THE SYNTHESIS AND PROPERTIES OF A BENZANNELATED DIHYDROPYRENE AND SEVERAL DERIVATIVES.

BY

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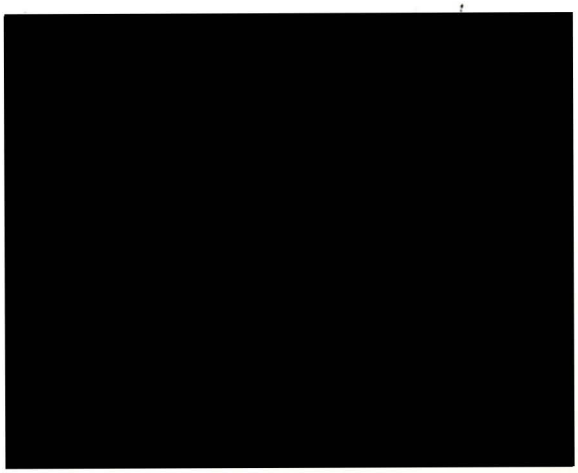
ABSTRACT

In this work we have synthesised a symmetrical benzannelated dimethyldihydropyrene and shown that it is aromatic both in terms of magnetic effects (diatropic and large 'Q' value) and classical reaction chemistry (in that it undergoes electrophillic substitution reactions). Synthetic procedures have been developed which allow a base-induced sulphinic acid elimination as an alternative to the better-known Hofmann type sulphonium salt elimination in the last step of the sequence to produce cyclophane-dienes. Also a method has been found whereby alkyl substituents may be introduced onto the bridge position of the phane-diene. The synthesis of the first terphenylophane is also described.

The phototautomerisation of the benzodimethyldihydropyrene and its derivatives has been studied, and it is found that the activation barriers between the phane-diene ⇌ dihydropyrene tautomers are somewhat higher (i.e. process is slower) than for the parent system.

The barriers to rotation in several substituted terphenyls have also been determined.



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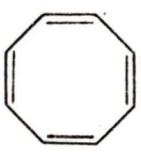
I. Introduction

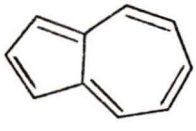
For more than 100 years the terms 'aromatic character' and 'aromaticity' have traditionally been used to refer to the properties of benzene and its derivatives. However care is required in using the phrase 'benzene-like properties' as a definition of aromaticity since both ground state properties (e.g. anisotropy of diamagnetic susceptibility) and transition state vs ground state (e.g. chemical reactivity) are involved. At the present time, reactivity does not seem a very useful criterion for aromaticity, since many non-benzenoid systems which are considered aromatic by other criteria, might not be so in terms of reactivity. The lack of understanding of what aromaticity actually is, is perhaps demonstrated best by the many syntheses of new and novel 'aromatic' systems that appear each year[1]. It would be preferable if both theoretical and synthetic chemists could agree on a general definition of aromaticity which would hold true for all new systems to be made in the future. The present status of aromaticity is given below, and although it is not suited to all the known examples, it does provide to a large extent some understanding of aromatic systems.

From a theoretical standpoint, Hückel's rule has been the most widely applied definition of aromaticity and states that 'those monocyclic co-planar systems of trigonally-hybridised atoms

which contain $(4n + 2)$ π-electrons will possess relative electronic stability[2] (n = integer)'. Both valence-bond (VB) theory and molecular orbital (MO) theory have been applied to aromatic systems, though in recent years VB theory which utilizes pure single and double bonds has proved less popular, perhaps due to difficulties in analysis[3]. Breslow and Dewar[4] have more recently extended the definition of aromaticity such that 'cyclic conjugated systems are considered aromatic if cyclic delocalisation of π-electrons makes a negative contribution to their heat of formation.' By definition, the opposite, cyclic delocalisation of π-electrons giving a positive contribution, i.e. net destabilisation, is referred to as 'antiaromaticity'. As a consequence, non-aromatic molecules show no net stabilisation or destabilisation in comparison to a linear model. Both Hückel theory (HMO) and Dewar self-consistent field (SCF) calculations[5] have been used on a wide variety of benzenoid and non-benzenoid systems, and allow some degree of classification into the above systems, e.g. olefinic in the case of cyclooctatetraene (1), to borderline for azulene(2), and essentially aromatic for fluoranthene(3). Even homoaromatic, species such as norbornyl cation(4) are covered to some extent.



(1)



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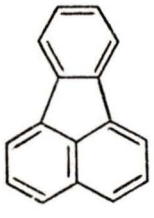
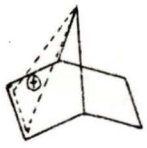


(3)

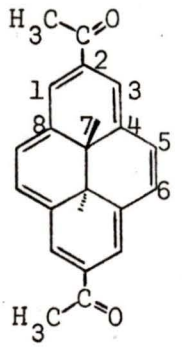


(4)

Unfortunately heats of combustion or hydrogenation are somewhat tedious and difficult to obtain, so support of theoretical calculations by thermodynamic data is sparse, and hence much disagreement on the value of MO calculations exists. Part of the problem may be that the so-called 'resonance or delocalisation energy' which is derived as the difference between observed thermodynamic data and that calculated on the basis of hypothetical models having alternating single and double bonds, is highly variable depending on method of calculation. It is probably better called 'stabilisation'[6a], because the latter takes account of σ-bond energy, steric strain, etc. as well as π-elctron delocalisation energy, and it is therefore not surprising that it is not necessarily a very useful criterion for aromaticity. Resonance energy is also markedly dependent on the model chosen, e.g. for benzene values of from 40-300 kj/mol have been quoted[6b]. Because of the above variability of theoretical calculations, it is preferable that some simple, easily determined experimental quantity should be used to define aromaticity.

In concept, although not necessarily in practice, diffraction methods (X-ray, electron and neutron) are the most fundamental, since they actually measure bond alternation, as well as deviations from planarity in conjugated systems. Examples where these methods have been used to determine whether bond alternation is present or

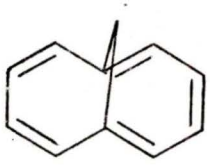
not are provided by benzene (all six C-C bonds equal at 139pm)[7], [18] annulene(8) (six long outer bonds at 141.9pm and twelve shorter inner bonds at 138.2pm)[8] and the nearly planar bridged [14] annulene, 2,7-diacetoxy-trans-10b,10c-dimethyl-10b,10c-dihydropyrene(5)(periphery bonds: C_1-C_2 138.6, C_3-C_4 138.9, C_4-C_5 140.1 and C_5-C_6 139.2pm)[9].



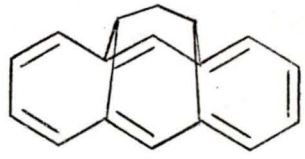
(5)

In contrast, [16] annulene[9] is non-planar and has alternating bonds (eight longer bonds at 145.4pm and eight shorter bonds at 133.3pm)[8]. Unfortunately such methods require considerable time in comparison to the more convenient and hence popular determination of chemical shifts in magnetic resonance spectra. Consequently, aromaticity is now more frequently discussed in terms of presence of an induced ring current, as evidenced in terms of chemical shift difference between inner and outer atom resonances than by other methods which are more directly associated with the criteria for aromaticity, such as lack of bond alternation mentioned above.

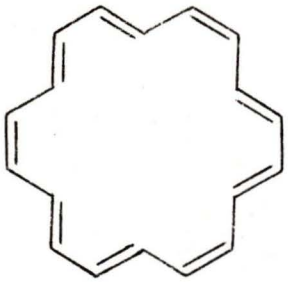
It is not absolutely certain that a ring current is responsible for the chemical shifts observed, rather than local anisotropies or local effects from σ bonds[10], e.g. fulvenes which are not normally considered aromatic, exhibit resonances at low field where external aromatic protons normally are found. Charge can also introduce ambiguities, e.g. the chemical shift of cyclooctatetraene and its aromatic dianion are almost identical[11]. However, despite a few problems such as these, there are an overwhelming number of examples where the ring current criteria for aromaticity appears satisfactory. Numerous examples can be found in Sondheimer's studies[8] on the annulenes, Nakagawa's results[12] on the more rigid cumulene-acetylene containing annulenes, and in the bridged [10] and [14] annulenes of Vogel[13], [14] annulenes of Boekelheide and Mitchell[14] and [18] annulenes of Boekelheide[15] where in each case there is a very large chemical shift difference between the deshielded outer and shielded inner protons in the (4n + 2) π-electron systems. Some selected examples are given in table 1.



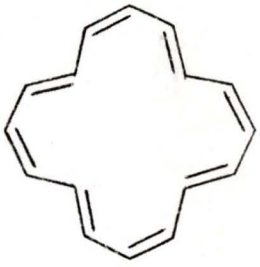
1,6-methano[10]annulene(6)



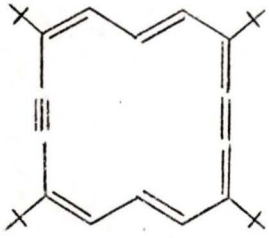
1,6:8,13-butanediylidene [14]annulene(7)



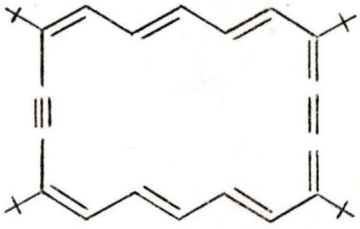
[18] annulene (8)



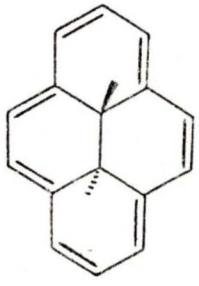
[16] annulene (9)



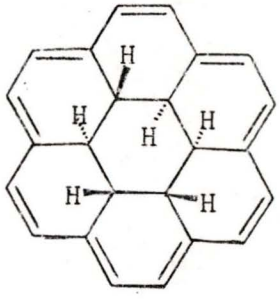
3,7,10,14-tetra-t-butyl-
1,8-didehydro [14] annulene(10)



3,9,12,18-t-butyl-1,10-
didehydro [18]annulene(11)



trans-10b,10c-dimethyl-10b,10c-
dihydropyrene(12)
(bridged[14]annulene)



12b,12c,12d,12e,12f,12g-
hexahydrocoronene(13)
(bridged [18] annulene)

Table I. Comparison of chemical shift differences for inner and outer protons in selected systems.

Compounds	temperature	chemical shifts inner 'H'(δ)	outer 'H'(δ)	Δδ	system
1. (6)[e]	ambient	-0.52 (methylene)	7.63, 6.95	8.15	4n+2
2. (7)[a]	ambient	0.52 (methylene) -0.96 (methine)	7.86, 7.34	7.34 6.82 8.82 8.30	"
3. (10)[b]	+35°C	-4.39	9.42	13.81	"
4. (12)[d]	ambient	-4.15 (methyl)	8.74, 8.24	12.89 12.39 11.65	"
5. (9)[e]	-120°C +30°C	9.47	5.40, 5.11 all 6.73	4.07 4.36	4n
6. (8)[e]	-60°C +100°C	-2.99	9.28 all 5.45	12.27	4n+2
7. (13)[c]	-97°C	-6.54- -7.96	9.55-9.30	16.09 17.26	"
8. (11)[b]	36°C	-4.39	9.42	13.81	"

a. see ref. 13 b. see ref. 12 c. see ref. 15 d. see ref. 14

e. see ref. 8

Diamagnetic susceptibility exaltation, Λ, is a quantity that has also been used[16] to define aromatic compounds. The molar susceptibility of a compound χ_m is measured, either using a Faraday Balance[17] or an nmr method[16], and is compared to a hypothetical calculated value χ'_m, derived using an increment system based on London diamagnetism for the cyclic polyene. The exaltation, Λ is then defined as $\Lambda = \chi_m - \chi'_m$, and is large and positive for aromatic systems (e.g. benzene=13.7; trans-10b,10c-dimethyl-10b,10c-dihydropyrene=81 (units of $-10^{-6}cm^3mol^{-1}$))[16].

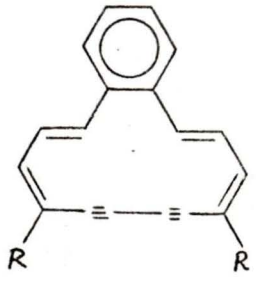
There has been some criticism of the value of this as a criterion for aromaticity however[18], and in any case because it is much more difficult to determine than a chemical shift, the method has not become very popular yet.

Some attempts have also been made to relate other physical properties to aromaticity, (e.g. dipole moments and electronic spectra)[19].

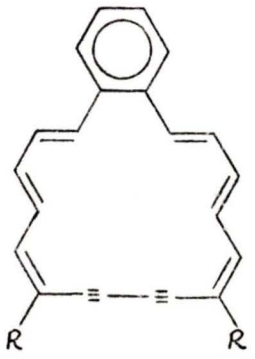
To summarise, the present most accepted definition of an aromatic compound is one in which all of the ring atoms of the cyclic system are involved in a single conjugated approximately planar system, which exhibits a diamagnetic ring current and shows a large magnetic susceptibility exaltation. Such compounds have also been called diatropic[20].

In the decade and a half following 1960 considerable efforts by a number of groups throughout the world have been made to understand aromaticity in larger monocyclic analogues of benzene. Although attention had been given to polycyclic syatems containing many fused benzene rings[21], compounds containing one or two benzene rings fused to a macrocyclic ring (i.e. a benzannulene) were virtually unknown. Several tri- and higher benzannelated annulenes had been known for a number of years[22] but all of these showed no detectable aromaticity in the macro ring. It was thus of considerable interest to attempt to prepare a stable $(4n + 2)\pi$ - electron system which was fused to a benzene ring to determine whether the macro ring would still be aromatic or not. During the period 1974-1975 several such systems appeared in the literature, perhaps prompted in part by a growing interest of theoretical chemists[23] in such systems, and partly by a realization that when only one or two benzene rings annelate the macrocyclic syatem, is the aromaticity of the large ring still likely to be observable. Thus at this time Sondheimer et al[24] prepared (14) and (15), Nakagawa and group[12] (16), and Mitchell (17a,b), (18a,b) and (19a,b)[22g,25]. Whereas the above examples can be used to compare diatropicities, they unfortunately are not very suitable for either chemical reaction studies (i.e. they are all not very stable) and because they lack symmetry, application of a theoretical test

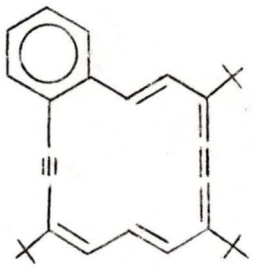
of aromaticity, such as Günthers Q test[23] (see section II-3b below), is made extremely difficult. There was thus much incentive to



(14)(R=H or CH_3)



(15)(R=H or CH_3)



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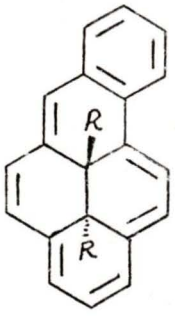
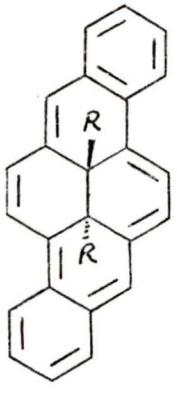
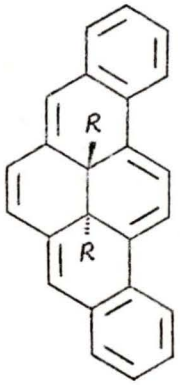


(17a)(R = H)
(17b)(R=CH_3)



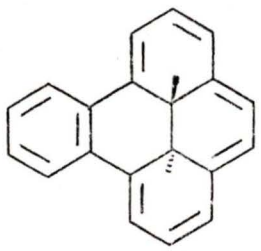
(18a)(R = H)
(18b)(R=CH_3)



(19a)(R = H)
(19b)(R=CH_3)

synthesise a stable and symmetrical benzannulene. We elected to attempt the synthesis of (20), since its parent, trans-10b,10c-

dimethyl-10b,10c-dihydropyrene(12), synthesised originally by Boekelheide and Phillips[26] is not only strongly diatropic (internal methyl protons at δ-4.25) but classically aromatic as well, in that it is stable and undergoes electrophilic aromatic substitution reactions[27]. Moreover this system has the advantage that Mitchell and Boekelheide have developed a synthetic sequence which gives access to a wide range of derivatives and related systems.[14,29] The object of this work was thus the synthesis of the benzannulene (20), and a preliminary investigation of its physical and chemical properties.



