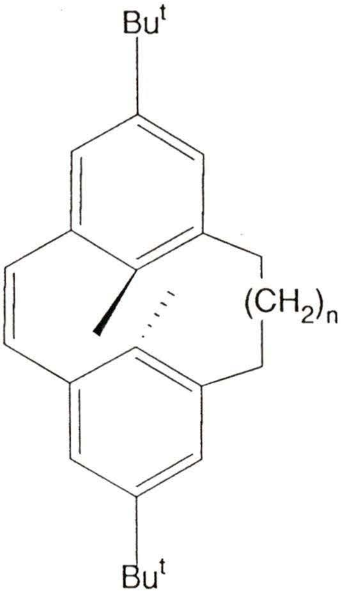


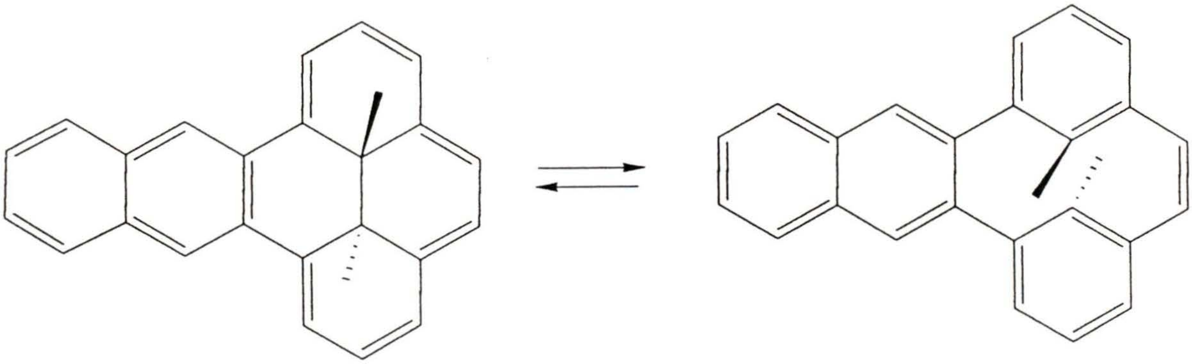
85 n = 0

86 n = 1

87 n = 2

More recently the emphasis seems to have shifted to application-oriented photochromic materials. In the early 1970's, a number of patents have been obtained utilizing the photochromic property of substituted dimethyldihydropyrenes.[77] The authors describe their applications as self-attenuating light valves in articles such as tinted safety glass and headlights for automobiles, in information retrieval apparatus devices and light meters. The potential for the utilization of photochromic compounds in energy storage[78] and optical information storage[79] has been discussed in the literature. The use of photofunctional crown ethers for ion extraction and ion transport has been reviewed by Shinkai and Manabe.[80] It has also been suggested that photochromic systems in general, might find engineering applications in relation to switch-functioned systems.[80] An entire volume has been devoted to a review of the subject.[81]

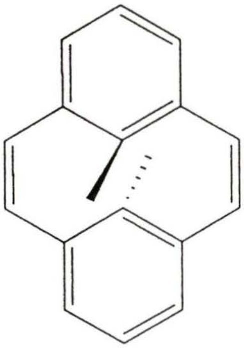
Like both the parent DMDHP **5** [68] and the benzo[e]-analogue **15**,[22] **25** exhibits photochromism as evidenced from the observation of repeated colourization-decolourization cycles. Solutions of **25** in cyclohexane are violet-purple (similar to aqueous solutions of $KMnO_4$), and decolourize quite rapidly to the cyclophanediene **28** (open-form) under a tungsten floodlight or under fluorescent light over a few hours. We find that solutions of **28** are indefinitely stable



25 **28**

at ambient conditions under fluorescent lighting, and **25** can be regenerated on demand in the presence of UV radiation.

The UV-VIS spectra of the DMDHP's **5**, **15** and **25**, are given in Figure 7, and those of the corresponding dienes, **88**, **89** and **28**, respectively, in Figure 8. A bathochromic shift is observed in the spectra of the DMDHP's in going from **5** to the benzo[e]- and naphtho[e]- compounds, **15** and **25**, respectively. A comparable series of 3,7,10,14-tetrasubstituted 1,8-didehydro[14]annulenes has been



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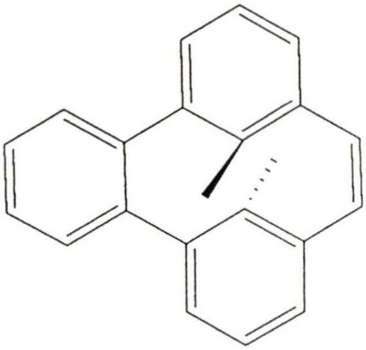

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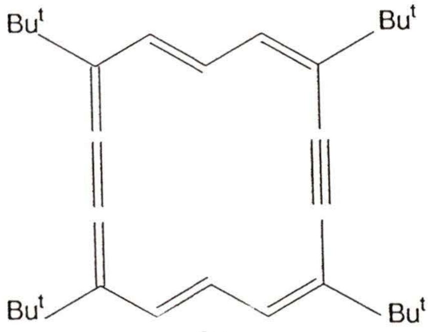
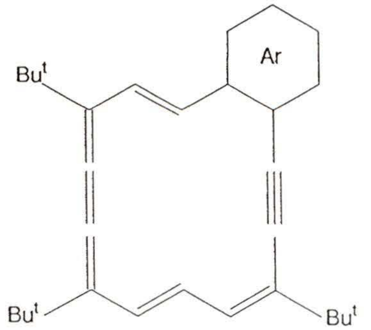
reported by Nakagawa's group during the 1970's. The synthesis and UV-VIS spectra of the parent tetra-*t*-butyl compound[82] **90** and that of the benzo-analogue, benzo[c]-

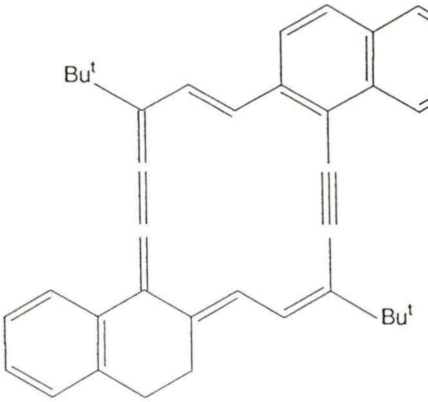


90

7,10,14-tri-*t*-butyl-1,8-didehydro[14]annulene[83] **91**, have been reported. Though the synthesis of the analogous naphtho-tri-*t*-butyldidehydro[14]annulene **92** has been reported,[84] its UV-VIS spectrum has not. However, we thought that we could substitute **92** by **93**,[85] for purposes of comparison of UV-VIS spectra, since the saturated ring should behave in much the same fashion as a *t*-butyl group.



Ar	
Benzene	91
Naphthalene	92



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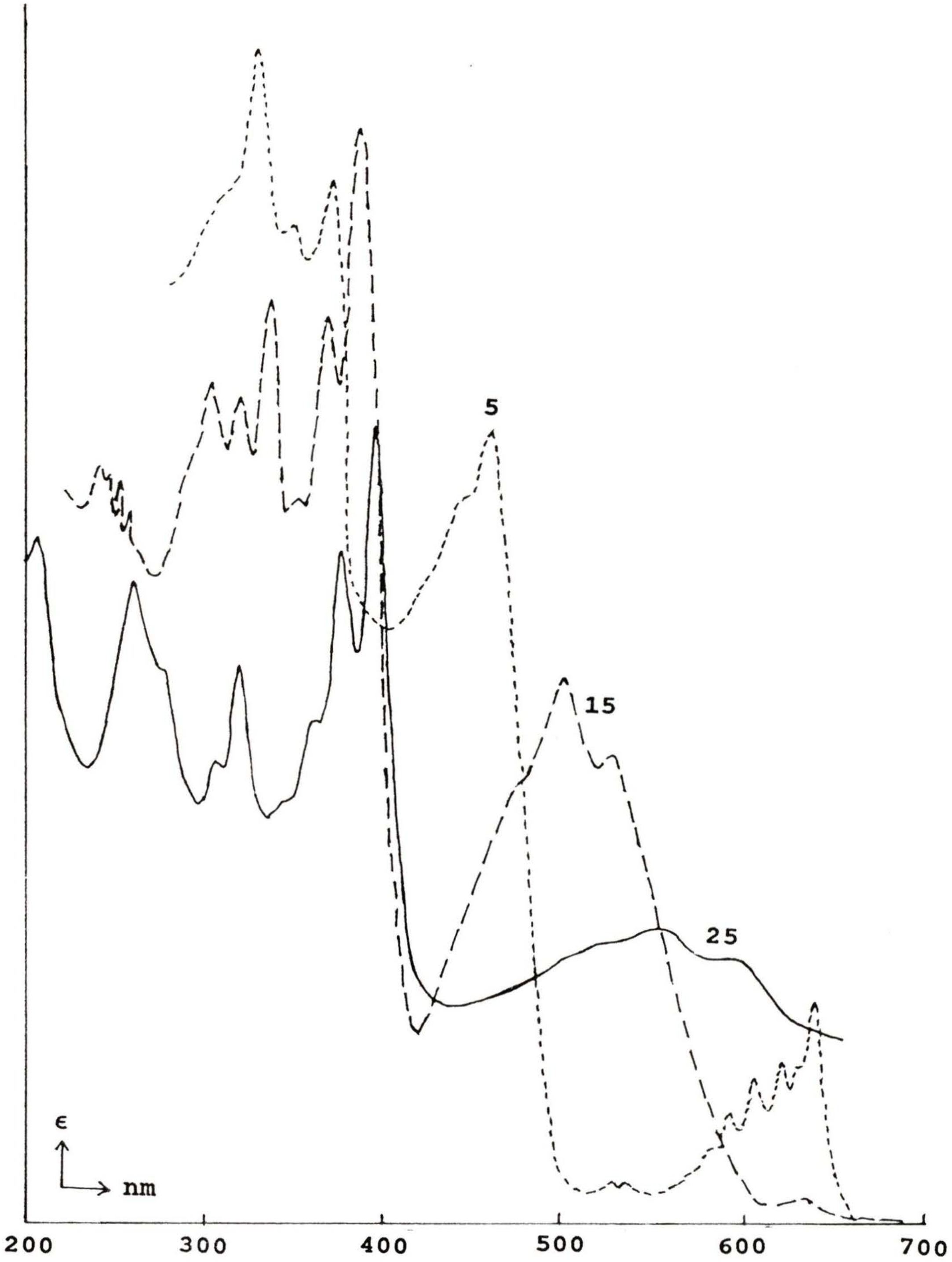