(20)

II. Results & Discussion

II-1. Synthesis of trans-12c,12d-dimethyl-12c,12d-dihydrobenzo(e)pyrene (20)

The synthetic scheme whereby we intended to synthesise (20) is shown in scheme I below. The first objective was the synthesis of the dibromide (28), the appropriate precursor to the thiacyclophane (29). Treatment of 2,6-dichlorotoluene (21a), with magnesium in tetrahydrofuran gave the mono-Grignard reagent (21b), which could be coupled with o-dibromobenzene in the presence of nickel(II) acetylacetonate as catalyst[28] to give the o-terphenyl (22) in 60% yield. The structure† of (22) was readily apparent from its simple pmr spectrum, which is temperature dependent and is discussed in detail in section II-8 below, and from its mass spectrum in which the molecular ion at m/e 326 showed a correct isotope pattern for two chlorine atoms, and indicated that two Grignard units had coupled with one dibromobenzene. As a minor product from this reaction, the quaterphenyl (23) was isolated in 3% yield as colourless crystals mp 173-175°C for which the molecular ion was at m/e 402($^{35}Cl_2$). Conversion of the dichloride (22) to the dinitrile (24) was readily accomplished by the von Braun reaction using cuprous cyanide in N-methylpyrrolidinone in 85-95% yield. In its

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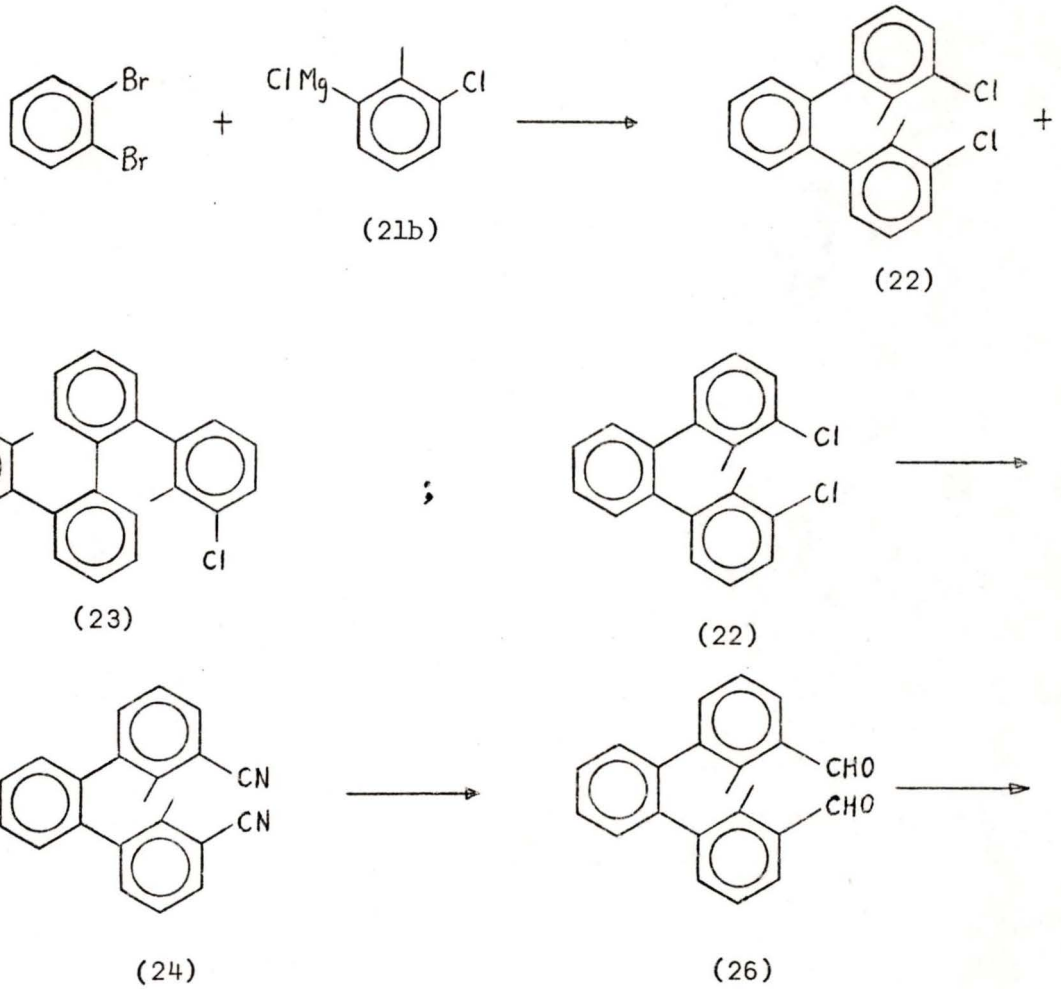
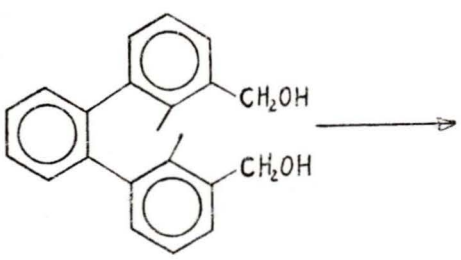
† Satisfactory elemental analyses were obtained for all new compounds unless otherwise stated. Any single, heavy or dotted line represents a methyl group in any structure, unless otherwise indicated.

ir spectrum, (24), mp 151-153°C, showed -C≡N stretch at 2240cm^{-1}. The mass spectrum, M^+ = 308, and pmr spectrum were consistent with conversion to the dinitrile. As a by-product, a small amount (ca 5%) of the mononitrile monochloride (25), mp 100-102°C was also obtained (M^+ = 317, correct isotope pattern for one chlorine atom).

Scheme I





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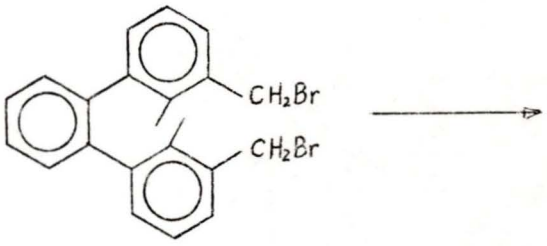

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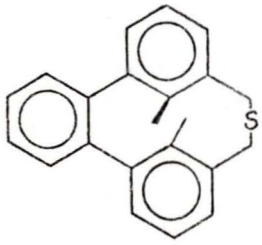

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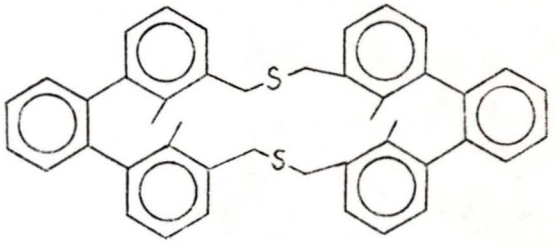

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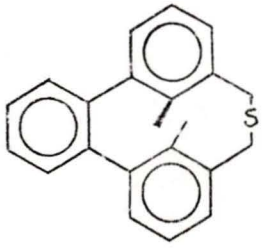

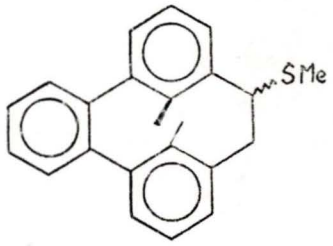

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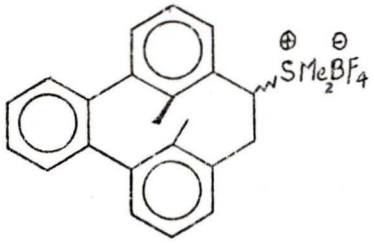
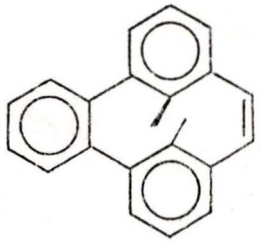




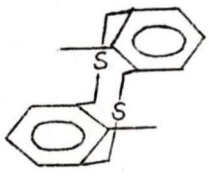
(32) (36)

Reduction of the dinitrile (24) to the dialdehyde (26) was achieved by diisobutylaluminium hydride in benzene in 86% yield. The dialdehyde (26), mp 141-143°C, showed the aldehyde protons at δ 10.2, in its pmr spectrum and the -C=O stretch at 1685cm^{-1} in its ir spectrum consistent with an aromatic aldehyde. The mass spectrum gave the molecular ion at m/e 314 with peaks indicating ready loss of -CH_3 and CO. All of the above terphenyls showed temperature dependant pmr spectra which are discussed in section II-8 below. Reduction of dialdehyde (26) with sodium borohydride in tetrahydrofuran led to the desired bis(hydroxymethyl) terphenyl (27), mp 135-137°C in essentially quantitative yield. The ir spectrum indicated an absence of -C=O stretch and showed the -OH stretch for the alcohol at 3250cm^{-1}. In its pmr spectrum, the -OH proton appeared at δ 1.62 and exchanged readily with deuterium oxide. The mass spectrum gave the molecular ion at m/e 318 as the base peak with ready loss of -CH_3 and H_2O. Treatment of diol(27) with phosphorus tribromide in benzene then led to the desired bis(bromomethyl) compound (28), mp 129-130°C, in 74% yield. The structure of (28) was readily apparent from the mass spectrum with M^+ at 444($^{79}Br_2$) with the 1:2:1 isotope pattern expected for a dibromide, and the singlet for the -CH_2Br protons at δ 4.35 in

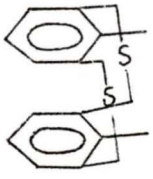
its pmr spectrum, characteristic of a benzyl type bromide. With the desired precursor to the thiacyclophane (29) now at hand, consideration could be given to the method of coupling. Whilst Mitchell & Boekelheide originally reported[29] the use of sodium sulfide to couple m-xylylene dibromides to thiacyclophanes, they subsequently[14,30] improved the coupling yields considerable by use of a thiol as one half of the molecule and a xylylene halide as the other. In our case however, it was not obvious how we would convert one bromine of (28) into a thiol group while leaving the other alone. Thus we attempted the sodium sulphide coupling directly. In the event, a good yield (48%) of (29) could be obtained by dropwise addition of sodium sulphide solution through one funnel, whilst the bromide solution (Ethanol-benzene) was added through a second funnel at the same rate. Chromatography of the product yielded the cyclophane (29), entirely as the anti-isomer mp 201-202°C. This was clearly indicated by its pmr spectrum in which the shielded internal methyl groups were at δ0.94. These can be compared with these of the known[14] syn and anti cyclophanes (34) and (33), given in table 2.

Table 2

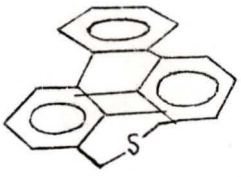
Chemical shifts (δ) of protons in thiacyclophanes.



(33)



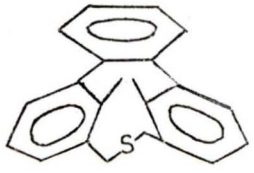
(34)



(29)

$-CH_3$	1.30	2.54	0.94
-ArH	7.0 - 7.4	6.66	7.0 - 7.75
$-CH_2$	3.68	3.80, 4.00	3.80 ,3.55

It is interesting that none of the corresponding syn-isomer (35) could be isolated, despite the fact that a 7:1 ratio for (33):(34) is obtained[14]. Molecular models indicate to us that the syn isomer is much

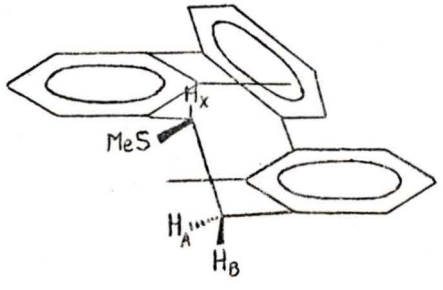


(35)

more crowded than the anti. The structure of (29) was confirmed by

an intense base peak for the molecular ion at m/e 316 in its mass spectrum. The coupling reaction also yielded 20% of the very insoluble dimer (30), mp 251-253°C, which showed a molecular ion at m/e 632 in its mass spectrum. The pmr spectrum was only obtained with difficulty and was quite complex (see experimental) and probably indicates severe folding of the molecule.

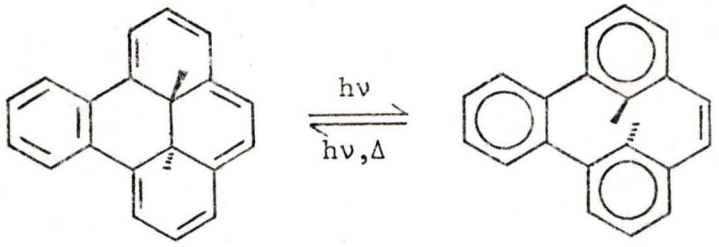
We decided firstly to investigate conversion of the thiacyclophane (29) into the cyclophane diene ⇌ dihydropyrene (36) ⇌ (20) by means of the Wittig rearrangement-Hofmann elimination sequence[14,31]. Wittig rearrangement of (29) using lithium diisopropylamide as base in tetrahydrofuran proceeded well and gave 80% of the ring contracted product (31), mp 165-166°C which pmr indicated to be a single isomer. The ABX system could be assigned[14] as follows:



(31)

H_X :δ 3.88, dd, J_{XB} = 11Hz; J_{XA} = 3Hz
H_A :δ 3.28, dd, J_{AB} = 11Hz; J_{AX} = 3Hz
H_B :δ 2.60, t, J_{BA} = J_{BX} = 11Hz

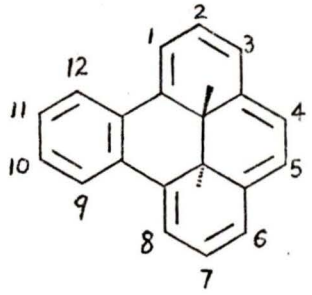
The -SMe signal at δ2.28 indicated this to be a pseudoequatorial substituent as shown†, and in agreement with this neither internal Ar-CH_3(δ0.80) is deshielded from the other as it would be if the -SMe were pseudoaxial. The fact that we obtain a single isomer is interesting, and may be because an axial -$S^{\oplus}$ produced in the Wittig rearrangement reaction would have too severe an interaction with the neighbouring aromatic methyl group. In the [2,2]cyclophane series, when an internal H is present, axial -$S^{\oplus}$ is produced[14]. Conversion of (31) to the sulphonium salt (32), mp. ca 287°C(dec) occured in 80% yield with dimethoxycarbonium fluoroborate $(MeO)_2CHBF_4$ and then treatment of the salt with potassium t-butoxide in tetrahydrofuran at reflux gave the desired dimethyldihydrobenzo(e)pyrene (20). This was isolated in 75% yield as deep purple-red crystals, mp 136-138°C. After standing for some time, crystals of (20) became pale on the surface which may indicate some conversion to the cyclophane diene form (36). This may be supported by the rather broad ir band



(20) (36)

† pseudo axial -SMe usually appear just below δ2[14]

at 1650cm^{-1}. In solution conversion between (20) and (36) is easy, since on exposure to light a solution of (20) converts to the colourless (36). This is discussed in more detail in section II-4 below. Preparation of a solution of (20) for uv spectral determination was therefore carried out in the dark. The uv spectrum is shown in Fig. 1, along with the parent dimethyldihydropyrene (12) for comparison. The major bands of (20) at 531 and 390 nm are bathochromically shifted from those of the parent (12) at 463 and 377 nm, consistent with the longer conjugated aromatic system in (20). The uv spectrum of the open tautomer (36) can be obtained by first exposing the solution to bright tungsten light to bleach it and then rapid determination of the spectrum. Compound (36) shows λ_{max}(log ε_{max}) 260(4.22), 253(4.26), 226(4.42). Since the conversion of (36) $\rightleftharpoons$ (20) is much slower than in all previous examples, this determination is made feasible, and is discussed in greater detail in section II-4 below. Both tautomers are readily discernible by pmr spectroscopy: The internal methyls of (20) appear highly shelded at δ-1.85, consistent



(20)

with a diatropic system. This point is discussed in greater detail below. The external protons are somewhat more difficult to assign: in benzo(e)pyrene(20), H-9, 12 are most deshielded[24,32], as indeed they are in phenanthrene itself and has been assigned in part to steric compression[33]. They are readily visible in the spectrum of (20) as the AA' part of an AA'XX' multiplet at δ8.70, and are easily distinguishable from H-1,8 which are also deshielded but occur as a doublet at δ8.18, J_{12}= 7Hz; presumably the meta-coupling J_{13} is too small to be observed. The protons, H-4,5 can be seen as a singlet at δ7.22. The remaining protons occur as multiplets: H-3, 6, 10, 11 at δ7.62-7.33 and H-2, 7 at δ7.14-6.94, and were assigned on the basis of spin-decoupling experiments and comparison to dimethyldihydropyrene (12)[14] itself. It is interesting that H-2, 7 are the most shielded external protons in both (12) and (20). This is consistent with greater π-electron density at these points. The latter is also indicated since 2, 7-substitution occurs under electrophilic conditions (see section II-3c below). By irradiation of the nmr sample with tungsten light, conversion to the tautomer (36) occurs. This tautomer has its internal methyl protons at δ1.41, the region anticipated for an anti-cyclophane. This proton chemical shift is further discussed in section II-3a

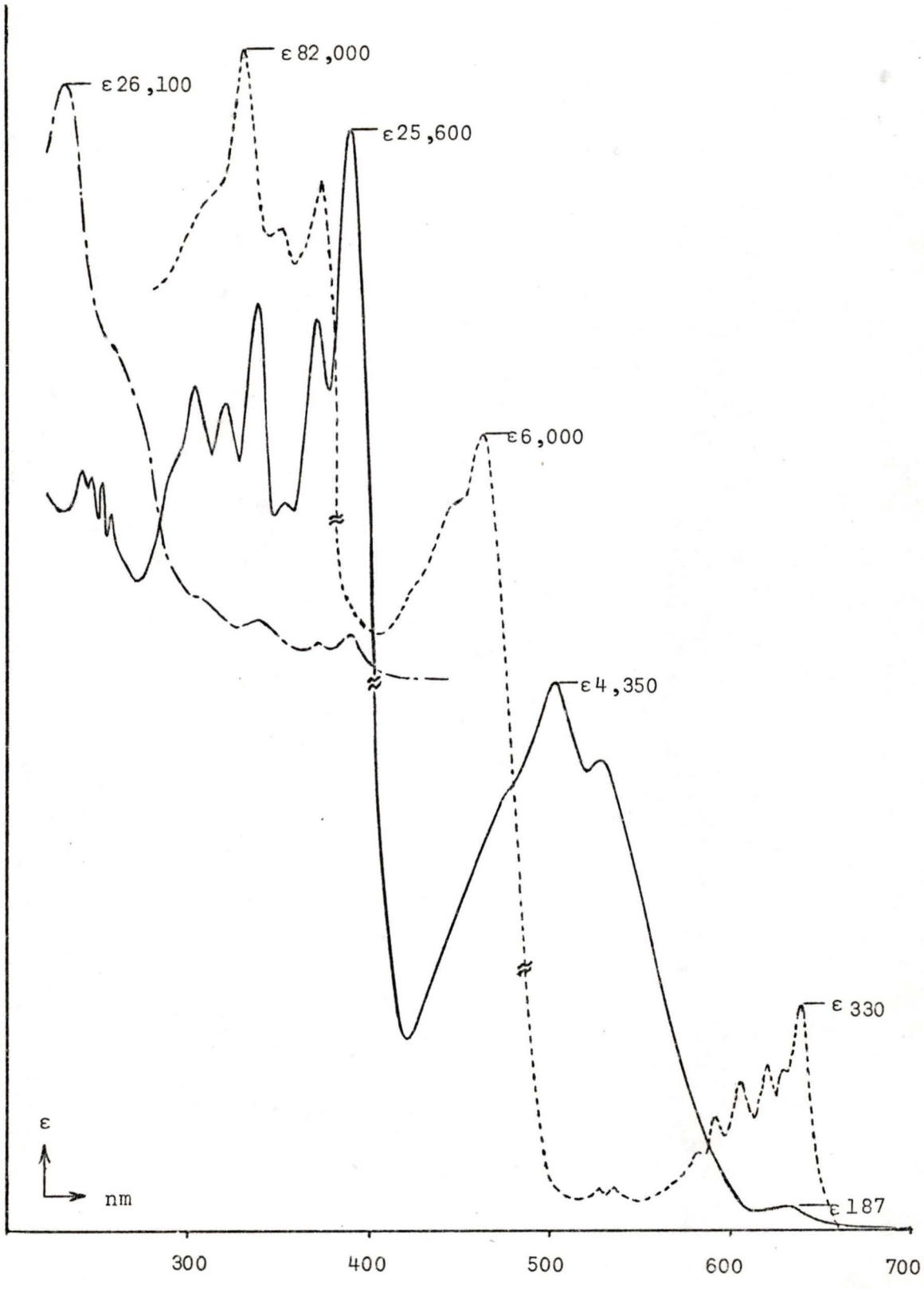


Figure 1. U. v. and visible spectra of (12) (------), (20) (———) and (36) (— - —) taken in cyclohexane using a Carey 17 spectrophotometer.

Fig. 2. pmr spectrum of trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene(60MHz,δ)

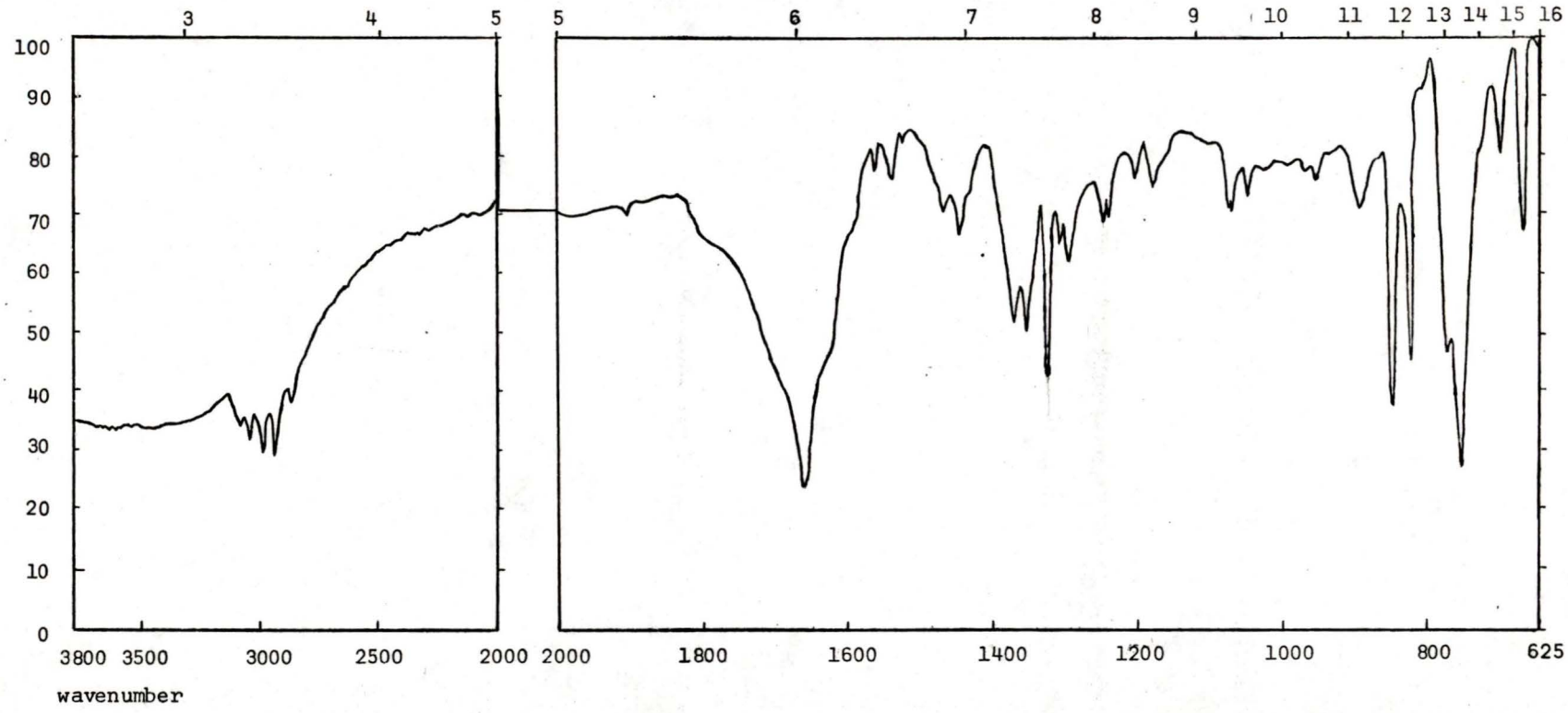
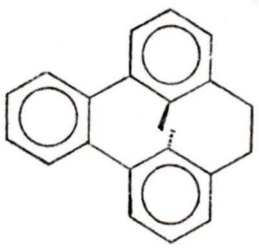


Fig. 3, ir spectrum of trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene(KBr)

below. Final proof for the structure of (20) is obtained from the mass spectrum, where the molecular ion is found at m/e 282 with very strong peaks corresponding to loss of one and two methyl groups. A detailed comparison of the diatropicity and chemical properties of (20) is given in section II-3 below.

II-2. Other synthetic routes

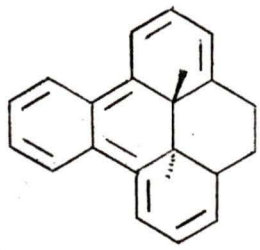
Before the optimum conditions used above were found, and because we were interested in determining whether any alternative to the Hofmann elimination was possible, we investigated a number of other routes to (20). Since compound (37) is effectively a [2,2]metacyclophane-1-ene, and Boekelheide and Blaschke[34] have shown that [2,2]metacyclophane-1-ene can be photoisomerised to



(37)

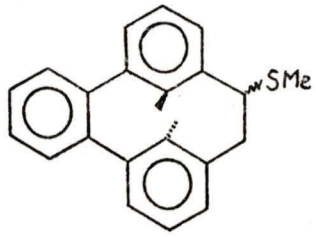
9,10,10b,10c-tetrahydropyrene, we thought it worthwhile to

determine whether (37) would isomerise to the analogous (38) which might then easily be dehydrogenated to the aromatic (20).



(38)

Lithium reduction of the Wittig product (31) in liq. ammonia led to a mixture containing the cyclophane (37) and further ring reduced products, which could not be separated by chromatography. Raney Nickel (W-7) however, cleanly produced the cyclophane (37), mp 156-157°C, in 85% yield. The structure of (37) follows from its mass spectrum, molecular ion at m/e 284 and pmr spectrum in which the bridge protons now appear as an AA'BB' multiplet at δ3.15-2.40, and the internal methyls are exceptionally shielded at δ0.67. These are compared with other cyclophanes in table 3.



(31)

Table 3

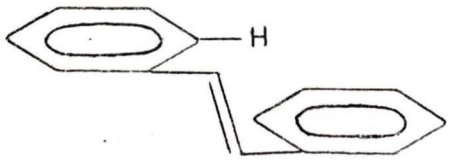
Internal proton chemical shifts (δ) of cyclophane, cyclophane-1-ene and cyclophane-1,9-diene for several metacyclophanes.

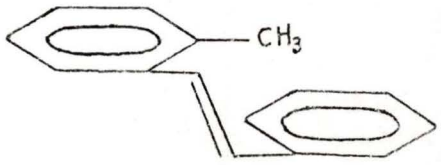
	Cyclophane	Cyclophane-1-ene	Cyclophane-1,9-diene
[2,2] Metacyclophane			
(internal H)	4.17[a]	5.62[b]	7.90[c]
8-methyl [2,2]MCP[e]			
(internal H)	3.72[d]	4.90[d]	
(internal Me)	0.48	0.78	
8,16-Dimethyl [2,2]MCP[e]			
(internal Me)	0.56[a]	0.79[d]	1.52[d]
8,20-Dimethylbenzo [2,2] MCP[e]			
(internal Me)	—	0.67	1.41

a. see ref. 35 b. see ref. 34 p.2748 c. see ref. 14 p.3511
d. see ref. 36 e. MCP: Metacyclophane

It is interesting that the benzene ring of (37) appears to have somewhat less of a deshielding effect than a double bond. However in view of the huge effects that are observed with internal hydrogens, it may be that some change in the geometry is the major

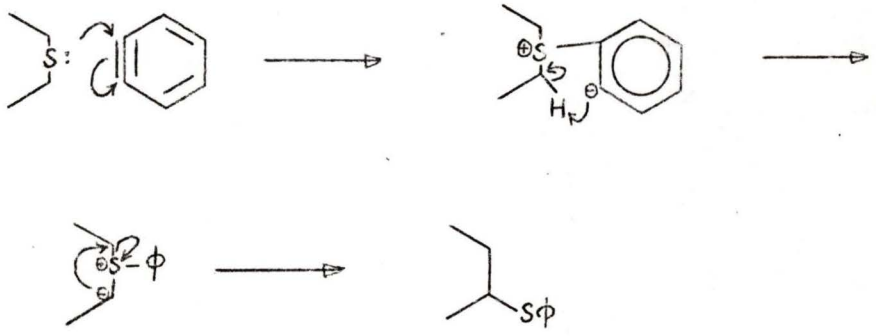
cause, (i.e. that the methyl protons are too far out from the double bond.).





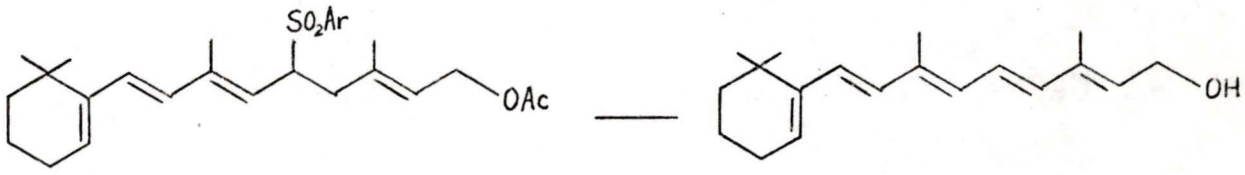
The attempts to phototautomerise(37) to (38) and subsequently dehydrogenate to pyrene (20) failed under a variety of conditions (see experimental).

An alternative to the Wittig rearrangement is a benzyne-induced Stevens rearrangement[37]. Treatment of (29) with benzyne generated[38] in situ from anthranilic acid and isoamyl nitrite gave an 86% yield of the phenylsulphide (39)(see P.30).



mechanism of Stevens benzyne rearrangement

Since the pmr spectrum of (39) showed a similar ABX pattern to that of (31), we assumed that the analogous isomer was present. Further proof of structure of (39) was provided by Raney Nickel reduction to (37) (96% yield) identical to the previously obtained sample. Since it is not very convenient to alkylate a phenyl sulphide (to effect a Hofmann elimination) Boekelheide carried out a sulphoxide elimination to introduce the double bond[37]. However, such eliminations require relatively high temperatures, and are not very convenient on a larger scale. Whereas a sulphinate anion ($RSO_2^{\ominus}$) might not be such a good leaving group as the better known sulphonates, e.g. tosylate $ArSO_3^{\ominus}$, we anticipated that the elimination would be feasible in our systems, since M. Julia and P. Ward have reported[39] base induced sulphinate elimination from sulphonyl vitamin A precursor (40) to give vitamin A alcohol (41).



(40) (41)

Thus oxidation of the benzyne product (39) with hydrogen peroxide in acetic acid gave the sulphone (42) in 80% yield as a fairly insoluble white powder, mp 238-239°C. The pmr spectrum

of (42) was somewhat surprising in that H_X and H_A are almost at the same chemical shift (δ 3.92 and 3.70 respectively) with H_B at δ2.95. Thus conversion of -Sφ into $-SO_2\phi$ has had a marked deshielding effect on H_B and H_A but not on H_X, which has actually undergone some shielding. An analogous situation is found for the $-SO_2Me$ compound (see below) except that H_X is not much affected see table 4.

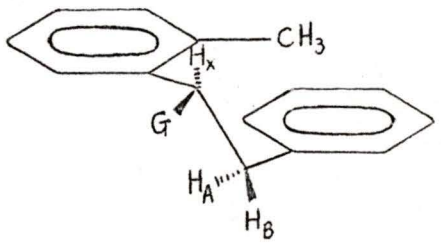
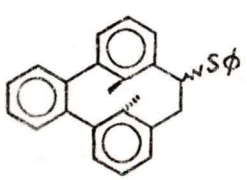


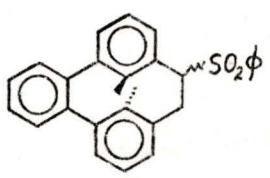
Table 4

Proton chemical shifts (δ) of H_X, H_A, H_B and internal methyl of several thiosubstituted cyclophanes

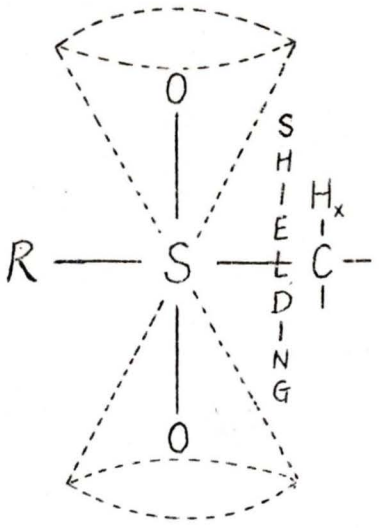
Compound	G	H_X	H_A	H_B	$-CH_3$
(31)	-SMe	3.88	3.28	2.60	0.80
(43)	$-SO_2Me$	3.85	3.72	2.88	0.72,0.70
(39)	-Sφ	4.23	3.25	2.60	0.72,0.67
(42)	$-SO_2\phi$	3.92	3.70	2.95	0.67,0.47



(39)



(42)



Examination of models suggests that H_X is in the shielding cone[40] of the $-SO_2R$ group, whereas H_A and H_B fall in the deshielding region. Presumably the effect is not as marked for H_X when R = Me because Me is less sterically demanding than ϕ.

The structure of the sulphone(42) was however confirmed by mass spectrometry, molecular ion at m/e 424 with the base peak corresponding to loss of $-SO_2\phi$. The ir spectrum showed the $-SO_2$ bands[40] at 1320 and 1155cm^{-1}. The elimination of ϕSO_2H from (42) can be effected by use of potassium t-butoxide in refluxing tetrahydrofuran. The reaction failed in a variety of other solvents(N,N-dimethylformamide, dioxane, pyridine) or with other bases such as potassium hydroxide. The resulting pyrene (20) was obtained in 84% yield and was identical to the previous sample. With this success, the analogous elimination

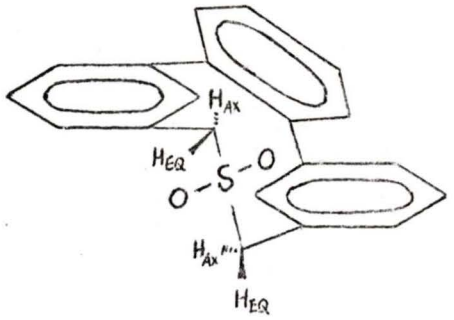
of methanesulfinic acid ($MeSO_2H$) was tried: conversion of (31) to sulphone (43) using again hydrogen peroxide and acetic acid proceeded in 93% yield. Sulphone (43), M^+ at m/e 362, (base peak corresponding to loss of $-SO_2Me$), also showed ir bands at 1295 and 1140cm^{-1} corresponding to $-SO_2$ stretch. Despite several attempts, the maximium yield of (20) obtained in the elimination reaction with potassium t-butoxide and tetrahydrofuran was only 47%.