Figure 7 : UV-VIS Spectra of **5**, **15** and **25** in cyclohexane.

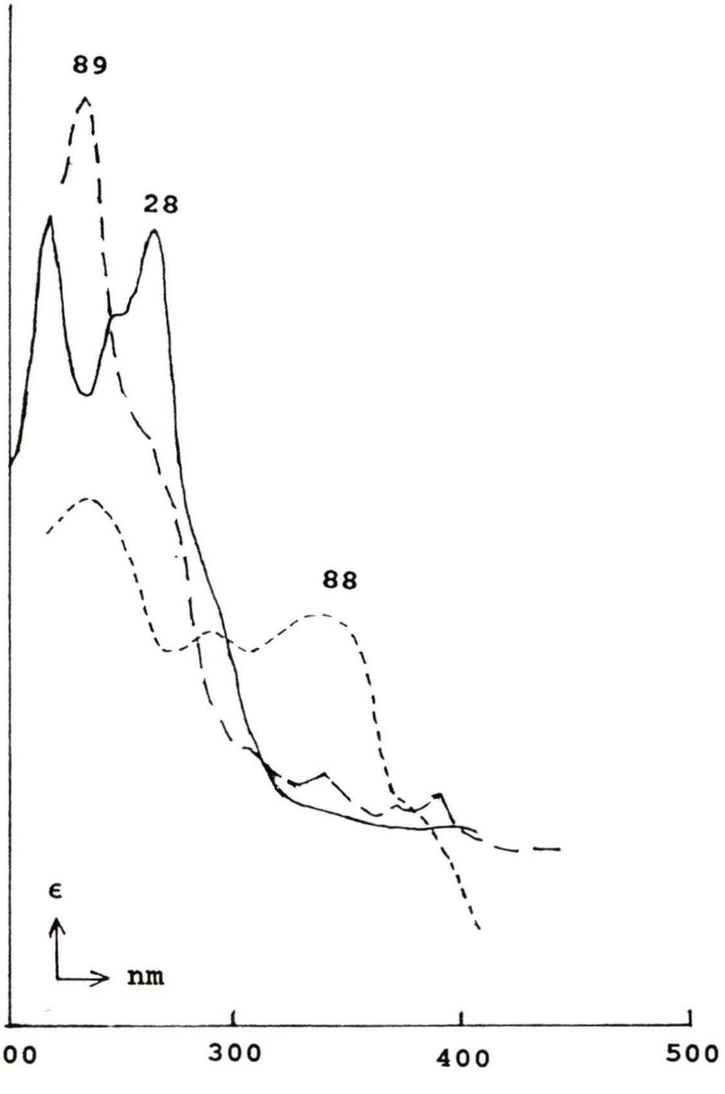


Figure 8 : UV-VIS Spectra of **88**, **89** and **28** in cyclohexane.

The UV-VIS spectra of **90, 91** and **93** are presented in Figure 9. Once again, a bathochromic shift similar to that of the DMDHP's (Figure 7) is observed. Earlier, the effect of annelation to cause a bathochromic shift to higher wavelengths has been noted.[86]

For a useful photochromic system, the prerequisites are high quantum yield, high reversibility and large structural change.[80] The interconversion between **25** and **28** is accompanied by a large structural change and as noted above is easily reversible, essentially to a photostationary equilibrium, in either direction. Thus, two of the three criteria being satisfied (the quantum yield not being measured for the purposes of this study), we decided to study the photochemical stability of **25** to assess its potential for use as a switch-type device. A degassed (freeze-thaw method) solution of **28** was subjected to 20 cycles of UV and visible light, a cycle consisting of 30 seconds of visible light followed by 20 seconds of UV light and the spectrum determined initially and at 5-cycle intervals. Monitoring the reaction at 399 nm, and using the absorbances relative to the initial spectrum as a measure of the extent of decomposition of **25**, we observed 28, 58, 76 and 83% decomposition at the end of 5, 10, 15 and 20 cycles, respectively. It was observed that even by the end of five and ten cycles, there was visually detectable loss in the

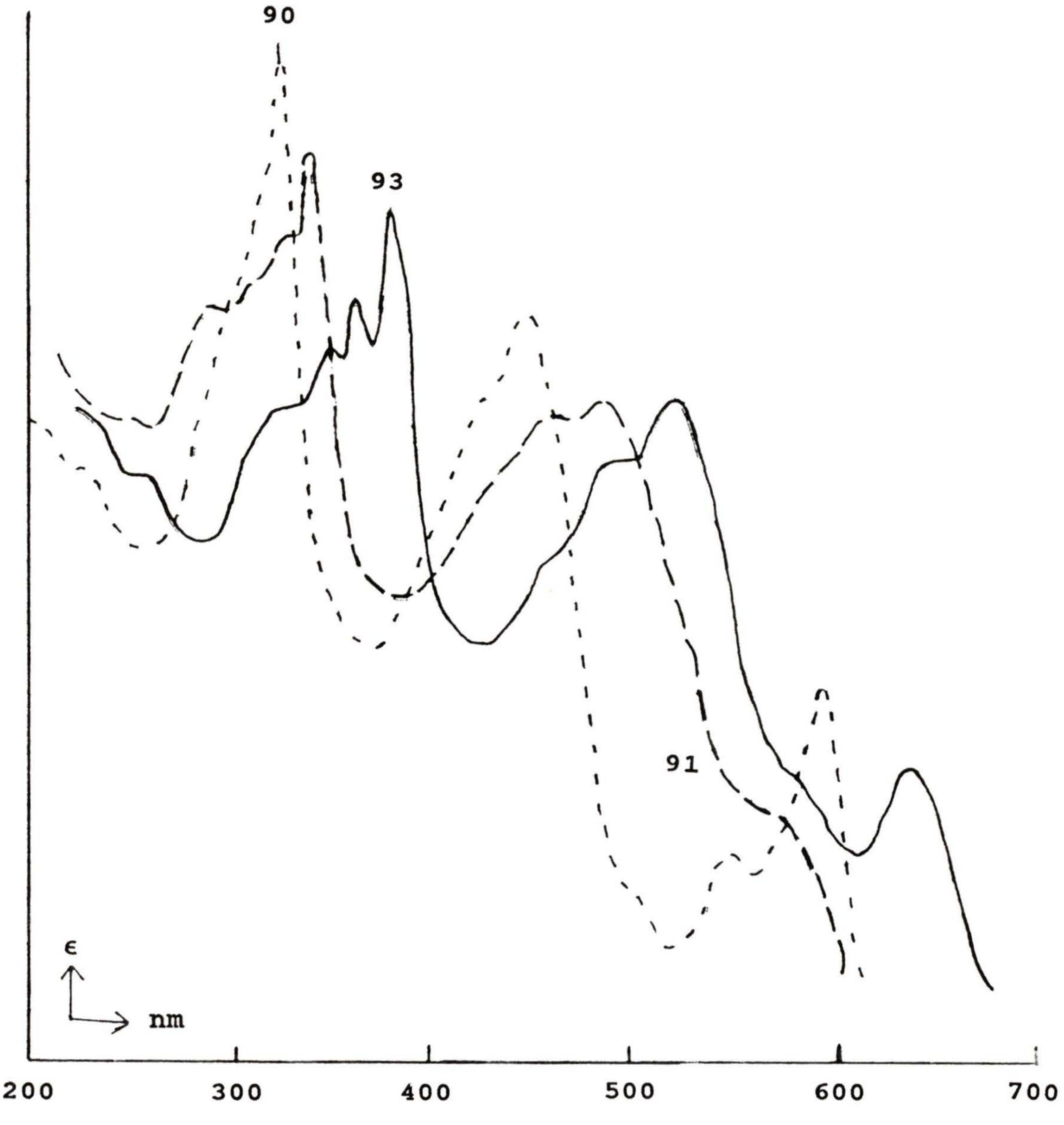
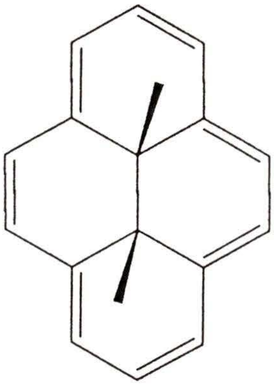


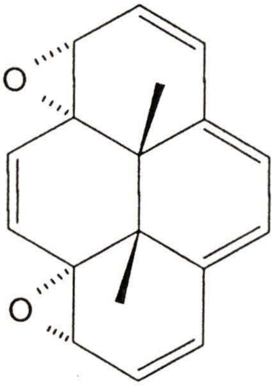
Figure 9 : UV-VIS Spectra of **90, 91** and **93** in THF-d_8.

intensity of the violet colour of the DMDHP **25** and that by the end of fifteen cycles, the solution had essentially decolourized. At this stage, the photodecomposition product seems to be essentially naphthalenoid, with the characteristic features of the DMDHP moiety being lost.