At this time it came to our notice that Paquette[41] had reported that sulphone (44) can be converted into alkene(45)

(44) (45)

directly by treatment with n-butyllithium and then lithium aluminum hydride in refluxing dioxane. A variety of other examples, including dibenzyl sulphone into stilbene, was also reported. Thus the sulphide (29) was converted into the sulphone (46) in

quantitative yield as above using hydrogen peroxide and acetic acid. The sulphone grouping in (46) differentiated the equatorial and axial protons of the methylene bridges considerably. Models indicate the axial protons fall into the shielding cone of the $-SO_2-$ and these protons appear at δ4.16(d, J = 14 Hz), whereas the equatorial protons are deshielded at δ4.45. The $-SO_2-$ stretch in the ir spectrum is found at 1315 and 1115cm^{-1}. Because of its high mp 310-312°C, the mass spectrum was obtained using



(46)

chemical ionization and gave MH^+ at m/e 349.

On reaction of (46) with n-butyl lithium and lithium aluminum hydride in refluxing dioxane only a small amount of reduced sulphide (29) could be detected; no(20) was found. Paquette notes that a lowering of substitution around the sulphone (44) lowers

the conversion to the alkene. Possibly this has some bearing here. If the mechanism of this reaction involves a 3-membered ring like the Ramberg-Bäcklund rearrangement, then failure may be because of the steric difficulty of generating the 3-membered ring across the cyclophane. Mitchell[42] has noted that the Ramberg-Bäcklund rearrangement fails for metacyclophanes.

II-3. The properties of trans-12c,12d-dimethyl-12c,12d-dihydrobenzo(e)pyrene (20)

II-3a. Diatropicity

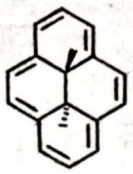
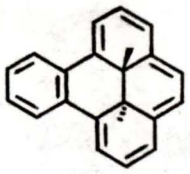
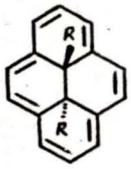
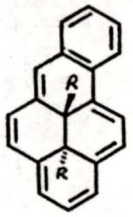
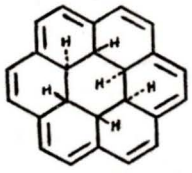
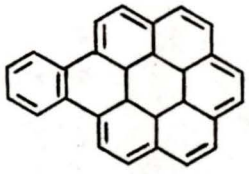
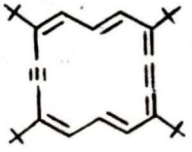
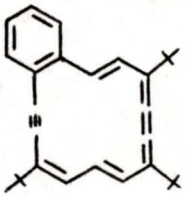
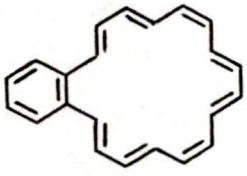
In the introduction, we indicated the most widely applied criterion for aromaticity is that the compound under test should show diatropism. Indeed benzopyrene (20) with its highly shielded internal protons at δ-1.85 and deshielded external protons at δ8.7-6.9 is diatropic. It is however considerably less diatropic than the non-benzannelated parent, trans-10b,10c-dimethyl-10b,10c-dihydropyrene, (12), where the internal methyls are at δ-4.25. Comparison of other monobenzannelated annulenes and their corresponding parents is made in table 5.

Table 5

Chemical shifts (δ) of internal and external protons in selected annulenes and monobenzannelated annulenes

Table 5

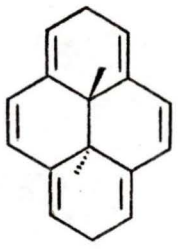
Chemical shifts (δ) of internal and external protons in selected annulenes and monobenzannelated annulenes

set 1.	 (12)		 (20)	
	internal-CH_3	-4.25	-1.85	$\Delta\delta$ 2.4
	external-H	8.7-8.1	8.7-6.9	
set 2,3.	 (12)&(47)		 (17a,17b)	
	internal-CH_3	-4.25	-1.60	$\Delta\delta$ 2.65
	internal-H	-5.5	-1.35	$\Delta\delta$ 4.15
	external-H(R=Me)	8.7-8.1	8.7-7.1	
	external-H(R=H)	8.6-7.9	7.8-7.2	
set 4.	 (13)		 (48)[a]	
	internal-H	-6.54- -7.96	-1.0- -2.6	$\Delta\delta$ 5.3-5.5
	external-H	9.55-9.30	9.9-7.4	
set 5.	 (10)		 (16)	
	internal-H	-4.39	0.81-0.71	$\Delta\delta$ 5.1-5.2
	external-H	9.42	9.08-7.74	
set 6.	 (8)		 (49)[b]	
	internal-H	-2.99	4.75-4.95	$\Delta\delta$ 7.7-8.0
	external-H	9.28	8.05-6.64	

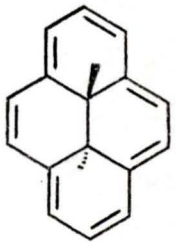
a. see ref. 15. b. see ref. 32b

To determine the change in diamagnetic ring current on benzannelation the difference in shifts ($\Delta\delta$) between the internal protons can be compared with the shift Δ of the parent from a suitable model,

eg.



(50)



(12)

$\delta(CH_3)$=0.95 $\delta(CH_3)$=-4.25

Δ=5.2[+]

The apparent percentage reduction of ring current for

(20) = $\frac{(\Delta\delta)}{\Delta} = \frac{2.4}{5.2} \times 100\% = 46\%$

This calculation is carried for the above examples in table 6.

Table 6

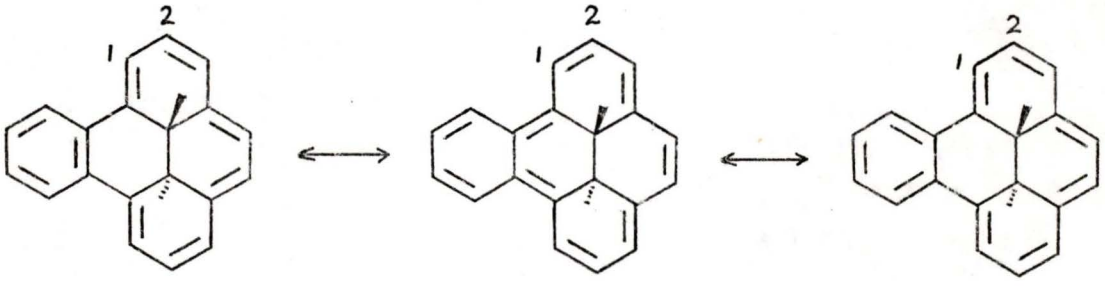
Calculations of the apparent percentage reductions of ring current for monobenzannelated annulenes.

	($\Delta\delta$)	Model	Δ	($\Delta\delta$)/Δ x 100
set 1.	2.4	0.95[+]	5.2	46%
set 2.	2.65	0.95[+]	5.2	51%
set 3.	4.15	2.86[+]	8.35	50%
set 4.	5.3 - 5.5	2.25[+]	8.8-10.2	53-60%
set 5.	5.1 - 5.2	6.5[*]	10.9	47-48%
set.6.	7.7 - 8.0	6.5[*]	9.5	81-84%

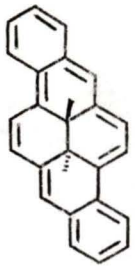
+ see ref. 15 * see ref. 40

Clearly most of the systems have their apparent ring current reduced by approximately 50%. It would appear that the effect on our system, (20) is least, though we can not tell how significant this is. The question then becomes "why does such an apparent reduction of ring current occur?"

Mitchell has suggested[25] that this is because the Kekulé structures of the benzannulene are no longer equivalent(or identical)

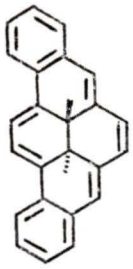


i.e. bond 1-2 has 2/3 single bond character and 1/3 double bond character, assuming all three structures are equally contributing. In other words, complete electron delocalisation does not occur, with a consequent reduction of ring current and hence reduction in shielding of internal substituent. To support this argument the dibenzo systems shown below have been prepared, and those with



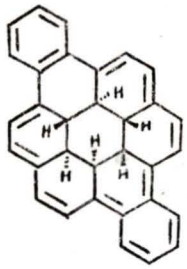
(18a)[a]

δ -3.58
internal-CH_3



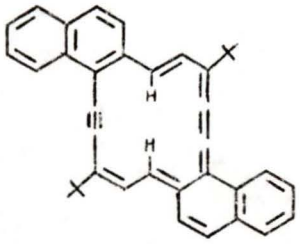
(19b)[a]

δ 0.02
internal-CH_3



(51)[b]

δ -3.5- -5.3
internal-H



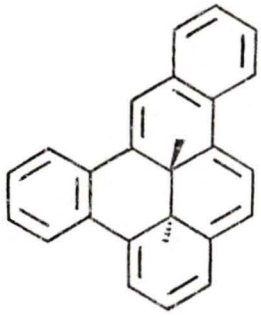
(52)[c]

δ -3.45
internal-H

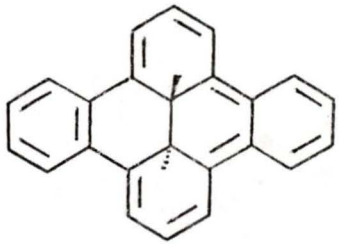
a. see ref. 25. b. see ref. 15. p.2454. c. see ref. 12. p.917.

symmetrical Kekulé structures (i.e. peripheral bonds 50% double, 50% single) are all strongly diatropic, whereas (19) which lacks symmetrical Kekulé structures is only weakly diatropic.

Such ideas could be further strengthened by preparation of



(53)



(54)

(53) and (54), since (53) lacks symmetrical Kekulé structures and hence could be expected to show its internal $-CH_3$ at δ0.3 whereas (54) should be diatropic and have its internal $-CH_3$ at δ-3.9.

Our initial attempts at the synthesis of (54) are noted in section II-7 below.

The above results are also further supported by chemical shifts of ^{13}Cmr spectra as shown in table 7.

Table 7

Chemical shifts from ^{13}Cmr spectra of several dimethyldihydropyrenes (downfield form TMS)

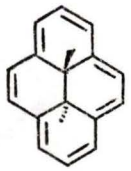
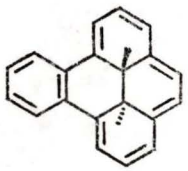
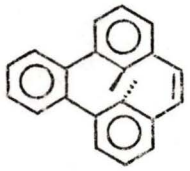
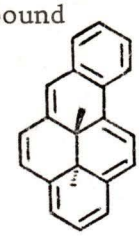
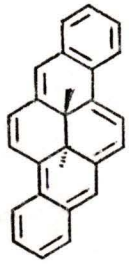
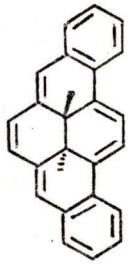
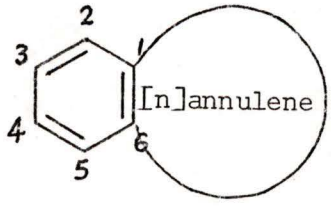
	internal-CH_3	internal bridge
 (12)	14.0	30.0
 (20)	16.8	35.2
 (36)	19.5	---

Table 7 continued

compound	internal-CH_3	internal bridge
 (17b)	17.0,17.7	35.5,36.0
 (18b)	15.9	32.8
 (19b)	19.2	39.5

II-3b Q-Test

Günther[23] has proposed a method where by the benzene nucleus of benzannulenes may be used as a probe for the π-electronic structure of the annulene itself.



In this analysis, it is assumed that the bond orders of the C(2)-C(3) and C(3)-C(4) bonds of the benzene ring depend only on that π-electronic structure, which is influenced by the nature of the condensed annulene system.

From HMO or SCF calculations, the bond orders P_{23} and P_{34} can be calculated, and their ratio $Q=P_{23}/P_{34}$ used as a parameter to classify the [n]annulene ring†. Thus when the [n]annulene is a $(4q + 2)\pi$ system, Q is predicted to lie between 1.14 and 1.20, and for a $4q\pi$ system, Q is predicted to lie between 0.96 and 1.03. These figures are based on HMO calculations and are modified somewhat for SCF calculations. Clearly a $(4q + 2)\pi$ [n]annulene has a much greater effect on the benzene ring (i.e. it localises the bonds) than does a $4q\pi$ system.

Table 8

Predicted Q values for benzo[n]annulenes based on SCF calculations.

n	Q
6	1.262
8	0.930
10	1.196
12	0.984
14	1.143
16	1.016
18	1.108

To verify this equation some relationship between bond order and a measurable quantity is required. It has been shown[23] that

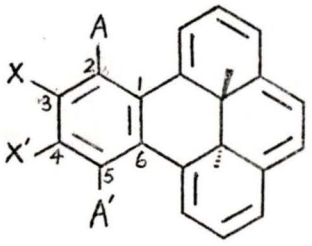
† The integer n refers to the total number of π-electrons of the annulene ring (q = 1,2,3 & 4) in this section.

estimates of bond order can be made from vicinal H-H (^{3}Jcis) coupling constants. For benzenoid hydrocarbons the relationship is

$$P_{\mu,\nu}(SCF) = 0.104\,^3J_{\mu,\nu} - 0.120 \qquad \text{eq[1]}$$

Thus by measurement of ^{3}Jcis in the C_2-C_3 and C_3-C_4 bonds in the benzo[n]annulene, an experimental determination of Q can be made.

Thus far experimental evidence of the validity of this test has only been obtained for n=6,8 and 10.[44] System (20) would present the first evidence for a macrocyclic annulene. Fortunately the AA' part of the AA'XX' spectrum is well removed from the rest



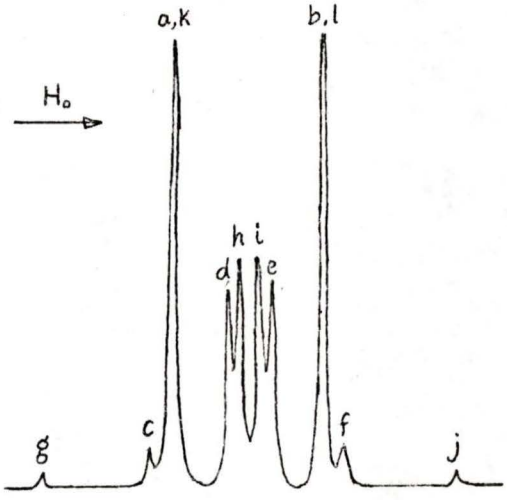
(20)

of the protons and sufficiently resolved for analysis. The coupling constants are obtained as follows:[45]

For simplicity let

$$J_{23} = J_{45} = J$$
$$J_{34} = J_X$$
$$J_{24} = J_{35} = J'$$
$$J_{25} = J_A$$

Then the spectrum should appear as



where $N = J + J'$ $\quad L = J - J'$

$K = J_A + J_X$ $\quad M = J_A - J_X$

then $N = a - b$

L $N = \sqrt{(c-f)(d-e)} = \sqrt{(g-j)(h-i)}$

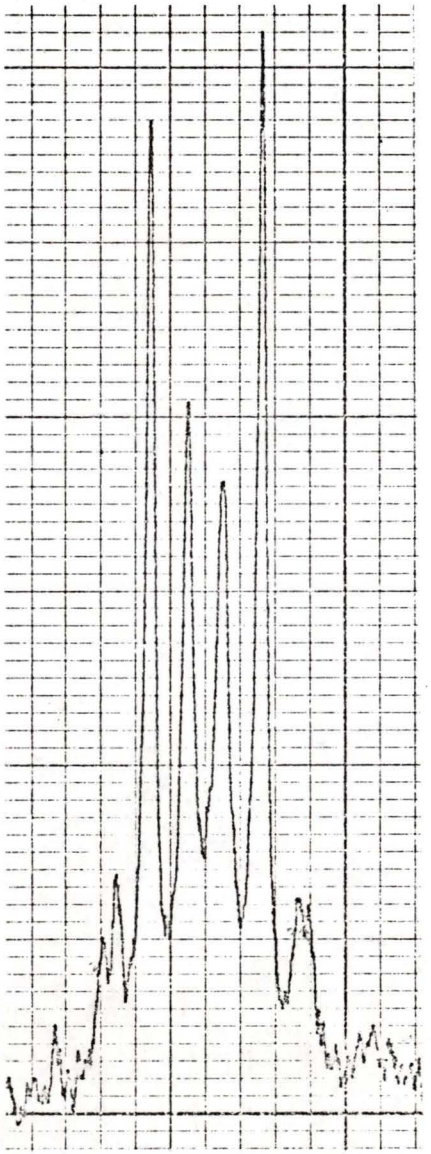
$K = g-h = i-j$

$M = c-d = e-f$

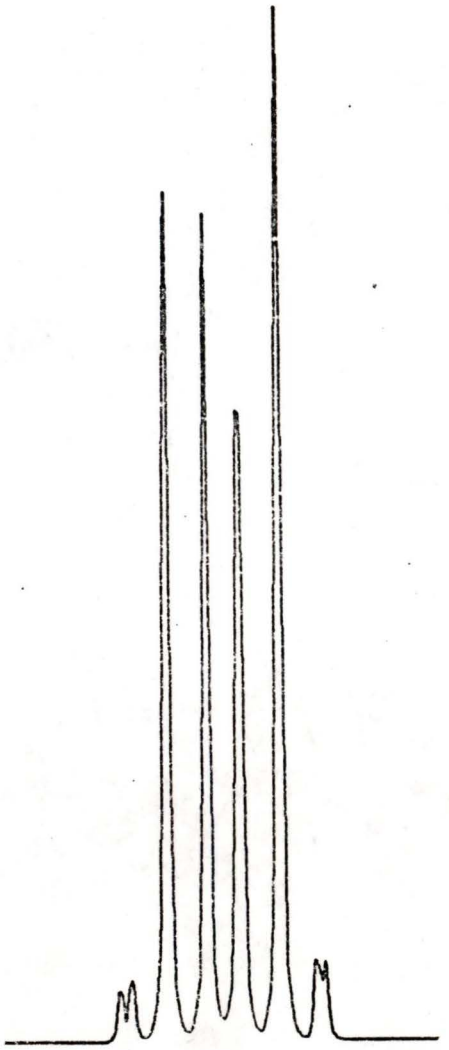
Our initial estimates obtained for these coupling constants were $J = 8.28$Hz, $J_X = 6.83$Hz, $J' = 1.39$Hz and $J_A = 0.50$Hz.

These were refined by iteration using the computer program (obtained from Dr. K. R. Dixon) which then produced the simulated spectrum shown in Fig. 4, in good agreement with the actual spectrum.

Fig. 4. AA' part of the actual and simulated AA'XX' spectrum of (20)



Actual spectrum of (20)



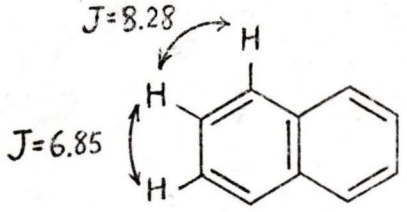
Simulated spectrum of (20)

The values thus obtained were

J_{23} = 8.26 Hz J_{34} = 6.93 Hz

J_{24} = 1.37 Hz J_{25} = 0.49 Hz

Application of equation [1] then gives for (20), Q = 1.23, verifing Günther's hypothesis. An interesting comparison can be made with naphthalene where Q = 1.252.



Günther's predictions based on SCF calculations suggest Q will decrease for a $(4q + 2)\pi$ system as the [n]annulene increases. From table 8 the values predicted for n = 6 and n = 14 are 1.262 and 1.143, whereas those found are 1.252 and 1.232.

This would suggest that bond alternation in [n]annulenes is not setting in as fast as predicted, i.e. the aromaticity of (12) is not much less than that of benzene.

II-3c. Chemical Reactions.

Whereas the pmr and ^{13}Cmr spectra discussed above clearly indicate (20) to be diatropic, the classical description of an

aromatic compound might still be viewed as 'one that undergoes electrophilic substitution reactions'. In this regard, attempts have been made to electrophilically substitute most of the major novel aromatic systems that have recently been prepared. Thus Sondheimer[46] showed that [18]annulene could by nitrated and acylated, and Boekelheide[27] and Vogel[47] did the same for trans-10b,10c-dimethyl-10b,10c-dihydropyrene (12) and 1,6-methano [10]annulene (6), respectively. However thus far no benzannulene has been successfully electrophilically substituted. With the encouragement of the relatively strong diatropism for (20) above, and the fact that (20) seems to be a reasonably stable benzannulene, we decided to attempt substitution reactions on it.

Treatment of (20) with copper(II)nitrate trihydrate and acetic anhydride at $0^{o}C$ gave mainly the mononitro derivative (55), as dark blue crystals mp 163-164^{o}C. Compound (55) could be isolated in 35% yield. The structure was assigned on the basis of the mass spectrum, M^{+} at m/e 327 with peaks corresponding to loss of $-CH_3$, two-CH_3's, CH_3 and NO_2, and two $-CH_3$'s and NO_2's. In the ir spectrum the $-NO_2$ bands could be seen at 1485 and 1285cm^{-1}. The uv spectrum (Fig. 5) showed a bathochromic shift with respect to (20), the main visible λmax shifting to 592nm from 502nm, a somewhat greater shift than for (12). The pmr spectrum showed the aromatic protons

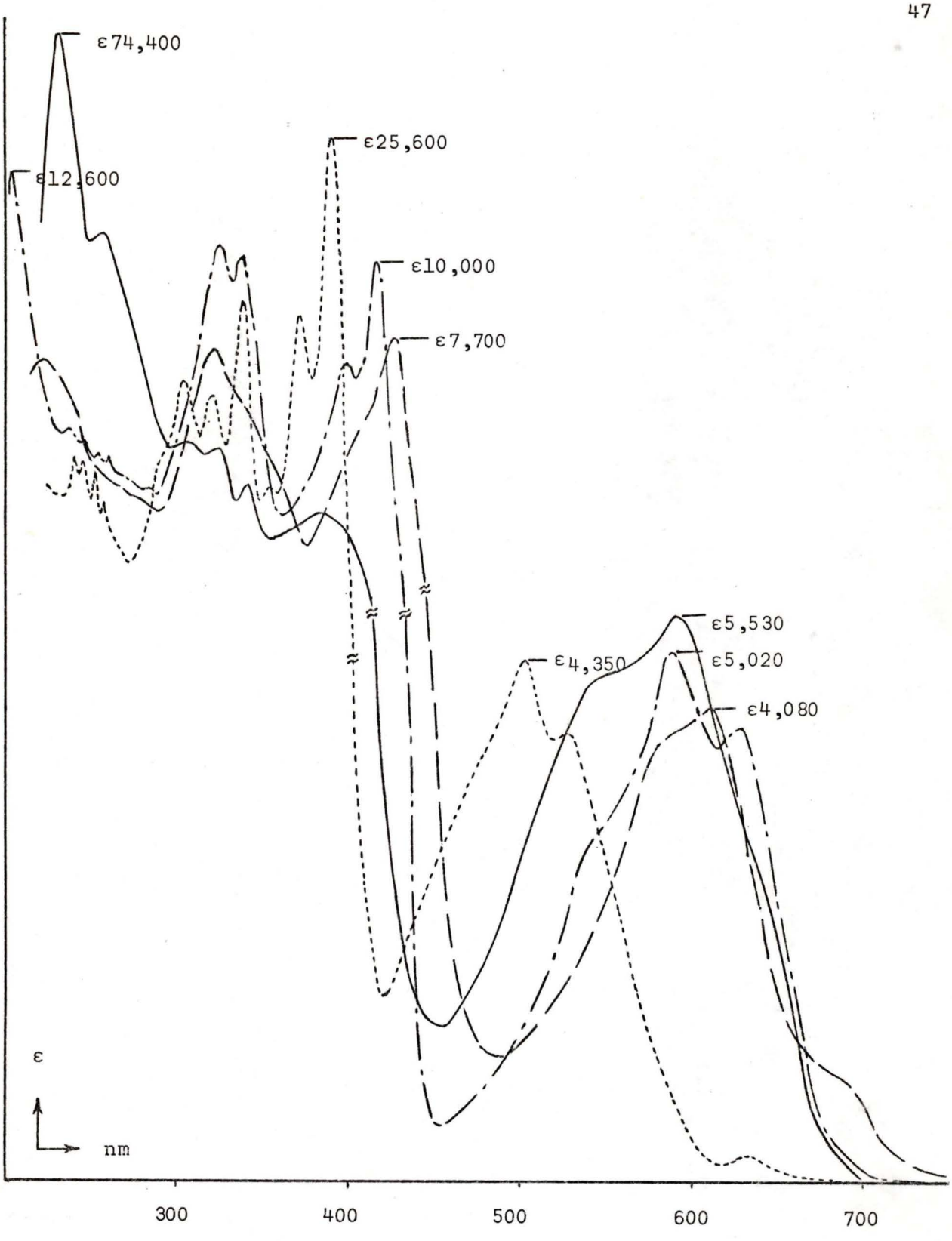
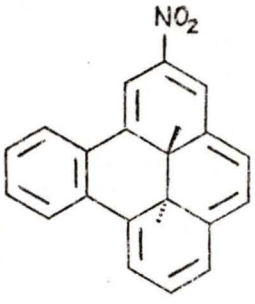


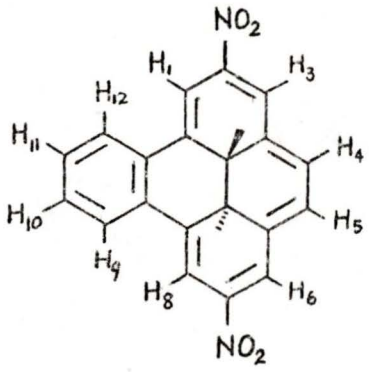
Figure 5 . U. v. and visible spectra of (20) (·-·-·-·-), (55) (———), (56) (—·—·—) and (57) (— —) taken in cyclohexane using a Carey 17 spectrophotometer.

to be more spread out (δ9.2-7.3) in comparison to (20), presumably because of local deshielding by the nitro group. The internal methyl protons remain at δ-1.85 as in (20) and are unresolved from each other. This at first sight was surprising, but those for nitro-(12) are also unresolved, and hardly affected in chemical shift[27]. The chemical shift of the methyl group in toluene is also almost the same as in the nitrotoluenes[48]. We tentatively assigned (55) as the 2-nitro derivative on the basis of the disubstitution product below.

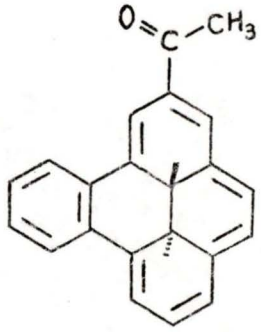
When the nitration was carried out at 20°C, the dinitro derivative (56) was the major product, isolated in 20% yield as dark blue crystals mp 197°C(dec), molecular ion, MH^+ = 373. The ir spectrum of (56) was considerably simpler than that of the mononitro derivative (55), showing only three major bands below 1000 cm^{-1}. This suggests that the molecule is symmetrical, and both the pmr and ^{13}Cmr spectra strongly support this argument. The latter shows only 5 peaks corresponding to aromatic carbons



(55)



(56)



(58)

bearing a hydrogen atom. The pmr spectrum supports the 2,7-dinitro structure shown for (56) and shows a 2H doublet at δ9.09 with J = 1.5 Hz assigned to protons H-1,8. The adjacent nitro group strongly deshields H-1,8 and they show a typical meta-coupling to H-3,6. The AA' part of the AA'XX' of H-9,12-10,11 can still be seen at δ9.2-8.6, consistent with nitration occurring in the 14π ring. The large singlet at δ7.92 for H-4,5 is also clearly visible, with H-3,6 appearing at δ8.71 as a doublet (J = 1.5 Hz) deshielded by the nitro group from their position in(20) (ca δ7.5). We believe that this spectrum is not consistent with any other substitution pattern. Further this is the same substitution pattern that the parent (12) shows itself[27]. The internal methyl protons show a small downfield shift to δ-1.60. The uv spectrum of (56) is shown in Fig. 5 and is further bathochromically shifted from (55).

When excess cupric nitrate was present (e.g. 4-5 equivalents) at room temperature, the major product was a trinitro derivative (57)[†], isolated in 18% yield as dark green crystals, dec 198°C, possibly as a mixture of isomers. The mass spectrum indicated three nitro groups to be present, MH^+ = 418, and the uv spectrum, Fig. 5, was further bathochromically shifted from (56). The pmr spectrum showed

[†] Analysis obtained by high resolution mass spectrometry.

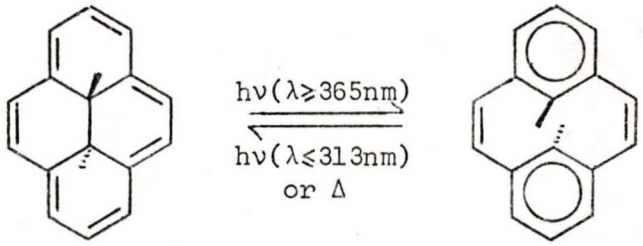
the aromatic protons even more deshielded, δ9.7-7.85, and the two internal methyls appeared as singlets at δ-1.50 and -1.55.

The benzannulene (20) could be acetylated using acetic anhydride and a few drops of boron trifluoride etherate as catalyst at room temperature to give the monoacetyl derivative (58) in 76% yield as dark purple crystals, mp 140-142°C. The structure was assigned on the basis of its mass spectrum, molecular ion at m/e 324, with peaks corresponding to facile loss of $-CH_3$; CH_2CO and CH_3; CH_3CO and CH_3. The pmr spectrum showed the aromatic protons at δ9.2-7.1, the $-COCH_3$ at δ2.80 and the internal methyl protons at δ-1.67. In the uv spectrum the longwavelength maximum is at 538 nm, bathochromically shifted from the parent (20) at 502 nm, but nowhere near as much as for the nitro compound at 592 nm. This is consistent with results on the parent system (12) : substituent (λmax) H(204 nm), $COCH_3$(246 nm) and NO_2(269 nm).[49]

Thus (20) can clearly undergo electrophilic substitution reactions, and is the first benzannulene where this has been successful.

II-4. The photochemistry of the benzannulene (20) and its derivatives.

One of the more interesting aspects of trans-10b,10c-dimethyl-10b,10c-dihydropyrene (12) is its reversible photochemical valence tautomerisation into [2,2]metacyclophane-1,9-diene (59).

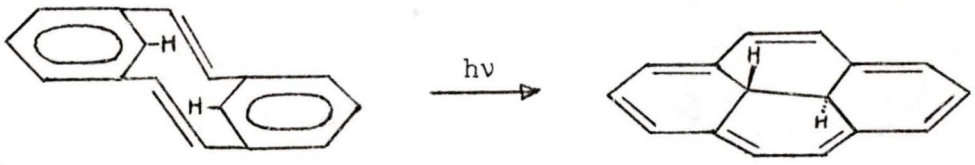


(12) (59)

This is a specialised example of the more general cis-stilbene 4a,4b-dihydrophenanthrene isomerism studied by Fischer[50] and others[51], of which [2,2]metacyclophane-1-ene ⇌ 9,10,10b,10c-tetrahydropyrene[52] is a further related example.

The photochemistry of (12)⇌(59) has been well studied by Blattman and Schmidt[53] and has been shown to be a fully reversible photoequlibrium, with (12) being the thermodynamically more stable tautomer by about 11 kj/mol(ΔG^{o}_{f298}). Thus far the tautomerisation has been observed in ca 30 derivatives of (12)[53]. Schmidt has suggested that the tautomerisation is in agreement with Woodward-Hofmann rules except that one would not then expect the thermal back reaction, a process forbidden by the symmetry allowed for the photochemical transformation. Schmidt has suggested the

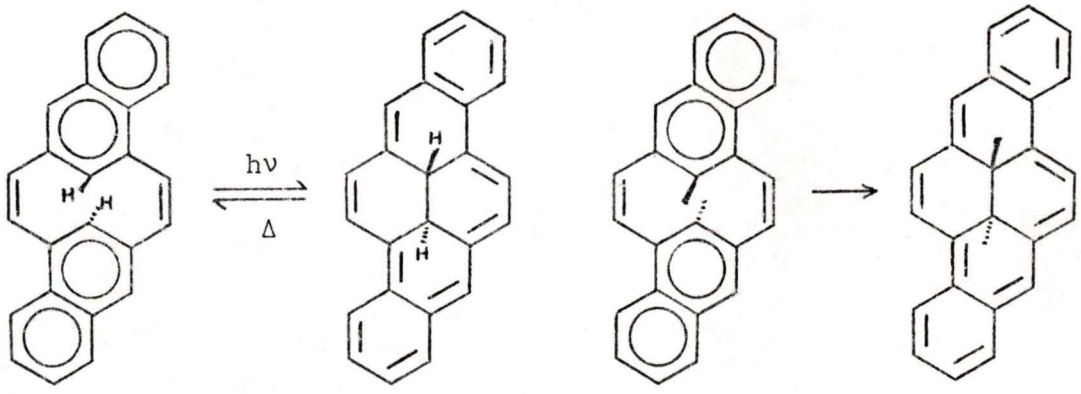
photoisomerisation is fast because the energy difference between reactant and product is small and because these systems have a fairly low activation energy (ca 97 kj/mol). According to Fischer[52], in view of the rigid structure of the molecule, the geometry of the excited state cannot be very different from the ground state, unlike the cis-stilbene ⇌ dihydrophenanthrene case where rotation of the phenyl rings is involved. In the case of (12)⇌(59), (12) is the thermodynamically more stable. This suggests that it is advantageous to disrupt two benzene ring π-delocalisations and relieve the strain present in the cyclophane (59) to form the 14π electron delocalised system of (12). This is very finely balanced. For example in the case of 10b,10c-dihydropyrene (47), itself, the cyclophane diene form (60) can readily be isolated[14], whereas in the methyl substituted case,



(60) (47)

only the dihydropyrene form can be isolated. Presumably this is because of the small size of -H relative to $-CH_3$ and hence

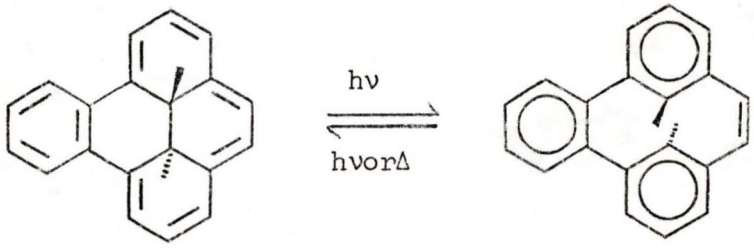
the slight reduction in strain energy in (60) relative to (47) compared to (59)—(12). Mitchell has reported[54] that in the case of the dibenzannulene (18a), the thermodynamically more stable isomer is in fact the open form (61), whereas in the case of the



(61) (18a) (62) (18b)

methyl substituted examples (18b) and (62), the more stable isomer is the closed form (18b).

It was thus of considerable interest to investigate the photochemistry of (20).