Another factor to be taken into consideration in such systems is their sensitivity to oxygen. Oxygen is known to add to *cis*-DMDHP, **94** to yield the bis(epoxide) **95**, though *trans*-DMDHP, **5**, is known to be inert under the same conditions, presumably due to steric hindrance by the two methyl groups in the case of **5**.[87] However, we thought that in the case of **25**, oxygen might add across the middle ring, in a fashion similar to that of anthracene, generating a benzene and a DMDHP moiety. Merely passing oxygen into a solution of **25** for a period of three minutes (the time required for the conversion of **94** to **95**)[87] produced no change whatsoever in the UV-VIS spectrum. Such a solution



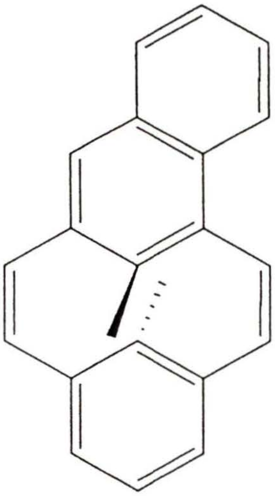
94



95

saturated with oxygen, when subjected to UV radiation (254 nm) for various periods of time, upto a total of a minute, showed virtually no change in either the intensities or characteristics of the spectrum. This information being very preliminary, it might be instructive to carry out similar studies in a cell sealed under vacuum, before drawing any conclusions as to the potential usefulness of **25** in switch-type devices.

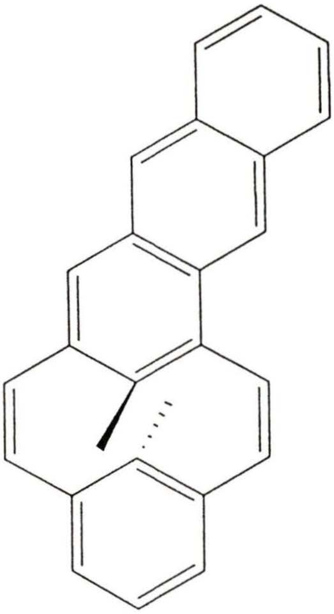
Finally attention is drawn to the effect that the position of annelation has on photochromic properties. Earlier, Mitchell and co-workers had reported that whereas the interconversion of benzo[e]DMDHP **15** to **89** was facile,[22] there was no evidence for any substantial (> 4%)[23] conversion of benzo[a]DMDHP **16** to **96**. This has been rationalized on the basis that the energy balance between disturbing the π-systems of the naphthalene and benzene



96

rings of **96** and forming the new π-system of **16**, the formation of the new sp^3-sp^3 bond, together with relief of strain in going from **96** to **16** is in favour of the formation of **16**.[22]

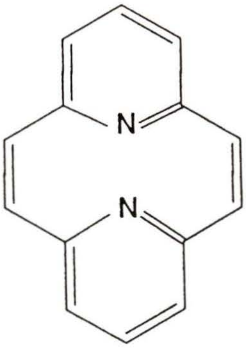
Similar observations are obtained for the naphthannelated compounds **25** and **65**. Naphtho[a]DMDHP, **65**, shows no tendency to interconvert with the corresponding cyclophanediene **97**,[52] whereas, the interconversion between the naphtho[e]-analogue **25** and **28** is facile. Thus, it is clear that the position of annelation is very significant in determining the photochromic properties in the DMDHP series, this probably being the only series where such an effect has been noted.



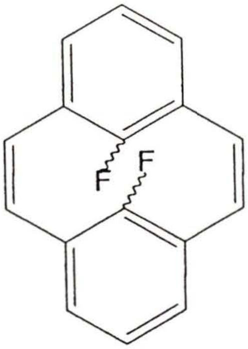
97

4.2 UV-VIS Spectroscopic determination of the barrier to the isomerization of 28 to 25

Blattmann and Schmidt[69] have studied the thermal conversion of a diene to the dihydropyrene for a number of derivatives of **5**. In all the cases studied, the process was found to be reversible and the closed form observed to be thermodynamically more stable. Though the closed form is commonly the more stable isomer, quite a few exceptions to this generalization are known. Boekelheide and Lawson[88] reported the synthesis of [2.2](2,6)pyridinophane-1,9-diene, **98**, which shows no tendency to convert to the corresponding dihydropyrene. Another exception is *anti*-8,16-difluoro-[2.2](1,3)cyclophane-1,9-diene, **99b**. The *anti*-isomer **99b** was reported by Boekelheide and Anderson in 1973 (then thought to be *syn*, **99a**), which on heating gave 1-fluoropyrene, presumably involving the *trans*-difluorodihydropyrene **100b**, as the transient intermediate.[89] A crystallographic investigation by Hanson,[90] showed the conformation to be *anti*, *i.e.*, **99b**. Authentic **99a** was synthesized by Bodwell,[91] and it does close to **100a**. Finally, among the exceptions is a series of dienes bridged by an one-atom bridge. Nakasuji *et al.*[92] have reported the synthesis of **101**, and Boekelheide and co-workers, the synthesis of **102** [93] and **103**.[94] Renfroe has also reported a hexasubstituted derivative of **101**.[95] Like **98** and **99b**,

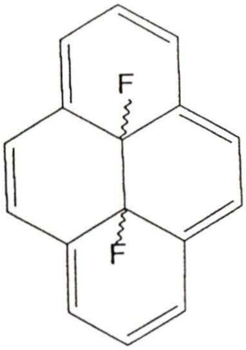


98



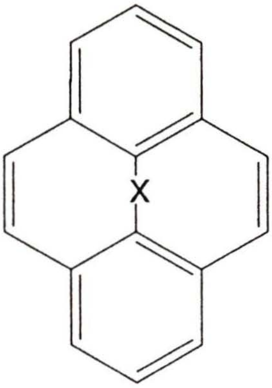
99

a syn / cis
b anti / trans



100

compounds **101** - **103**, prefer to remain as the respective dienes. However, in keeping with the general trend, in the case of both the parent DMDHP **5** and the benzo-analogue **15**, the closed form is the thermodynamically more stable isomer. This is also true of **25**, as evidenced by the fact that solutions of **28** left in the dark or heated, give a purple solution of **25**.



X	
CH_2	**101**
O	**102**
NH	**103**

Given the facility with which the two forms are interconvertible, we decided to determine the barrier to the isomerization of **28** to **25** by using UV-VIS spectroscopy.

Earlier, the barrier to the formation of **5** from the corresponding open-form compound **88**, has been determined by using UV-VIS spectroscopy.[69]

A solution of **25** was bleached repeatedly with tungsten light until there was no further change in the UV-VIS spectrum, and the solution left to equilibrate at the desired temperature. The solution was bleached just before the start of the kinetic run to ensure maximal conversion to the open-form compound **28**. The kinetics was followed at the absorption maximum at 399 nm and the data are compiled in Table 13. An Arrhenius plot (ln k *vs.* T^{-1}) yielded a slope of -12,673 K, from which the activation energy, E_a, is calculated to be 105.4 ± 1.5 kJ mol^{-1}, since the slope is equal to $-E_a/R$. This compares favourably with the values of 97 kJ mol^{-1} and 105 kJ mol^{-1}, for **5** [69] and **15**,[22,41] respectively. The fact that the E_a of **15** as determined by ^1H NMR spectroscopy and that of **25**, determined by UV-VIS spectroscopy are so similar is indeed striking. The similarity between the E_a values for **15** and **25** can be rationalized on the basis that the extra annelating ring in the case of **25** is not expected to add much to the existing strain in the case of **15**.