(20) (36)

On closure of (36) to (20), the π electron delocalisation of

three benzene rings must be at least partially disrupted. The relief of strain however might be somewhat greater than for (59), because of the constraints of the fused benzene ring. It is thus difficult to predict which form would be the more stable. In fact (20) is the tautomer isolated, and is the one formed when solutions of (36) are heated, and hence must be the thermodynamically more stable. However the conversion (36) → (20) is much slower than for (59) → (12), indicating a larger activation barrier, perhaps for the reasons mentioned above.

The reaction rate for (36) → (20) and the energy of activation for this reaction can be measured as follows: From the rate equation for a first order reaction

$$\frac{-d[A]}{dt} = k[A] \qquad \text{eq[2]}$$

where [A] is the concentration and k is the first order rate constant, integration gives

$$\ln(A_o/A)^{\dagger} = kt$$

$$\text{or} \quad \log(A_o/A) = \frac{k}{2.303} \times t$$

Thus k can be calculated as 2.303 × slope of a plot of $\log(A_o/A)$ vs t.

The concentration of (36) or (20) could be estimated either from uv or pmr spectra. Whereas Balttman and Schmidt[53] found uv

---

† $[A_o]$ refers to the initial concentration of the open tautomer (fully converted).

to be most convenient, in our systems we found pmr methods to be preferred.

The dihydropyrene was dissolved in C_6D_6 and irradiated with visible light to convert to the colourless cyclophane-diene form, and the thermal return was followed by recording the integration† of the internal $-CH_3$ signals of both forms at suitable intervals.

The results for the parent (20), the nitro derivative (55), the acetyl derivative (58) and the methyl-derivative (66) (see section II-5 below) are given in Table 9 and in graphical form in Fig. 6 & 7.

Table 9

Rate constants of valence tautomerisation for parent (20) and its derivatives. ($k \times 10^4 min^{-1}$)

Compound	k_{22^o}	k_{32^o}	k_{42^o}
(20)	0.78	4.4	11
(55)		600	
(58)		135	
(66)		4.3	

The dinitro compound (56) was too fast to measure by this method.

As can be seen from table 9 the order of rate constants is nitro pyrene (55) > acetyl pyrene (58) > parent pyrene (20) > methyl pyrene (66). This is consistent with the results of

† or by cutting out and weighing the peaks

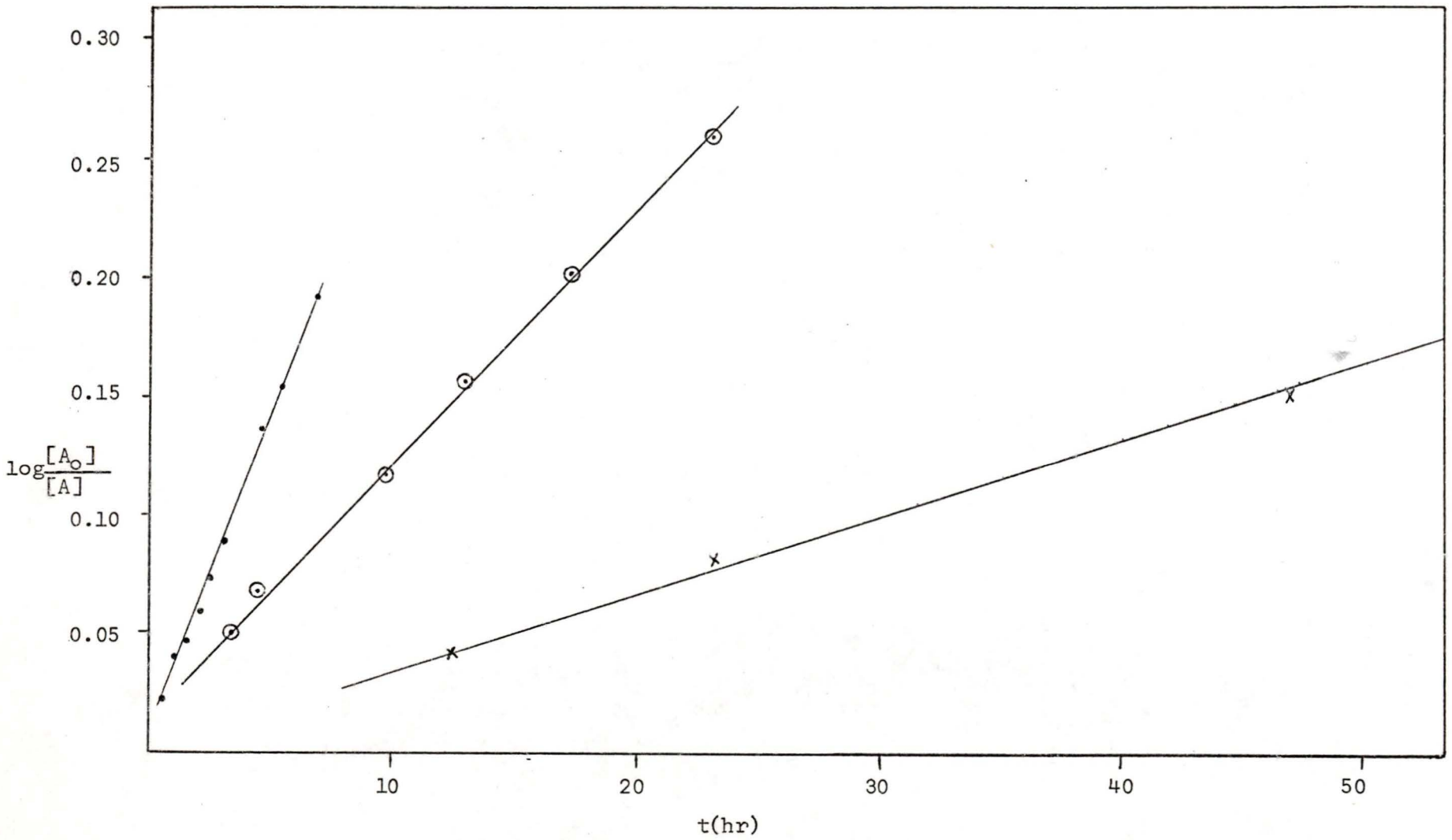


Fig. 6. Log[A_o]/[A] plotted against time for valence tautomerisations of parent (20) at 22°C(-×-×-), 32°C(-o-o-) and 42°C(-•-•-). The rate constants for the tautomerisation are calculated from the slope × 2.303 of the straight lines.

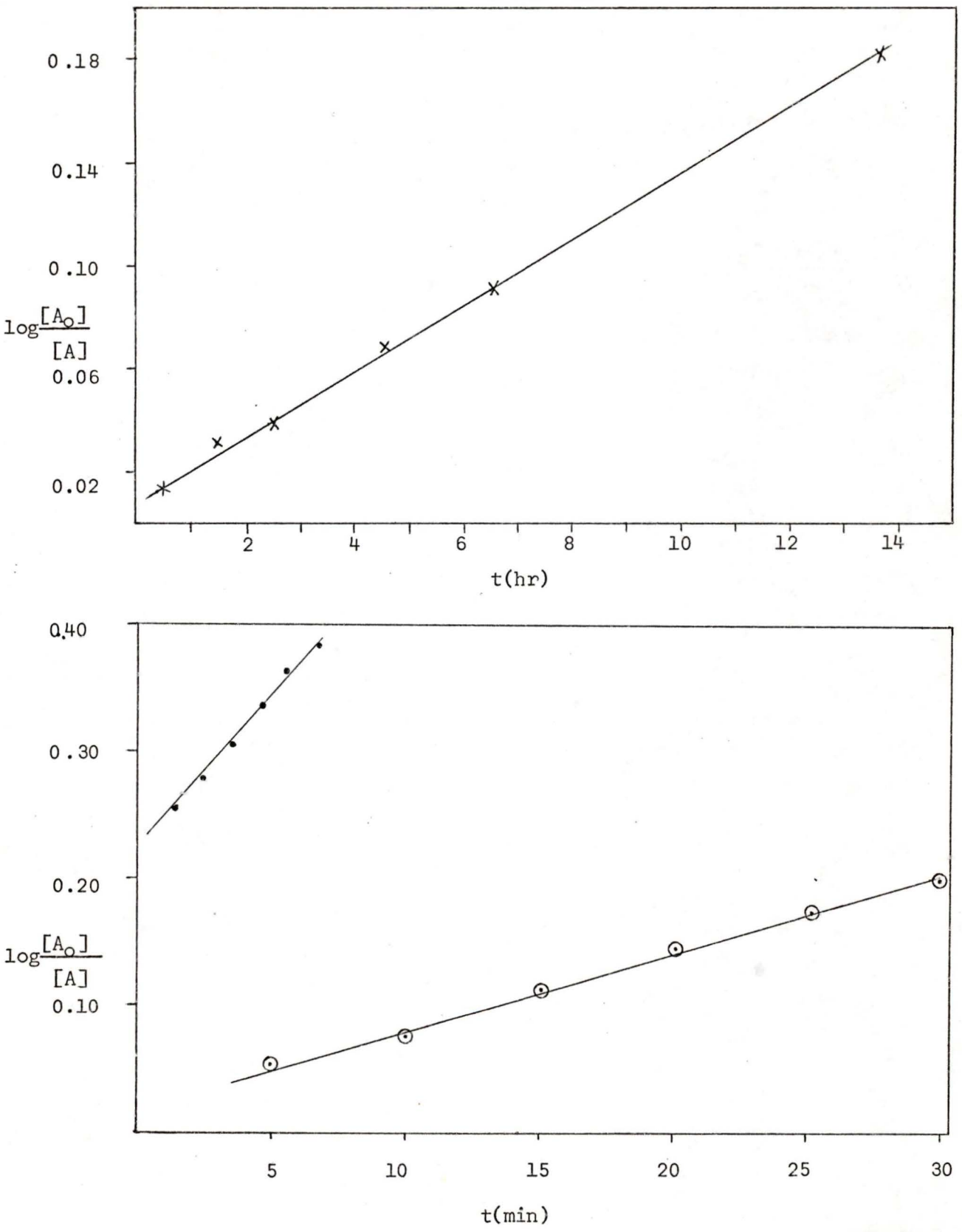


Fig. 7. Log$[A_o]/[A]$ plotted against time for valence tautomerisations of nitro-(55)(•—•), acetyl-(58)(o—o) and methyl-(66)(×—×) at 32°C. The rate constants for the tautomerisation are calculated from the slope × 2.303 of the straight lines.

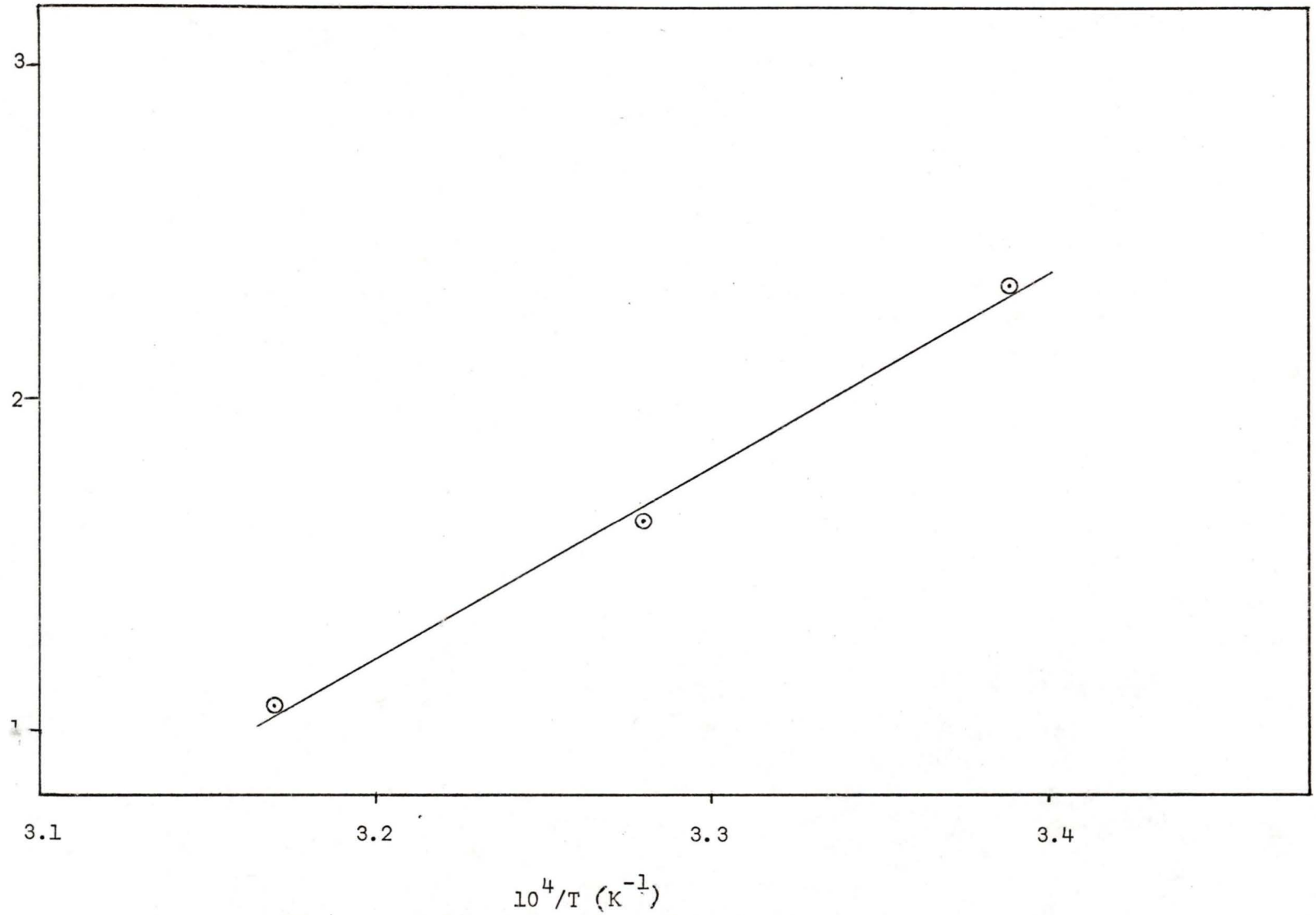


Fig. 8. -Logk plotted against reciprocal absolute temperature for valence tautomerisation of trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene. The activation energy of the tautomerisation is calculated from the slope × 2.3R of the straight line.

Schmidt[57]. The rate constant reported for the parent (12) is $10 \times 10^{-4} min^{-1}$ at 30°C, which is faster than for (20), in agreement with our observations.

For (20), rate constants were estimated at three different temperatures such that an approximate value of the energy of activation for (36)→(20) could be obtained. From the plot of -log k vs 1/T(Fig.8), E_{act} is obtained as the slope × 2.303R and is estimated to be 105 kj/mol. This is somewhat higher than that reported[53] for (59)⇌(12) (96.6 kj/mol) in agreement with our observations. As a result system (36)→(20) is somewhat unusual for a dimethyldihydropyrene in that the open cyclophane diene form (36) can be almost completely obtained in solution, permitting somewhat easier than normal spectral data collection for these compounds. The chemical shifts of spectra are given in table 10.

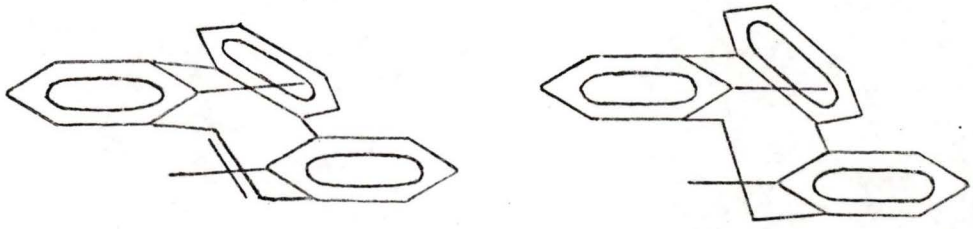
Table 10

Chemical shifts from pmr spectra of several cyclophane-diene tautomers (90 MHz, δ).

Compound	External ArH	Bridge=CH	Other 'H'	Internal CH_3
Parent-(36)	8.1-6.9	6.63(s)		1.41(s)
5-acetyl-(63)	7.8-6.7	6.49(s)	2.52(s,-$COCH_3$)	1.41,1.37(s)
5-nitro-(64)	7.8-6.7	6.48(s) 6.46(s)		1.41(s)
1-methyl-(65)	7.7-6.4	6.22(bs)	2.21(s,-CH_3)	1.28,1.25(s)
(59)*	7.0-6.2	6.24		1.52(s)
(37)	7.8-7.0		3.1-2.4(-CH_2-)	0.67(s)

* see ref. 14 page 1549

From the table it can be seen that the shielding of the internal $-CH_3$ protons is not very dependent on substituents, however the other methyl protons in table 10 are considerably deshielded from those of the saturated cyclophane (37). This is probably partly because the protons are deshielded by the near perpendicular double bond, and partly because the double bond introduces a change in geometry. Models suggest less distortion in (36) than (37), i.e. the $-CH_3$ is not pushed so far over the face of the opposite benzene ring.