Table 13: Kinetic data for the conversion of **28** to **25**

$T(K)$	T^{-1} ($\times 10^3$ K^{-1})	k ($\times 10^6$ s^{-1})	$\ln k$
298.15	3.354	8.448 ± 0.05	-11.682
308.15	3.245	32.26 ± 0.50	-10.342
323.15	3.095	210.7 ± 2.0	-8.465
333.15	3.002	747.3 ± 7.0	-7.199

SUMMARY AND CONCLUSIONS

The synthesis of the title compound **25** has been achieved in 9 steps from 2,3-dibromonaphthalene, **37** in an overall yield of 3.9%. This represents the first synthesis of a naphthannelated DMDHP, with the DMDHP **25** being the more stable isomer compared with the corresponding cyclophanediene **28**.

An improved correlation has been devised for predicting the chemical shift(s) of the internal methyl protons of various DMDHP's, based on the change in RE when a delocalized aromatic moiety is fused onto a DMDHP with the change in shielding of the DMDHP`s methyl protons. The anisotropy introduced by [a]- or [e]-annelation can also be taken into account. The synthesis of compounds **66 - 69** are awaited to further test the validity of these correlations.

The X-ray structural determination of the teraryl **31** clearly demonstrates for the first time the existence of *syn*- and *anti*-conformers in the teraryl series, which had been postulated from solution studies. The barrier to rotation in the teraryls **31** and **43** have been determined by ^{13}C and ^{1}H VT NMR, respectively, and found to be slightly higher than that for the corresponding benzo-analogues.

Naphtho[e]DMDHP, **25**, is found to be photochromic like its benzo-analogue, **15**. A bathochromic shift is observed in going from the parent DMDHP **5** to **15** and **25**, similar to that observed in the benzene, naphthalene, anthracene series. The DMDHP **25** is found not to be overly sensitive towards oxygen, but undergoes decomposition during prolonged exposure to UV light. More studies, preferably in a cell sealed under vacuum are necessary before drawing any conclusions as to the potential usefulness of **25** in switch-type devices. In this regard, the effect that [e]-annelation has on photochromism has been noted.

The photoisomerization of **28** to **25** has been studied by UV-VIS spectroscopy and the activation barrier determined to be very similar to that observed in the case of the benzo-analogue **15**. This is as would be expected, since the extra annelating ring in the case of **25** is not expected to add much to the existing strain already present in the case of **15**.

EXPERIMENTAL

1 Instrumentation

All melting points were determined on a Reichert 7505 (Austria) melting point apparatus coupled to an Omega Engineering Model 199 chromel-alumel thermocouple and are uncorrected. Infrared spectra, calibrated with polystyrene, were recorded on a Perkin-Elmer 283 spectrophotometer as KBr discs. The observations are reported in wavenumbers (cm^{-1}). Unless otherwise mentioned, both ^1H NMR (250.1 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded in $CDCl_3$ solutions on a Bruker WM 250 instrument with TMS as the internal standard. Both electron impact (EI) and chemical ionization (CI, CH_4 carrier gas) mass spectra were recorded on a Finnigan 3300 mass spectrometer. Microanalysis were performed by Canadian Microanalytical Services Ltd. (Vancouver, B.C.). All evaporations were carried out under reduced pressure on a rotary evaporator. All organic layers were washed with water and dried over anhydrous sodium sulphate or potassium carbonate, as necessary. The X-ray structure determination was attempted by Dr. G. W. Bushnell and Kathy Beveridge. The proton numbering scheme for the teraryls is as shown in Section 3.2.

2 Preparation of Compounds

2.1 2,3-Dibromonaphthalene, 37

2,3-Dibromonaphthalene was prepared as described by Danish and co-workers[35] and purified following the method of Prill:[36]

To the residue after filtering off the excess HCCP was added 1.5 molar equivalents of maleic anhydride in toluene and refluxed for 17h. After cooling, the reaction mixture was washed repeatedly with aqueous NaOH and finally with water. The organic layer was dried and evaporated. The residue was then chromatographed over basic alumina using petroleum ether as eluant to give 85% of **37** as shiny white plates, m.p. 139-141°C (lit.[96] m.p. 140°C). IR, ^{1}H NMR data, and ^{13}C NMR data were in excellent agreement with those reported in the literature.[37,38] These were further supported by mass spectral data which had the correct isotopic pattern for the two bromine atoms and elemental analysis. The above procedure is suitable for preparing **37** in 100-gram quantities.

2.2 2,3-Bis(3-chloro-2-methylphenyl)naphthalene, 31

A solution of 2,6-dichlorotoluene (60.4 g, 48.2 mL, 0.375 mol) in dry THF (100 mL) was added dropwise over 1 h to a mixture of Mg turnings (9.12 g, 0.375 mol) , 1,2-

dibromoethane (1.5 mL, 17 mmol) and dried THF (200 mL) that had been gently warmed under N_2 in oven-dried glassware. The mixture was heated under reflux for 2-3 h until most of the Mg dissolved.

The Grignard reagent thus formed was cooled to room temperature and a solution of 2,3-dibromonaphthalene, **37** (32.0 g, 112 mmol) and Ni(acac)$_2$ (2.33 g, 9 mmol) in dried THF (400 mL) was added over 45 minutes. The reaction mixture was heated under reflux for 3 h.

The reaction mixture was cooled and the THF was evaporated. The residue was dissolved in diethyl ether (800 mL) and 3M HCl (100 mL) was added. The organic layer was washed with water (2 x 600 mL), dried and evaporated. The resulting brown oil was preadsorbed onto silica gel (50 g) and chromatographed over a column of silica using petroleum ether as the eluant to yield the product, **31**, 11.54 g (27%). A portion was recrystallized from DMSO to yield white needles, m.p. 155-156°C (lit.[43] m.p. 149-151°C, cyclohexane); ^{1}H NMR, δ, 7.89 (*AA'*XX', 2H, H-4',7'), 7.78 (d, J = 7.5 Hz, 2H, H-6,6"), 7.56 (AA'*XX'*, 2H, H-5',6'), 7.25 (m, 2H, Ar*H*), 7.00 (m, 4H, Ar*H*), 2.15 (s, 6H, -CH_3); ^{13}C NMR, (see text for VT experiment), ppm, 142.6, 142.1, 138.7, 138.4, 135.0, 134.7, 134.2, 132.5, 132.3 (quarternary aromatic *C*), 129.9, 129.7, 129.2, 128.3, 128.1, 128.0, 127.7, 126.5, 125.8, 125.5 (aromatic secondary *C*), 18.4, 17.9 (-CH_3); IR (cm^{-1}), 1546 (s), 1462 (m), 1419 (s,br), 1365 (m), 1317 (m), 1175 (m), 1140 (m), 1124(m), 1065 (m), 1046 (s), 1013 (s), 993 (s), 950 (m), 889 (s), 883 (s), 795(s), 785 (s), 775 (s), 750(s), 743(s), 715 (s), 707 (s), 596 (m), 472 (s); MS, CI, *m/e* (relative intensity), 377 (100, M + 1, $C_{24}H_{18}{}^{35}Cl_2$, correct isotopic pattern), 405 (27, M + 29), 417 (12, M + 41); EI, 376 (100, $M^{+\cdot}$).

Analysis Calcd. for $C_{24}H_{18}Cl_2$: C 76.40, H 4.81.
Found: C 76.29, H 4.86.

Eluted subsequently was the rearranged product, 1-chloro-11H-benzo[b]fluorene, **42**, 0.27 g (1%), obtained as white crystals from $CHCl_3$, m.p. 198-200°C; ^1H NMR, δ, 8.16 (s, 1H, Ar*H*), 7.87 (m, 4H, Ar*H*), 7.40 (m, 4H, Ar*H*), 4.07 (s, 2H, -CH_2-); ^{13}C NMR, ppm, 143.0, 141.8, 140.2, 139.9, 133.4, 132.9, 131.4 (quarternary aromatic *C*), 128.6, 128.2, 127.9, 127.3, 125.7, 125.6, 123.5, 118.8, 118.5 (aromatic secondary *C*) and 36.0 (-CH_2); IR (cm^{-1}), 1553 (w, br), 1483 (w), 1451 (m), 1446 (4), 1421 (m), 1392 (w, br), 1325 (w), 1305 (w), 1180 (w), 1158 (m), 1127 (w,br), 1103 (w), 992 (m), 943 (m), 891 (w), 862 (s), 825 (m), 815 (m), 775 (s), 735 (s), 717 (s), 572 (w), 470 (m); MS, CI, *m/e* (relative intensity), 251 (100, M + 1, $C_{17}H_{11}{}^{35}Cl$), 279 (24, M + 29), 291 (5, M + 41); EI, 250 (42, $M^{+\cdot}$, $C_{17}H_{11}{}^{35}Cl$), 252 (13, $M^{+\cdot}$, $C_{17}H_{11}{}^{37}Cl$), 215 (100, M - ^{35}Cl/M - ^{37}Cl).

<u>Analysis</u> Calcd. for $C_{17}H_{11}Cl$: C 81.44, H 4.42.
Found: C 81.45, H 4.48.

2.3 2,3-Bis(3-cyano-2-methylphenyl)naphthalene, 44

A mixture of 3,3'-dichloro-2,2'-dimethyl-*o*-terphenyl, **31** (7.25 g, 19 mmol), cuprous cyanide (4.56 g, 51 mmol) and NMP (100 mL) was refluxed for 8 hours. Two additional portions of CuCN (each 4.56 g) were added at 8 h intervals.

The reaction mixture was then cooled to *ca.* 100°C and poured onto ice (200 g) and ammonium hydroxide (≈30%, 800 mL). After mixing thoroughly, the mixture was filtered and the residue washed well with dilute NH_4OH and was then air-dried. The precipitate thus obtained was extracted with CH_2Cl_2 for 18 h using a Soxhlet extractor. The solvent was evaporated to yield a brown oil which was preadsorbed onto silica gel and chromatographed over a column of silica gel using petroleum ether/CH_2Cl_2 mixtures as the eluant.

Eluted first with petroleum ether, was the starting material, **31**, 0.5 g (7%). With petroleum ether/CH_2Cl_2 (7:3) was eluted 2-(3-chloro-2-methylphenyl)-3-(3-cyano-2-methylphenyl)naphthalene, **43**, 0.3 g (4%). A portion was recrystallized from ethanol as white crystals, m.p. 161-163°C; ^{1}H NMR, δ, 7.88 (*AA'*XX', 2H, H-4',7'), 7.75 (t, J = 7.92 Hz, 2H, H-5,5"), 7.56 (AA'*XX'*, 2H, H-5',6'), 7.47

(dd, J = 0.03 Hz, J = 0.01 Hz, 1H, Ar*H*), 7.25(m, 2H, Ar*H*), 7.12 (m, 1H, Ar*H*), 6.95 (m, 2H, Ar*H*), 2.30, 2.28 (s,s, total 3H, $-C_6H_3(CN)(CH_3)$, 2.09 (s, 3H, $-C_6H_3(Cl)(CH_3)$; ^{13}C NMR, ppm, 142.2, 142.1, 141.7, 141.6, 139.9, 139.8, 138.4, 138.2, 137.3, 136.9, 135.2, 134.9, 132.6, 132.5, 132.4, 132.3, 118.3, 113.6, 113.2 (aromatic quarternary *C*), 135.6, 134.2, 134.1, 131.8, 131.7, 129.9, 129.8, 129.6, 129.5, 129.2, 128.4, 128.2, 127.7, 127.7, 126.9, 126.8, 126.0, 125.7, 125.6, 125.3 (aromatic secondary *C*), 19.2, 18.7, 18.4, 17.9 (internal $-CH_3$); IR (cm^{-1}), 2211 (s, -C≡N stretch), 1563 (w, br), 1546 (m, br), 1461 (m, br), 1413 (s, br), 1365 (s), 1023 (m, br), 1007 (m), 990 (m), 955 (w), 945 (w), 905 (m, br), 885 (s, br), 816 (w), 794 (s), 775 (s), 745 (s, br), 715 (s), 705 (s), 475 (s), 445 (m); MS, CI, *m/e* (relative intensity), 368 (100, M + 1, $C_{25}H_{18}{}^{35}ClN$, correct isotopic pattern), 396 (18, M + 29), 408 (5, M + 41); EI, 367 (100, $M^{+\cdot}$, $C_{25}H_{18}{}^{35}ClN$), 369 (33, $M^{+\cdot}$, $C_{25}H_{18}{}^{37}ClN$).

<u>Analysis</u> Calcd. for $C_{25}H_{18}ClN$: C 81.62, H 4.93.
Found: C 81.30, H 4.99.

Eluted next was the product, **44**, 5.9 g (86%). A portion was recrystallized from DMSO, m.p. 173-175°C (lit.[43] m.p. 181-183°C, benzene/methanol); ^1H NMR, δ, 7.89 (*AA'*XX', 2H, H-4',7'), 7.76 (d, J = 7.1 Hz, 2H, H-6,6"), 7.58 (AA'*XX'*, 2H, H-5',6'), 7.48 (dd, J = 0.03 Hz, J = 0.01 Hz, 2H, H-5,5"), 7.17 (m, 4H, Ar*H*), 2.28 (s, 6H, -C*H*$_3$); ^{13}C NMR, ppm, 141.7, 141.2, 139.7, 136.9, 136.6, 132.6, 132.4, 118.1, 118.0, 113.8, 113.4 (aromatic quarternary *C*), 135.5, 134.0, 131.9, 131.8, 129.9, 129.5, 127.7, 127.1, 125.8, 125.5 (aromatic secondary *C*), 19.2, 18.7 (internal -*C*H$_3$); IR (cm^{-1}), 2211 (s, -C≡N stretch), 1563 (m, br), 1460 (m, br), 1421 (s, br), 1370 (m, br), 1277 (w), 1265 (w, br), 1180 (w), 1123 (w), 1065 (w), 1005 (m), 993 (w), 955 (m, br), 885 (s, br), 825 (w), 805 (m), 787 (s, br), 763 (m), 740 (s, br), 715 (s), 545 (m), 524 (m), 475 (s), 445 (s), 415 (m); MS, CI, *m/e* (relative intensity), 359 (100, M + 1), 387 (21, M + 29), 399 (5, M + 41); EI, 358 (100, $M^{\ddagger}$).

Analysis	Calcd. for $C_{26}H_{18}N_2$:	C 87.12,	H 5.06.
	Found:	C 87.21,	H 5.16.

2.4 2,3-Bis(3-formyl-2-methylphenyl)naphthalene, 29

A solution of DIBAL-H (16.9 mL, 25% solution in hexanes) was added to the dinitrile **44** (3.0 g, 8.4 mmol) dissolved in dry benzene (50 mL) over 30 minutes at room temperature with vigorous stirring. After 21 h, the viscous yellow gel was quenched with methanol (5 mL), 1:1 MeOH/H$_2$O (5 mL) and 10% HCl (5 mL) with ice-bath-cooling, such that the resulting solution was slightly acidic.

The mixture was extracted with benzene (3 x 50 mL), washed with water, dried and evaporated. The resulting yellow solid was preadsorbed onto silica gel and chromatographed over a column of silica gel using CH_2Cl_2 as eluant to yield the product **29**, 2.75 g (90%). A portion was recrystallized from benzene to yield white crystals, m.p. 202-204°C (lit.[43] m.p. 204-206°C, CCl_4); ^1H NMR, δ, 10.21, 10.19 (s,s, total 2H, -C*H*O), 7.89 (*AA'*XX', 2H, H-4',7'), 7.78 (d, J = 9.5 Hz, 2H, H-6,6"), 7.66 (dq, J = 1.6 Hz, J = 3.7 Hz, 2H, Ar*H*), 7.56 (AA'*XX'*, 2H, H-5',6'), 7.30 (t,t, J = 0.03 Hz, J = 0.01 Hz, 2H, H-5,5"), 7.20 (m, 2H, Ar*H*), 2.40, 2.37 (s,s, total 6H, -C*H*$_3$); ^{13}C NMR, ppm, 192.8 (-*C*HO), 142.5, 142.0, 138.3, 138.3, 138.1, 137.8, 134.4, 134.1, 132.6, 132.4, 128.3 (aromatic quarternary *C*), 136.8, 135.3, 131.6, 131.2, 130.0, 129.4, 127.7, 126.7, 125.4, 125.1 (aromatic secondary *C*), 17.0, 16.5 (internal -*C*H$_3$); IR (cm^{-1}), 1663 (s, br, C=O stretch), 1561 (m, br), 1385 (w), 1365 (m), 1278 (w), 1265 (w, br), 1230 (s, br), 1185 (w), 1118 (w), 948 (w), 883 (m, br), 825 (m), 787 (m, br), 741 (s), 715 (m), 695 (w), 477 (m); MS, CI, *m/e* (relative intensity), 365 (100, M + 1), 393 (20, M + 29), 405 (4, M + 41); EI, 364 (100, $M^{+\cdot}$).

<u>Analysis</u> Calcd. for $C_{26}H_{20}O_2$: C 85.69, H 5.53.

Found: C 86.03, H 5.46.

2.5 2,3-Bis(3-(hydroxymethyl)-2-methylphenyl)naphthalene, 36

The dialdehyde **29** (2.75 g, 7.5 mmol) in THF (15 mL) was added to a stirred suspension of $NaBH_4$ (0.23 g, 6 mmol) in wet THF (15 mL) at room temperature for 20 h. The reaction mixture was decomposed with H_2O (5 mL) and 10% HCl (5 mL). The aqueous layer was saturated with NaCl, extracted with CH_2Cl_2, washed with water, dried and evaporated to yield the product **36**, 2.72 g (98%). A portion was recrystallized from benzene to yield white crystals, m.p. 155-157°C; ^1H NMR, δ, 7.87 (*AA'*XX', 2H, H-4',7'), 7.76 (d, J = 9.1 Hz, 2H, H-6,6"), 7.51 (AA'*XX'*, 2H, H-5',6'), 7.13 (m, 6H, Ar*H*), 4.59, 4.56 (s,s, total 4H, $-CH_2-$), 2.07 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 1.56 (s (broad), 2H, -O*H*); ^{13}C NMR, ppm, 141.7, 141.2, 139.9, 139.4, 138.8, 138.6, 134.1, 134.0, 132.5, 132.2 (aromatic quarternary *C*), 131.2, 129.8, 129.5, 129.0, 127.6, 126.4, 126.3, 126.2, 124.8, 124.6 (aromatic secondary *C*), 63.8, 63.7 ($-CH_2-$), 16.4, 15.9 (internal $-CH_3$); IR (cm^{-1}), 3351 (s, br, -OH stretch), 1567 (w), 1461 (m), 1413 (s, br), 1362 (m), 1314 (w), 1155 (w), 1124 (w), 1103 (w), 1065 (w, br), 1019 (m), 1004 (s), 987 (s), 953 (m), 879 (s), 785 (s), 754 (m), 736 (s), 716 (s), 478 (m); MS, CI, *m/e* (relative intensity), 369 (100, M + 1), 397 (21, M + 29); EI, 368 (100, $M^{\dot{+}}$).