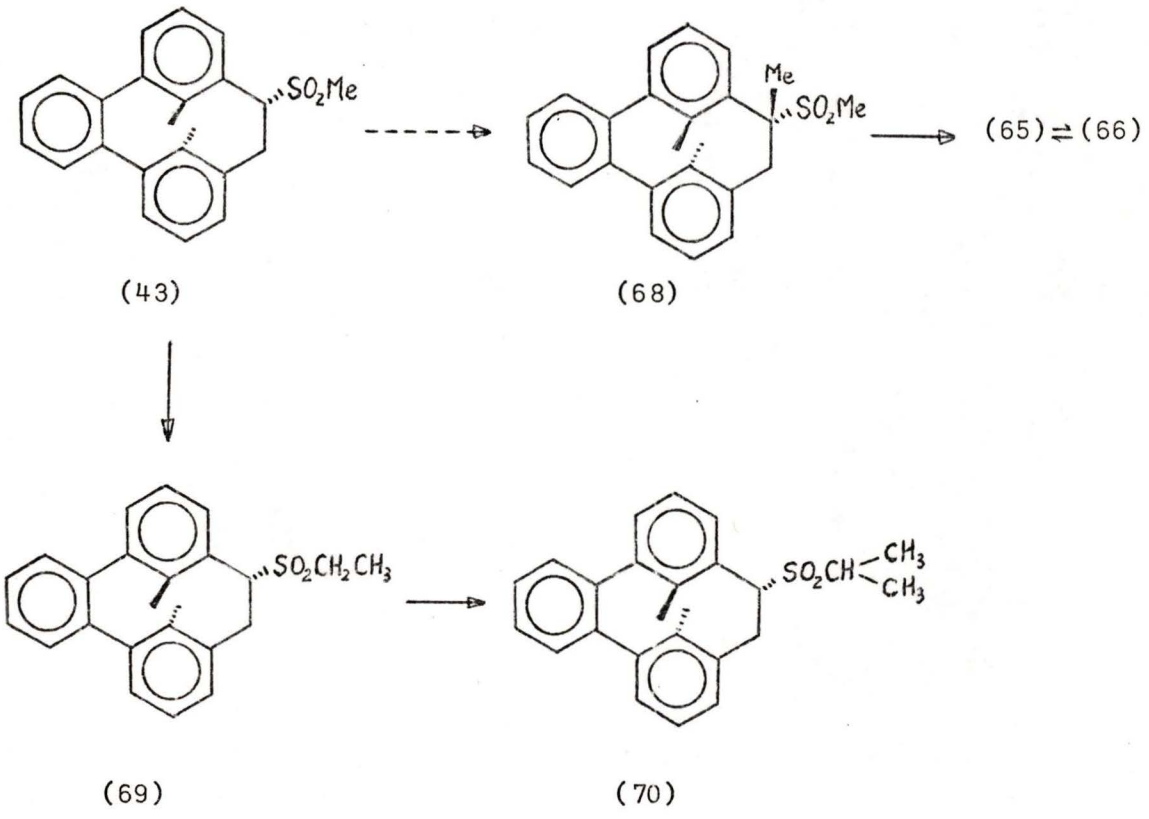


(36) (37)

II-5. Synthesis of a methyl-substituted benzodihydropyrene: 4,12c,12d-trimethyl-12c,12d-dihydrobenzo(e)pyrene(66).

Boekelheide and Sturm[55] reported the synthesis of 4,10b,10c-trimethyl-10b,10c-dihydropyrene (67) by a rather long and involved route. It occurred to us that it might be possible to introduce

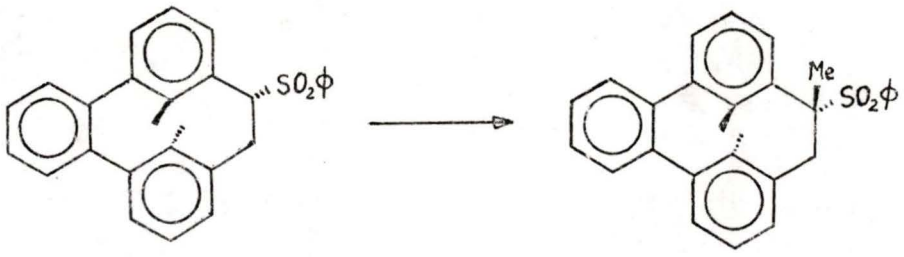
an alkyl substitutent at the cyclophane bridge positions by making use of the sulphur atom in the starting thiacyclophanes. We thought that it should be possible to alkylate the sulphone (43), since a sulphone is a strong electron-withdrawing group and should be able to stabilise an adjacent anion[56]. It was thus projected that methylation of (43) would yield (68) which on elimination would give (65)⇌(66).



However, when the reaction was carried out, methylation proceeded entirely at the methyl side of the sulphone to give the ethyl sulphone(69) and then the isopropyl sulphone (70), rather than at the hoped for benzyllic side of the sulphone. Presumably although the latter side of the sulphone is more acidic, it is more sterically hindered. The ethylsulphone(69) was isolated in 69% yield, mp 198-200°C. The structure of (69) was readily assigned on the basis of the pmr spectrum which showed a $-\underline{CH}_2-CH_3$ quartet at δ3.21 and the $-CH_2-\underline{CH}_3$ triplet at δ1.34, and the mass spectrum which gave molecular ion at m/e 376 and the base peak at m/e 283 corresponding to loss of $-SO_2Et$. With excess lithium diisopropylamide and methyl iodide, the isopropylsulphone (70) was obtained in 65% yield, mp 242-244°C; the pmr was somewhat more complicated (see experimental), but the $-CH\begin{smallmatrix}\underline{CH}_3\\ \underline{CH}_3\end{smallmatrix}$ groups could clearly be seen as doublets at δ1.47 and 1.23. The mass spectrum gave a molecular ion at m/e 390 with base peak again at m/e 283 corresponding to loss of $-SO_2CH(CH_3)_2$.

To overcome this problem we substituted the phenyl sulphone (42) which can only alkylate on the desired side to give (71).

In fact (71) was obtained in 89% yield, as colourless crystals which decomposed at 218°C. The pmr spectrum of (71) showed the



(42) (71)

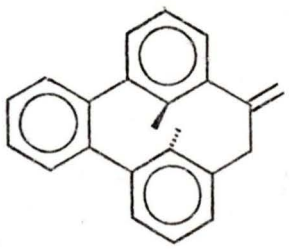
aromatic protons at δ8.1-7.0; the methylene bridge protons were separated, one deshielded by the $-SO_2\phi$ to δ3.67 and the other at δ2.62(1H each, d, J=15Hz), and the bridge substituted $-CH_3$ appeared at δ1.70. The internal methyl groups were well separated at δ1.23 (deshielded by $-SO_2\phi$) and δ0.72. The ir spectrum showed the $-SO_2-$ stretch at 1290cm^{-1}. The molecular ion at m/e 438 was rather weak in the mass spectrum, the base peak at m/e 297 corresponding to loss of $-SO_2\phi$.

Treatment of a refluxing solution of sulphone (71) in tetrahydrofuran with potassium t-butoxide gave two products in a 1:9 ratio (pmr). The major product was the desired purple dihydropyrene (66) obtained in 77% yield mp 158-159°C. The pmr spectrum showed quite similar aromatic protons to those of the parent (20), with H-9,12 appearing at δ9.0-8.7, H-1,8 at δ8.35 and 8.30 (d,7Hz each),

remaining ArH at δ 8.0-7.0, the bridge $-CH_3$ at δ 2.61, and the internal methyls shielded at δ -1.90 and -1.95. The uv spectrum showed the expected bathochromic shift for methyl substitution[57]. The mass spectrum showed the molecular ion at m/e 296 with facile loss of one and two $-CH_3$ groups.

To separate the minor product from the purple dihydropyrene it was necessary to chromatograph the reaction mixture on a column wrapped in foil such that (66) was not irradiated and converted into its photo tautomer (65), which travelled almost identically to the minor product on t.l.c.

The minor product, obtained in 9% yield as colourless crystals, mp 143-145°C, was assigned the structure of the exomethylene compound (72) on the basis of its pmr and mass spectrum. In the latter, the molecular ion at m/e 296 indicated it to be an isomer

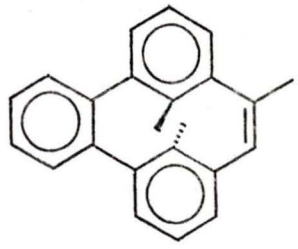


(72)

of (65). It also readily lost one and then two $-CH_3$ groups. The

pmr spectrum clearly indicated it to be a cyclophane with its internal $-CH_3$ groups at δ0.76 and 0.67. The vinyl protons appeared as broad singlets at δ5.28 and 4.96, with the methylene bridge $-CH_2-$ as an AB superimposed dd(=t) at δ3.46 (J=14Hz) and the aromatic protons at δ7.8-6.8. Presumably the exomethylene group deshields one of the internal $-CH_3$ groups slightly.

This elimination is interesting in that it indicates that there is not a very great difference in the stabilities of the two alkenes (65) and (72). At first sight this is somewhat



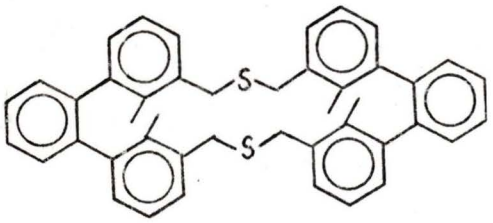
(65)

surprising since (65) is trisubstituted and if planar would be conjugated, and hence considerably favoured over (72). The observed ratio indicates that conjugation in (65) must be severely limited as predicted by models.

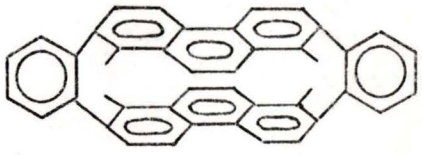
This synthesis has demonstrated that it is feasible to use the sulphone grouping as a method to introduce at least alkyl

substituents into the ring at the 4,(5) positions, and that a methyl group on the bridge does not interfere with the photovalence tautomerisation (see section II-4 above).

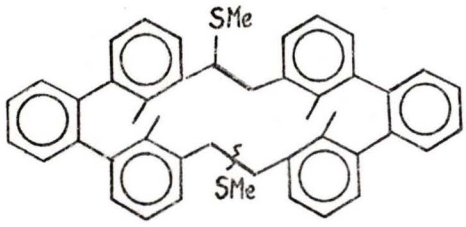
II.6. Attempted conversion of the dithiacyclophane (30) to a macrocyclic unsaturated system. The preparation of a terphenylophane.



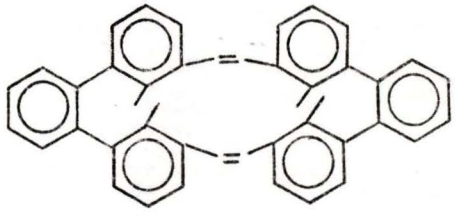
(30)



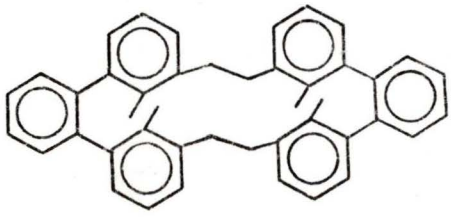
(74)



(75)



(73)

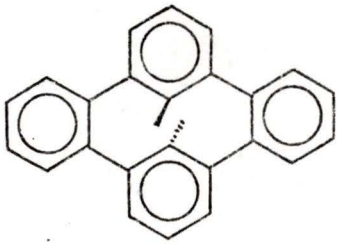


(76)

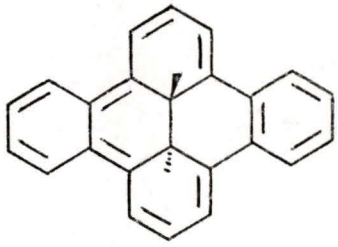
Since the coupling reaction to give (29) also gave 20% of the dimer (30), we thought it worthwhile to attempt conversion to the unsaturated macrocyclic system (73), since this was a possible precursor to the novel polycyclic system (74).

Some considerable difficulty was met in trying to effect the Wittig rearrangement of (30). Finally after much experimentation it was found that very slow addition of lithium diisopropylamide in tetrahydrofuran to (30) followed by quenching with methyl iodide gave (75). We were unable to characterise the product (75) as such, but could effect a Raney Nickel removal of the -SMe groups to give the cyclophane (76) in 46% yield, mp 245-246°C. The structure was confirmed by the molecular ion (base peak) in the mass spectrum at m/e 568 corresponding to $C_{44}H_{40}$. The pmr spectrum showed the aromatic protons at δ7.6-6.6(m), the bridge $-CH_2-$ protons at δ3.1-2.3(m) and the internal methyl groups shielded to δ1.90. The shielding of the latter is considerably less than for cyclophane (37), being close to the value observed for an open 2,2"-dimethyl-o-terphenyl(see section II-8 below), reflecting the less rigid structure of (76) in comparison to (37). This represents the first example of a terphenylophane. We were not able to convert (75) into the unsaturated system (73) by means of either a Hofmann elimination of the sulphonium salt, or through a sulphoxide elimination.[37a]

II-7. Approaches to the dibenzannulene (77).



(77)

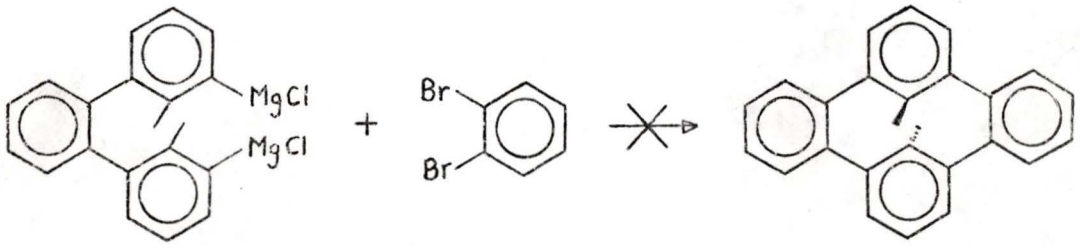


(54)

It should be of considerable interest to synthesise the o,m,o,m-cyclophane (77) to determine whether valence tautomerisation to the dibenzodihydropyrene (54) will occur. Further, (54) would provide additional results to test Mitchell's[25] hypothesis on the significance of symmetrical Kekulé structures to diatropicity. Since (54) has symmetrical Kekulé structures, one would expect the system to be highly diatropic, hence the internal methyl protons should appear between δ-3 and -4. Such a system would also be interesting to apply the 'Q' test to. Our observations on the monobenzannelated system (36)⇌(20) have suggested that benzofusion on the bridge has enhanced the stability of the open form (36). It is thus conceivable that (77) might be more stable than (54), since to form (54) the delocalisation of 3-4 benzene rings must

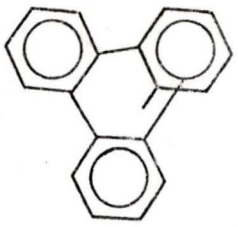
be interupted. If this is the case, (77) would be the first example where the cyclophane-diene tautomer is more stable than the dimethyldihydropyrene.

Conceptually the synthesis of (77) seemed simple, if a coupling between the bis-Grignard reagent (78) and o-dibromobenzene could be made to succeed.



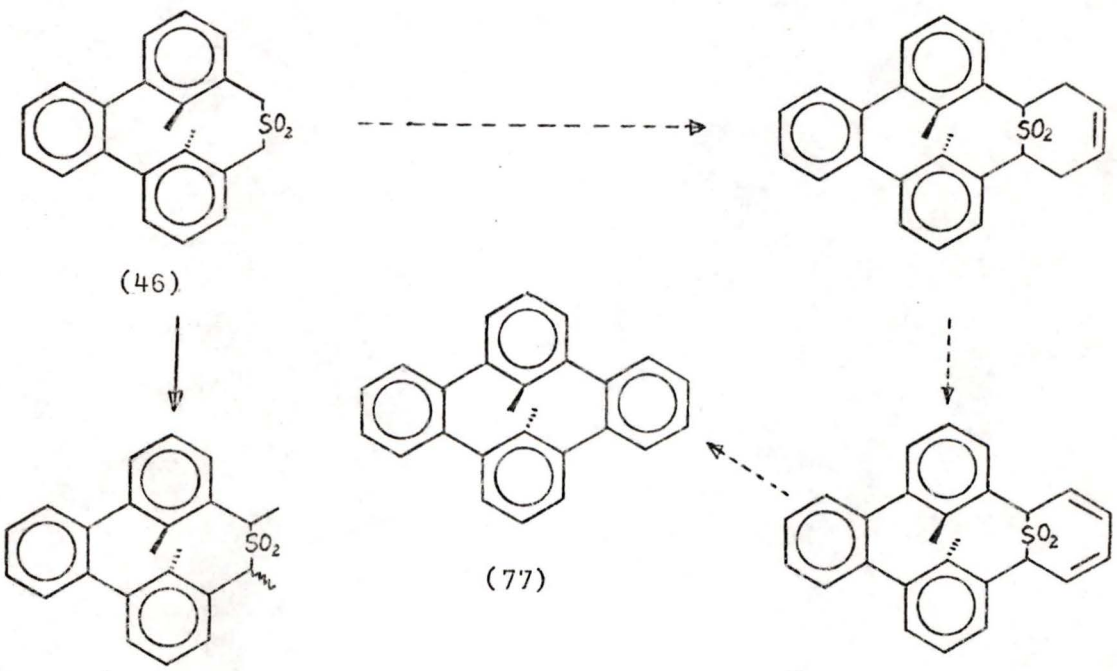
(78) (77)

Unfortunately in our hands this coupling failed, despite successful generation of the bis-Grignard (78) as evidenced by the hydrolysis product, 2,2'-dimethyl-o-terphenyl, (79), mp 84-86°C. The mass spectrum of (79) showed the molecular ion (as the base peak) at m/e 258. The pmr spectrum showed the aromatic protons at δ7.2-6.7 and the methyl protons at δ1.87. These are shielded with respect to toluene, and presumably reflect the propeller nature of a terphenyl:



(79)

An alternative approach to (77) might be through the sulphone (46), if it could be successfully bis-alkylated with a suitable dihalide, e.g. as shown in the scheme below:



(46)

(77)

(80)

As an initial attempt to test the feasibility of such an approach, the sulphone (46) was treated with excess lithium diisopropylamide in tetrahydrofuran and then quenched with methyl iodide, to yield 74% of the bis-methylated sulphone (80), mp(dec) 240°C. The mass spectrum of (80) gave the MH^+ ion at m/e 377 with ready loss of SO_2 and H to give the base peak at m/e 312. The pmr spectrum clearly showed the methine $-C\underline{H}\begin{matrix}\nearrow CH_3\\ \searrow SO_2-\end{matrix}$ protons at δ4.30 (quartet, J = 7 Hz), the methyl $-CH\begin{matrix}\nearrow \underline{CH}_3\\ \searrow SO_2-\end{matrix}$ protons at δ1.74 (doublet, J = 7 Hz), and the internal methyl protons at δ0.98, confirming the assigned structure. The ir spectrum showed the $-SO_2-$ stretch at 1300cm^{-1}.