Analysis Calcd. for $C_{26}H_{24}O_2$: M = 368.1776.

Found: M = 368.1695.

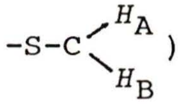
2.6 2,3-Bis(3-(bromomethyl)-2-methylphenyl)naphthalene, 34

A mixture of HBr (48%, 1.5 mL) and conc. H_2SO_4 (0.5 mL) was added to a solution of the bis(hydroxymethyl) compound **36** (1.0 g, 2.7 mmol) in benzene (10 mL) and stirred at room temperature for 18 h. The reaction mixture was cooled with an ice-bath, cold water (20 mL) added and extracted with benzene (3 x 15 mL). The organic layer was washed with H_2O, 10% $NaHCO_3$ and H_2O, dried and evaporated to yield the product **34**, 1.23 g (92%). A portion was recrystallized from a mixture of benzene and petroleum ether to yield white crystals, m.p. 148-149°C; ^{1}H NMR, δ, 7.88 (*AA'*XX', 2H, H-4',7'), 7.79 (d, J = 6.5 Hz, 2H, H-6,6"), 7.54 (AA'*XX'*, 2H, H-5',6'), 7.15 (m, 2H, H-5,5"), 7.01 (m, 4H, Ar*H*), 4.45, 4.44. 4.42 (s,s,s, total 4H, $-CH_2-$), 2.14 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$); ^{13}C NMR, ppm, 142.0, 141.5, 139.4, 139.1, 136.0, 135.3, 132.5, 132.3 (aromatic quarternary *C*), 130.8, 129.5, 129.1, 129.1, 128.9, 127.7, 126.4, 126.3, 125.2, 125.0 (aromatic secondary *C*), 33.2, 33.1 ($-CH_2$), 16.5, 16.1 (internal $-CH_3$); IR (cm^{-1}), 1431 (m, br), 1361 (m), 1243 (m), 1195 (m), 1175 (w), 1115 (w), 995 (m), 953 (w), 940 (w), 880 (m), 803 (m), 792 (s), 735 (s), 715 (s), 668 (m), 645 (w), 560 (s, br), 470 (m); MS, CI, *m/e* (relative intensity), 493 (7, M + 1, $C_{26}H_{22}{}^{79}Br_2$), 495 (13, M + 1, $C_{26}H_{22}{}^{79}Br^{81}Br$), 497 (6, M + 1, $C_{26}H_{22}{}^{81}Br_2$), 521 (1, M + 29, $C_{26}H_{22}{}^{79}Br_2$), 523 (3, M + 29, $C_{26}H_{22}{}^{79}Br^{81}Br$), 525

(1, M + 29, $C_{26}H_{22}{}^{81}Br_2$), 535 (1, M + 41, $C_{26}H_{22}{}^{79}Br^{81}Br$); EI, 492 (2, $M^{+\cdot}$, $C_{26}H_{22}{}^{79}Br_2$), 494 (5, $M^{+\cdot}$, $C_{26}H_{22}{}^{79}Br^{81}Br$), 496 (2, $M^{+\cdot}$, $C_{26}H_{22}{}^{81}Br_2$).

Analysis Calcd. for $C_{26}H_{22}Br_2$: C 63.18, H 4.49.
Found: C 63.60, H 4.54.

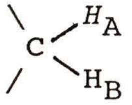
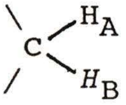
2.7 *Anti*-9,25-dimethylnaphtho[10,11-b]-2-thia[2.3]-metacyclophan-10-ene, 33

A solution of the bis(bromomethyl) compound **34**, (1.15 g, 2.3 mmol) in benzene (100 mL) was added at the same rate as a solution of $Na_2S.9H_2O$ (0.60 g, 2.53 mmol) dissolved in N_2-purged H_2O (32 mL) and N_2-purged ethanol (68 mL), into vigorously stirred N_2-purged 95% ethanol (300 mL) under N_2 over 26 h. The mixture was stirred for an additional 4 h and then evaporated. The residue was extracted with CH_2Cl_2 (250 mL) and H_2O (250 mL). The CH_2Cl_2 layer was dried and evaporated. The residue was preadsorbed onto alumina and chromatographed over alumina using dichloromethane/petroleum ether (1:3) as the eluant, to yield exclusively the *anti*-conformer of **33**, 0.23 g (27%). A portion was recrystallized from cyclohexane to yield white crystals, m.p. 198-200°C; ^1H NMR, δ, 8.11 (s, 2H, H-3',8'), 7.93 (*AA'*XX', 2H, H-4',7'), 7.53 (AA'*XX'*, 2H, H-5',6'), 7.39 (dd, J = 6.6 Hz, 2.2 Hz, 2H, H-5,5"), 7.19 (m, 4H, Ar*H*), 3.76 (*AB* quartet, 4H, J_{AB} = 13.0 Hz,  $-S-C\begin{smallmatrix}H_A\\H_B\end{smallmatrix}$), 0.95 (s, 6H, $-CH_3$);

^{13}C NMR, ppm, 140.5, 139.6, 139.4, 134.4, 133.2 (aromatic quarternary *C*), 131.6, 129.8, 127.8, 127.8, 126.2, 125.9 (aromatic secondary *C*), 30.5 ($-CH_2-$), 17.5 ($-CH_3$); IR (cm^{-1}), 1571 (w), 1553 (w, br), 1467 (w), 1451 (w), 1431 (s, br), 1409 (s, br), 1367 (m), 1313 (w), 1264 (w), 1251 (w), 1175 (w), 1152 (w), 1117 (w), 1062 (w), 1016 (m), 1003 (w), 942 (m), 892 (s), 877 (s), 785 (s), 756 (m), 737 (s), 722 (s), 716 (s), 654 (w), 566 (s), 555 (s), 506 (w), 471 (s), 405 (w); MS, CI, *m/e* (relative intensity), 367 (100, M + 1), 395 (17, M + 29), 407 (7, M + 41); EI, 366 (100, $M^{+\cdot}$).

Analysis Calcd. for $C_{26}H_{22}S$: C 85.20, H 6.05.
Found: C 84.67, H 6.12.

2.8 Wittig rearrangement of the thiacyclophane 33

A solution of LDA prepared from di-*i*-propylamine (0.12 g, 0.17 mL) and *n*-butyllithium (0.1 g, 1.6 mmol, 0.15 mL of 1.6M solution in hexanes, Aldrich) in dry THF (10 mL) was added to a solution of the thiacyclophane **33**, (0.15 g, 0.4 mmol) in dry THF (15 mL) under an argon atmosphere with stirring over 10 minutes. The solution was stirred for an additional 30 minutes and MeI (0.28 g, 2.0 mmol) was added to the resultant reddish-brown solution until the colour was discharged. The reaction mixture was extracted with CH_2Cl_2 (100 mL) and H_2O (100 mL). The organic layer was washed with 5% HCl (100 mL) and H_2O (100 mL), dried and evaporated. The yellow crystals thus obtained were chromatographed over a column of silica gel with petroleum ether/CH_2Cl_2 (3:2) as the eluant to yield the product **45**, 0.15 g (94%). A portion was recrystallized from cyclohexane to yield colourless crystals, m.p. 143-144°C; ^1H NMR, δ, 8.18 (s, 2H, H-3',8'), 7.93 (*AA'*XX', 2H, H-4',7'), 7.83 (dd, J = 7.1 Hz, J = 1.8 Hz, 1H, H-4"), 7.53 (AA'*XX'*, 2H, H-5',6'), 7.21 (m, 4H, Ar*H*), 7.08 (m, 1H, H-5"), 3.83 (dd, 1H, J_{BX} = 11.0 Hz, J_{AX} = 3.0 Hz, -CH_XSMe), 3.22 (dd, 1H, J_{AB} = 12.0 Hz, J_{AX} = 3.0 Hz,  $>C<^{H_A}_{H_B}$), 2.53 (t, 1H, J_{BX} = 11.0 Hz, J_{AB} = 12.0 Hz,  $>C<^{H_A}_{H_B}$), 2.18 (s, 3H, -SCH_3), 0.68 (s, 6H, -CH_3); ^{13}C NMR, ppm, 141.0, 140.8, 140.6, 140.5, 139.0, 138.5, 136.8, 136.3, 133.4 (aromatic quarternary *C*), 131.3, 130.6, 128.5, 127.8, 127.5, 126.3, 125.9, 125.6, 124.7 (aromatic secondary *C*), 54.4 (-*C*-SMe), 45.4 (-CH_2-), 16.9, 16.8 (internal -CH_3), 15.7 (-SCH_3); IR (cm^{-1}) 1551 (w), 1464 (w), 1416 (s, br), 1364 (w), 1312 (w), 1247 (m), 1116 (w), 1070 (m, br), 1010 (m, br), 937 (w), 885 (s), 874 (s), 787 (s), 765 (s), 736 (s), 707 (s), 641 (w), 576 (w), 554 (m), 508 (w), 474 (m); M.S., C.I., *m/e* (relative intensity), 381 (100, M + 1), 409 (13, M + 29), 421 (3, M + 41); EI, 380 (31, $M^{\ddagger}$), 317 (100,

$C_{25}H_{17}$).

Analysis Calcd. for $C_{27}H_{24}S$: C 85.22, H 6.36.

Found: C 84.72, H 6.47.

2.9 *Anti*-sulphonium salt, 32

Borch's reagent, $(MeO)_2CHBF_4$,[42] (0.13 g, 0.76 mmol) was added slowly to a solution of the Wittig rearrangement product **45** (0.16 g, 0.4 mmol) in CH_2Cl_2 (10 mL) at -30°C under an atmosphere of argon, which was stirred without further cooling for 10 h. Ethyl acetate (1 mL) was then added and after stirring for 12 h, the white precipitate was filtered, washed with CH_2Cl_2 and dried to yield the product **32**, 0.18 g (90%) as a white powder. The compound decomposed at 239°C. IR (cm^{-1}), 1609 (w, br), 1406 (m, br), 1367 (w), 1068 (s, br), 886 (w, br), 793 (m), 764 (w), 743 (m), 798 (m), 576 (w), 555 (w), 526 (w), 514 (w), 473 (w).

Analysis Calcd. for $C_{28}H_{27}BF_4S$: C 69.72, H 5.64.

Found: C 68.96, H 5.67.

2.10 *trans*-14c,14d-Dimethyl-14c,14d-dihydrodibenzo[de,qr]-naphthacene, 25

Potassium *t*-butoxide (0.02 g, 0.2 mmol) was added to a suspension of the *anti*-sulphonium salt, **32** (0.06 g, 0.1 mmol) in dry THF (10 mL) under an atmosphere of argon and heated at reflux for 25 minutes. The solution was evaporated, the residue extracted with distilled petroleum ether (10 mL), washed with 10% HCl (10 mL), H_2O (2 x 20 mL), dried and evaporated. The residue was dissolved in the minimum quantity of distilled petroleum ether and chromatographed over deactivated silica gel (5% w/w H_2O). Both the slurry used for packing the column and the eluant (petroleum ether) were degassed for 30 minutes. Elution with petroleum ether gave the dihydropyrene **25**, 0.036 g (90%). A portion was recrystallized from MeOH, to yield lustrous red-purple crystals, m.p. 103-105°C; ^1H NMR (C_6D_6), δ, 8.94 (s, 2H, H-9,14), 7.94 (*AA'*XX', 2H, H-10,13), 7.73 (d, 2H, J = 6.6 Hz, H-1,8), 7.41 (AA'*XX'*, 2H, H-11,12), 7.03 (d, 2H, J = 9.0 Hz, H-3,6), 6.72 (dd, 2H, J = 2.4 Hz, J = 4.0 Hz, H-2,7), 6.72 (s, 2H, H-4,5), -0.49 (s, 6H, $-CH_3$); ^{13}C NMR (THF-d_8), ppm, 140.3, 136.8, 132.6, 129.2 (aromatic quarternary *C*), 128.6, 127.0, 126.4, 124.2, 123.8, 123.0, 118.4 (aromatic secondary *C*), 38.8 (bridge *C*), 19.2 (internal $-CH_3$); IR (cm^{-1}), 1716 (m, br), 1433 (w), 1406 (w), 1270 (w, br), 885 (w), 785 (s), 727 (s); MS, CI, *m/e* (relative intensity), 333 (100, M + 1), 361 (12, M + 29), 373 (3, M + 41), 317 (19, M - 15), 302 (6, M - 30); EI, 332 (37, $M^{+\cdot}$), 317 (98, M - 15), 302 (100, M - 30); UV-VIS (nm, ϵ), 260 (45,600), 275sh (33,600), 312sh (19,600), 320 (33,400), 350sh (14,700), 369sh (25,900), 380 (49,700), 399 (66,800), 526sh (4,200), 550 (4,590), 580sh (3,550).

Analysis Calcd. for $C_{26}H_{20}$: M = 332.1565.

Found: M = 332.1530.

A solution of **28** obtained by bleaching **25** with tungsten light exhibited the following UV-VIS spectrum: (nm, ϵ), 219 (69,100), 235sh (58,100), 267 (67,200).

REFERENCES

1. D. Lloyd, 'Studies in Organic Chemistry 16: Nonbenzenoid Conjugated Carbocyclic Compounds', Elsevier, New York, 1984, p 2.

2. E. Hückel, *Z. Physik*, **70**, 204-286 (1931).

3. W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203-3206 (1954).

4. V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653-658 (1956).

5. W. Huber, J. Lex, T. Meul and K. Müllen, *Angew. Chem. Int. Ed. Engl.*, **20**, 391-393 (1981).

6. E. Vogel, J. Sombroek and W. Wagemann, *ibid.*, **14**, 564-565 (1975).

7. J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859-866 (1961).

8. R. J. Abraham, R. C. Sheppard, W. A. Thomas and S. Turner, *Chem. Commun.*, 43-44 (1965).

9. F. Sondheimer, *Pure Appl. Chem.*, **7**, 363-388 (1963).

10. P. J. Garratt, 'Aromaticity', John Wiley and Sons, New York, 1986, p 101.

11. a) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 3510-3512 (1970).

    b) *Idem.*, *ibid.*, **96**, 1547-1557 (1974).

12. V. Boekelheide and J. B. Phillips, *Proc. Natl. Acad. Sci. U. S. A.*, **51**, 550-552 (1964).

    b) *Idem.*, *J. Am. Chem. Soc.*, **89**, 1695-1704 (1967).

13. A. T. Balaban, M. Banciu and V. Ciorba, 'Annulenes, Benzo-, Hetero-, Homo-Derivatives, and their Valence Isomers', CRC Press, Inc., Boca Raton, Florida, 1987, Vol. 1, pp 163-166.

14. F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765-5766 (1960).

15. V. Boekelheide and C. H. Tsai, *J. Org. Chem.*, **38**, 3931-3934 (1973).

16. Ref. 13, Vol. 2, p 168.

17. R. H. Mitchell, Y.-H. Lai and R. V. Williams, *J. Org. Chem.*, **44**, 4733-4735 (1979).

18. J. B. Phillips, R. J. Molyneux, E. Sturm and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 1704-1709 (1967).

19. R. H. Mitchell, M. Chaudhary, T. W. Dingle and R. V. Williams, *ibid.*, **106**, 7776-7779 (1984).

20. R. H. Mitchell, I. Calder, H. Huisman and V. Boekelheide, *Tetrahedron*, **31**, 1109-1111 (1975).

21. H. B. Renfroe, J. A. Gurney and L. A. R. Hall, *J. Org. Chem.*, **37**, 3045-3052 (1972).

22. R. H. Mitchell, J. S.-H. Yan and T. W. Dingle, *J. Am. Chem. Soc.*, **104**, 2551-2559 (1982).

23. R. H. Mitchell, R. J. Carruthers, L. Mazuch and T. W. Dingle, *ibid.*, **104**, 2544-2551 (1982).

24. R. H. Mitchell, R. J. Carruthers and L. Mazuch, *ibid.*, **100**, 1007-1008 (1978).

25. R. H. Mitchell, R. V. Williams and T. W. Dingle, *ibid.*, **104**, 2560-2571 (1982).

26. R. H. Mitchell, R. V. Williams, R. Mahadevan, Y.-H. Lai and T. W. Dingle, *ibid.*, **104**, 2571-2578 (1982).

27. a) T. L. Gilchrist, D. Tuddenham, R. McCague, C. J. Moody and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 657-658 (1981).

    b) R. McCague, C. J. Moody and C. W. Rees, *ibid.*, 497-499 (1982).

    c) Z. Lidert and C. W. Rees, *ibid.*, 499-500 (1982).

    d) R. McCague, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 165-174 (1984).

28. R. McCague, C. J. Moody, C. W. Rees and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1063-1065 (1982).

29. R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 1722-1728 (1979).

30. R. H. Mitchell, T. W. Dingle, P. R. West, R. V. Williams and R. C. Thompson, *J. Org. Chem.*, **47**, 5210-5214 (1982).

31. Y.-H. Lai, *J. Am. Chem. Soc.*, **107**, 6678-6683 (1985).

32. R. H. Mitchell and T. W. Dingle, private communication.

33. Y.-H. Lai and P. Chen, *Tetrahedron Lett.*, **29**, 3483-3486 (1988).

34. R. H. Mitchell and J. S.-H. Yan, *Can. J. Chem.*, **58**, 2584-2587 (1980).

35. A. A. Danish, M. Silverman and Y. A. Tajima, *J. Am. Chem. Soc.*, **76**, 6144-6150 (1954).

36. E. A. Prill, *ibid.*, **69**, 62-63 (1947).

37. C. S. LeHoullier and G. W. Gribble, *J. Org. Chem.*, **48**, 2364-2366 (1983).

38. J. Seita, J. Sandström and T. Drakenberg, *Org. Mag. Reson.*, **11**, 239-245 (1978).

39. '^{13}CNMR Spectra of Polycyclic Aromatic Compounds', K. Hayamizu and O. Yamamoto, Eds., Japan Industrial Technology Association, Tokyo, 1982.

40. C.-J. F. Du, H. Hart and K.-K. D. Ng, *J. Org. Chem.*, **51**, 3162-3165 (1986).

41. J. S.-H. Yan, M. Sc. Thesis, University of Victoria, 1978.

42. R. F. Borch, *J. Org. Chem.*, **34**, 627-629 (1969).

43. a) S. A. Weerawarna, Ph. D. Dissertation, University of Victoria, 1988.

    b) R. H. Mitchell and S. A. Weerawarna, *Tetrahedron Lett.*, **27**, 453-456 (1986).

44. R. H. Mitchell and Y.-H. Lai, *J. Org. Chem.*, **49**, 2534-2540 (1984).

45. N. Eisen and F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, **25**, 1026-1027 (1986).

46. H. Günther, *ibid.*, **11**, 861-874 (1972).

47. D. Cremer and H. Günther, *Liebigs Ann. Chem.*, **763**, 87-108 (1972).

48. M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, **91**, 6325-6333 (1969).

49. Serena Software, Box 3076, Bloomington, IN 47402, USA, supplies this programme (QCPE 318) suitable for an IBM-PC.

50. R. H. Mitchell and N. A. Khalifa, unpublished work.

51. M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789-795 (1969).

52. P. Zhou and R. H. Mitchell, private communication.

53. Y.-H. Lai and T.-G. Peck, private communication.

54. A. Maercker, *Org. React.*, **14**, 270-490 (1965).

55. a) F. R. Stermitz, in 'Organic Photochemistry', O. L. Chapman, Ed., Marcel Dekker, Inc., New York, 1967, Vol. 1, pp 247-282.

    b) F. B. Mallory and C. W. Mallory, *Org. React.*, **30**, 1-456 (1984).

56. a) H. Vogler, private communication.

    b) H. Vogler and R. H. Mitchell, *Tetrahedron*, **41**, 3771-3777 (1985).

57. K. D. Bartle, D. W. Jones and R. S. Matthews, *Spectrochimica Acta*, **25A**, 1603-1613 (1969).

58. J. Bowen Jones and D. S. Brown, *Acta Cryst.*, C**39**, 764-766 (1983).

59. S. Galí, X. Solans, C. Miravitlles, M. Font-Altaba and O. Armet, *ibid.*, B**34**, 1011-1014 (1978).

60. J. H. Gall, D. D. MacNicol, P. R. Mallinson and P. A. Welsh, *Tetrahedron Lett.*, **26**, 4005-4008 (1985).

61. P. Wahl, C. Krieger, D. Schweitzer and H. A. Staab, *Chem. Ber.*, **117**, 260-276 (1984).

62. a) D. Gust, *J. Am. Chem. Soc.*, **99**, 6980-6982 (1977).

    b) D. Gust and A. Patton, *ibid.*, **100**, 8175-8181 (1978).

    c) A. Patton, J. W. Dirks and D. Gust, *J. Org. Chem.*,

44, 4749-4752 (1979).

63. a) R. L. Clough and J. D. Roberts, *J. Org. Chem.*, **43**, 1328-1331 (1978).

    b) *Idem.*, *J. Am. Chem. Soc.*, **98**, 1018-1020 (1976).

64. a) Y.-H. Lai, *J. Chem. Soc. Perkin Trans. II*, 1667-1670 (1986).

    b) P. J. Marriott and Y.-H. Lai, *J. Chromatogr.*, **447**, 29-41 (1988).

65. Y.-H. Lai, P. J. Marriott and B.-C. Tan, *Aust. J. Chem.*, **38**, 307-314 (1985).

66. K. A. Muszkat and E. Fischer, *J. Chem. Soc. (B)*, 662-678 (1967).

67. W. M. Moore, D. D. Morgan and F. R. Stermitz, *J. Am. Chem. Soc.*, **85**, 829-830 (1963).

68. H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130-131 (1965).

69. H.-R. Blattmann and W. Schmidt, *Tetrahedron*, **26**, 5885-5899 (1970).

70. V. Boekelheide and T. Miyasaka, *J. Am. Chem. Soc.*, **89**, 1709-1714 (1967).

71. H. Blaschke, C. E. Ramey, I. Calder and V. Boekelheide, *ibid.*, **92**, 3675-3681 (1970).

72. C. E. Ramey and V. Boekelheide, *ibid.*, **92**, 3681-3684 (1970).

73. R. Naef and E. Fischer, *Helv. Chim. Acta*, **57**, 2224-2233 (1974).

74. V. Boekelheide and W. Pepperdine, *J. Am. Chem. Soc.*, **92**, 3684-3688 (1970).

75. T. Yamato, K. Kobayashi, T. Arimura, M. Tashiro, K. Yoshihira, K. Kawazoe, S. Sato and C. Tamura, *J. Org. Chem.*, **51**, 2214-2218 (1986).

76. S. Murakami, T. Tsutsui, S. Saito, A. Miyazawa, T. Yamato and M. Tashiro, *Chem. Lett.*, 5-8 (1988).

77. a) L. A. R. Hall, J. A. Gurney and H. B. Renfroe, U. S. Patent 3,557,218, 1971.
    b) *Idem.*, U. S. Patent 3,697,604, 1972.
    c) *Idem.*, U. S. Patent 3,705,918, 1972.
    d) *Idem.*, U. S. Patent 3,716,595, 1973.

78. T. Laird, *Chem. Ind.*, **56**, 186-193 (1978).

79. H. G. Heller, *ibid.*, **56**, 193-196 (1978).

80. S. Shinkai and O. Manabe in, 'Topics in Current Chemistry **121**: Host Guest Complex Chemistry III', F. Vögtle and E. Weber, Eds., Springer-Verlag, New York, 1984, pp 67-104.

81. 'Techniques of Chemistry, Volume III: Photochromism', G. H. Brown, Ed., Wiley-Interscience, New York, 1971.

82. K. Fukui, T. Nomoto, S. Nakatsuji and M. Nakagawa, *Tetrahedron Lett.*, 3157-3160 (1972).

83. A. Yasuhara, T. Satake, M. Iyoda and M. Nakagawa, *ibid.*, 895-898 (1975).

84. Y. Aso, M. Iyoda and M. Nakagawa, *ibid.*, 4217-4220 (1979).

85. M. Iyoda, M. Morigaki and M. Nakagawa, *ibid.*, 3677-3680 (1974).

86. Ref. 10, pp 234-235.

87. D. Kamp and V. Boekelheide, *J. Org. Chem.*, **43**, 3475-3477 (1978).

88. V. Boekelheide and J. A. Lawson, *Chem. Commun.*, 1558-1560 (1970).

89. V. Boekelheide and P. H. Anderson, *J. Org. Chem.*, **38**, 3928-3931 (1973).

90. A. W. Hanson, *Acta Cryst.*, B**31**, 2352-2354 (1975).

91. G. J. Bodwell, M. Sc. Thesis, University of Victoria, 1986.

92. K. Nakasuji, M. Katada and I. Murata, *Angew. Chem. Int.*

Ed. Engl., **18**, 946-947 (1979).

93. a) B. A. Hess, Jr., A. S. Bailey and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 2746-2747 (1967).

    b) B. A. Hess, Jr., A. S. Bailey, B. Bartusek and V. Boekelheide, *ibid.*, **91**, 1665-1672 (1969).

94. B. A. Hess, Jr. and V. Boekelheide, *ibid.*, **91**, 1672-1678 (1969).

95. H. B. Renfroe, *ibid.*, **90**, 2194-2196 (1968).

96. W. P. Wynne, *Proc. Chem. Soc.*, **30**, 204 (1914).

VITA

Surname: VENUGOPALAN Given Names: Santhanagopalan

Place of Birth: Madras, India Date of Birth: 16 January, 1961

Educational Institutions Attended, with Dates of Entering and Leaving:

University of Madras, India	1978 TO 1981
University of Madras, India	1981 to 1983
University of Victoria, B. C.	1984 to 1989

Degrees, Diplomas, Etc., Awarded, with Dates and Names of Institutions:

B. Sc.	1981	University of Madras, India
M. Sc.	1983	University of Madras, India

Honours and Awards:

University of Victoria Fellowship, 1984/85

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Author [redacted]

(S. VENUGOPALAN).

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