The success of this bis alkylation makes the suggested route to (77) attractive to test in the future.

II.8. The barrier to rotation in 3,3"-disubstituted-2,2"-o-terphenyls.

The barrier to rotation in o-terphenyls appears not to have been measured. During the course of this work a number of 3,3"-disubstituted-2,2"-dimethyl-o-terphenyls have been prepared, which are ideally suited to the measurement of this barrier, since they exhibit temperature dependant pmr spectra.

Temperature dependant pmr spectra have been widely applied to obtain information about dynamic molecular structures; for example, to determine the energy barrier for conformer interconversion[58,59] and for rotation about sterically hindered C-C single bonds.[58,60,61] In general, since the practical range of variable temperature pmr measurements is from -180°C to +200°C, the range in barriers that can be studied is from about 20 to 110 kj/mol.

For spectra that are relatively simple, e.g. where the low temperature spectrum consists of two peaks and these collapse to a single peak at higher temperature, the coalescence temperature (Tc) method is often used. This method simply involves measurement of the coalescence temperature (Tc) of the peaks and their frequency separation $\Delta\nu$ at the lowest temperature; then the rate constant for the exchange at Tc can be calculated as

$$k_c = \frac{\pi\Delta\nu}{\sqrt{2}} \qquad [3]^{\dagger}$$

The free energy of activation ($\Delta Gc^{\neq}$) at the coalescence temperature can then be calculated from equation [3].[60]

$$\Delta Gc^{\neq} = 2.3\ R\ Tc\ (10.32 + \log Tc - \log k_c) \qquad [3]$$

Whilst this method is simple, it has limitations. In particular

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† For coupled nuclei $k_c = \frac{\pi}{\sqrt{2}} (\Delta\nu^2 + 6J^2)^{1/2}$

$\Delta G_c^{\neq}$ should only be compared within similar examples of the same system such that $\Delta S^{\neq}$ is constant or zero. Otherwise a complete lineshape analysis is preferred.

In the case we intended to study, all the examples are 3,3"-disubstituted-2,2"-dimethyl-o-terphenyls, and hence $\Delta S^{\neq}$ can be reasonably assumed to be more or less constant.

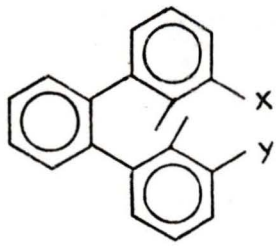
The pmr spectra were recorded at 90MHz for compounds (22), (24), (26), (25),(28) and (79) as dilute (10%) solutions in $CDCl_3$ from -70°C to +70°C. The results are shown in table 11.

Table 11

Thermodynamic data for the barrier to rotation in 3,3"-disubstituted-2,2"-dimethyl-o-terphenyls

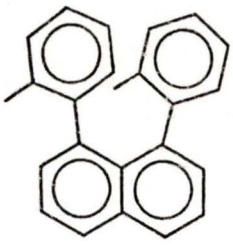
Compound	x	y	Δν(Hz)	kc(Hz)	Tc(°C)	$\Delta G_c^{\neq}$(kj/mol)
(22)	Cl	Cl	7.0	15.6	58	74.0
(24)†	CN	CN	5.6	12.5	42	70.9
(26)	CHO	CHO	7.2	16.1	62	74.8
(25)	Cl		6.0	13.4	42	70.1
		CN	5.1	11.4	38	70.2
(28)	CH_2Br	CH_2Br	<0.5	-	-	-
(79)	H	H	8.6	19.2	8	62.0

†(24)(Δν= 5.6 ± 0.5Hz,ΔG = 70.9 ± 0.3 kj/mol; Tc = 42 ± 2°C, ΔG = 70.9 ± 0.4 kj/mol)

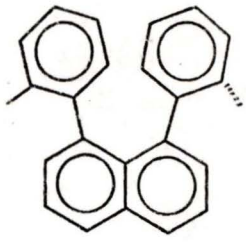


Clearly the rotation barrier is not much affected by the 3,3" substituents and is approximately 72 kj/mol. The values for the bis-bromomethyl compound could not be determined, probably because $\Delta\nu$ was too small to be observed. The substituent effect on the barrier decreases in the order of -CHO > -Cl> -CN, though this is rather samll.

To understand what is happening it is worth considering the analogous case of 1,8-di-o-tolylnaphthalene, (81a,b) where



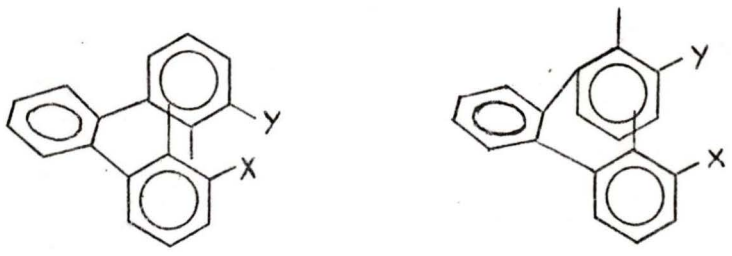
(81a)



(81b)

two isomers actually exist, and can be separated at low temperatures.[61b] The methyl protons of each isomer appear as a singlet, separated by $\Delta\nu$ = 2Hz, which coalesce to a single peak above 40°C. Cough and Roberts[61b] calculate $\Delta G_c^{\neq}$ = 101 kj/mol, somewhat higher than the values we obtain in our case. The corresponding values for 1,8-diphenylnaphthalene (82) and 2,2'-disubstituted biphenyls are 63 and ca 55 kj/mol respectively.[61c]

In our system the two singlets seen in the low temperature spectra thus probably correspond to



with the barrier to rotation being approximately 72 kj/mol, which is between that of (81) and (82). For compound (25), a separate barrier for each ring can be observed. These apparent barriers are smaller than for compounds (22) and (24) which is somewhat surprising and could possibly be explained by different angles between the o-substituents, if the effect is real.

III. Summary & Conclusions.

In this work we have synthesised a symmetrical benzannelated dimethyldihydropyrene and shown that it is aromatic both in terms of magnetic effects (diatropic and large 'Q' value) and classical reaction chemistry, in that it undergoes electrophillic substitution reactions. Synthetic procedures have been developed which allow a base-induced sulphinic acid elimination as an alternative to the better-known Hofmann type sulphonium salt elimination in the last step of the sequence to produce cyclophane-dienes. Also a method has been found whereby alkyl substituents may be introduced onto the bridge position of the phane-diene. The synthesis of the first terphenylophane is also described.

The phototautomerisation of the benzodimethyldihydropyrene and its derivatives have been studied, and it is found that the activation barriers between the phane-diene $\rightleftharpoons$ dihydropyrene tautomers are somewhat higher (i.e. process is slower) than for the parent system.

The barriers to rotation in several substituted terphenyls have also been determined.

IV. Experimental

All melting points were determined on a Kofler Hotstage and are uncorrected. The pmr spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin-Elmer R12A(60MHz) or R32(90MHz) spectrometer. ^{13}Cmr spectra were recorded on a Nicolet-TT-14 15.1MHz ft spectrometer in $CDCl_3$. Both are reported in ppm downfield from tetramethylsilane as internal standard. The ir spectra were recorded on a Pye-Unicam SP1000 spectrometer (only the medium and strong bonds are given) and the uv spectra on a Carey 17 spectrophotometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7 or Finnigan 3300 mass spectrometer at 70eV. using electron impact, except where the notation CI (chemical ionization) occurs. Analyses were performed by Dr. D. McGilivray of this department. All evaporations were carried out under reduced pressure on a rotary evaporatorator at ca. 40°C. All organic layers were washed with H_2O (unless otherwise stated) and dried with anhydrous sodium sulfate.

Preparation of Compounds

1. 3,3"-Dichloro-2,2"-dimethyl-o-terphenyl (22)

(a) Mono Grignard reagent of 2,6-dichlorotoluene: A solution of 2,6-dichlorotoluene (21a) (50.5g, 0.314 mol) in dry tetrahydrofuran (THF, 150 mL) was added dropwise over 30 min. to gently warmed Mg (7.63 g, 0.314 mol) under N_2. When the addition was complete the reaction mixture was heated under reflux for 3h and then diluted with a further portion of dry THF (150 mL).

(b) The Grignard reaction: A solution of o-dibromobenzene (37 g, 0.157 mol) in dry THF (100 mL) was added dropwise over 30 min. to the stirred Grignard reagent from (a) above held at -70°C under N_2, followed by $Ni(acac)_2$ [28a] (0.803 g, 20 mmol). The reaction mixture was then allowed to warm to room temperature over 1h before heating under reflux for 12h. After cooling, and addition of ice-water (300 mL), the organic layer was separated, washed with 10% aq HCl (300 mL), H_2O(2 × 300 mL), dried and evaporated. The resulting brown oil was preabsorbed onto silica gel (50 g) and chromatographed over a column(1.5m × 4cm) containing silica gel (800 g) using pentane as eluant to yield the product (22), (16-65 g(33%-60%). A portion was recorystallised from cyclohexane to yield colourless crystals, mp 102-104°C; pmr, δ, (60 MHz) 7.50-6.65(m, 10H,ArH) and two singlets at 2.11 and 2.05 (6H,-CH_3); ir (KBr) 1560(s), 1450(s),

1430(s), 1380(m), 1260(m), 1250(m), 1190(m), 1150(m), 1110(m), 1075(m), 1065(m), 1035(s), 1000(s), 950(m), 980(mw), 880(mw), 815(m), 797(s), 771(s), 760(s), 720(s), 715(s), 665(s) and 640(m)cm^{-1}; ms peaks at m/e relative intensity 326 (M^+, $C_{20}H_{16}{}^{35}Cl_2$, 57, correct isotope pattern), 291(M-Cl, 17) 256(M-Cl_2, 18), 166(M-$C_7H_6Cl_2$, 17), 165(M-$C_7H_7Cl_2$, 61), 126(59), 125(32) and 119(100).

Anal. Calcd. for $C_{20}H_{16}Cl_2$; C 73.61, H 4.94.

Found: C 73.35, 73.46, H 4.71, 4.88.

Eluted subsequently was 3,3"'-dichloro-2,2"'-dimethyl-o-quater phenyl (23) 1.90 g(3%),mp 173-175°C, as colourless crystals from cyclohexane; pmr, δ, (60 MHz) 7.5-6.3(m, 14 H, Ar-H), 1.65 and 1.48 (S, approx. 3H each, $-CH_3$); ir(KBr) 1565(m), 1470(m), 1450(m), 1430(m), 1155(m), 1115(m), 1060(m), 1040(m), 1005(m), 800(s), 785(s), 725(m) and 655(m); ms peaks at m/e (relative intensity) 402 (M^+, $C_{26}H_{20}{}^{35}Cl_2$, 100).

Anal. calcd. for $C_{26}H_{20}Cl_2$: C 77.61, H 4.98.

Found: C 77.47, H 4.99.

2. 3,3"-Dicyano-2,2"-dimethyl-o-terphenyl (24)

Cuprous cyanide (25.0g, 0.275mol) was added to a solution of 3,3"-dichloro-2,2"-dimethyl-o-terphenyl (22) (20.5g, 62.9mmol) in

N-methyl-2-pyrrolidinone (65mL). The reaction mixture was heated under reflux for 12h. Since TLC indicated the reaction was not complete, a further portion of CuCN(25.0g) in N-methyl-2-pyrrolidinone (65mL) was added, and reflux continued for a further 12h. After cooling to ca 100°C, the reaction mixture was poured onto ice (200g) and '880' ammonia (200mL). After mixing thoroughly, the mixture was filtered and the residue washed well with dil aq ammonia ('880'-H_2O 1:5), water and then was extracted with dichloromethane (3 × 300mL). The organic layer was washed with H_2O (2 × 500mL), dried and evaporated. The resulting brown oil was chromatographed over a column (1.5m × 4cm) of silica gel using pentane-dichloromethane (3:7) as eluant to yield firstly 3-chloro-3"-cyano-2,2"-dimethyl-o-terphenyl (25), 1.05g(5%), mp 100°-102°C; pmr, δ,(60MHz) 7.6-6.7(m, 10H, Ar-H), 2.30 and 2.25 (s, total 3H, -o-NC-ϕ-CH_3) and 2.10 and 2.05 (s, total 3H,-o-Cl-ϕ-CH_3) see text for variable temperature results; ir (KBr) 2240(m), 1570(m), 1455(s), 1430(s), 1385(m), 1040(m), 1000(m), 810(s), 800(s), 790(s), 770(s) and 730(s)cm^{-1}; ms peaks at m/e (relative intensity) 317(M^+, $C_{21}H_{16}{}^{35}ClN$, 100, correct isotope pattern), 312(M-CH_3, 16), 282(M-Cl, 57), 269(29), 268(26) and 240(27).

Anal. calcd. for $C_{21}H_{16}ClN$: C 79.37, H 5.04, N 4.41.

Found: C 79.58, H 5.01, N 4.43.

Eluted next was product (24), 18.5g (85-95%). A portion was recrystallised from absolute ethanol to yield white crystals of (24), mp 151-153°C; pmr, δ, (60MHz), 7.65-7.00 (m, 10H, Ar-H) and 2.30 and 2.25 (s, 6H total, $-CH_3$), variable with temp. see text); ir(KBr) 2240(m), 1450(m), 1425(m), 1380(m), 800(s), 770(s) and 725(s)cm^{-1}; ms peaks at m/e (relative intensity) 308(M^+, 100), 307(M-H, 35), and 292(M-H & CH_3, 47).

Anal. calcd. for $C_{22}H_{16}N_2$: C 85.68, H 5.23, N 9.09.
Found: C 85.48, H 5.19, N 8.67.

3. 2,2"-Dimethyl-o-terphenyl 3,3"-dicarboxaldehyde (26)

Diisobutylaluminum hydride (113 mmol), in hexane (68 mL) was added dropwise under N_2 to a solution of the dinitrile (24) (14.5g, 47.1 mmol) in dry benzene (140 mL) at room temperature with mechanical stirring. After 12h, the viscous pale yellow solution was decomposed slowly (using ice bath cooling) firstly methanol (7 mL), then by addition of methanol and water (1 : 1, 10.5 mL) and finally with conc. HCl (14 mL) and H_2O(24.5 mL),such that the resultant solution was slightly acidic.

The mixture was extracted with dichloromethane (3 × 500 mL). The organic layer was washed with H_2O(2 × 500 mL), dried and evaporated. The resulting brown oil was separated over a column (1.5 × 4cm) of silica gel using pentane-dichloromethane (1:9) as

eluant to yield the product (26), 12.7g (86%). A portion was recrystallised from carbon tetrachloride to yield white crystals of (26), mp 141-143°C: pmr, δ, (60MHz), 10.2 (s, 2H, -CHO), 7.70-7.00 (m, 10H, Ar-H), 2.40 and2.37 (s, total 6H, $-CH_3$ variable with temp. see test); ir(KBr), 1685(b,s), 1580(s), 1450(m), 1400(m), 1380(m), 1245(s), 850(s), 800(s), 770(s) and 720(s)cm^{-1}; ms peaks at m/e (relative intensity) 314(M^+, 100), 299(M-CH_3, 60), 243(M-2CO,-CH_3, 41) and smaller peaks.

Anal. calcd. for $C_{22}H_{18}O_2$: C 84.05, H 5.77.

Found: C 84.37, 84.55, H 5.52, 5.82.

4. 3.3"-Bis(hydroxymethyl)-2,2"-dimethyl-o-terphenyl(27)

A solution of the dialdehyde (26)(13.3g, 42.0 mmol) in undried tetrahydrofuran (95 mL) was added dropwise to a stirred slurry of $NaBH_4$ (1.2g, 31.7 mmol) in THF (15 mL) at RT.

After 12h, the mixture was decomposed with H_2O (5 mL) and HCl (5 mL). The aq. layer was saturated with NaCl and extracted with dichloromethane (3 x 300 mL). The organic layers were dried and evaporated to give crude product, dialcohol (27), 13g (98%). A portion of (27) was recrystallised from benzene to yield white

crystals, mp 135-137°C; pmr, δ, (60MHz), 7.5-6.7 (m, 10H, ArH), 4.53 (s, 4H, $-CH_2OH$), 2.00 (s, 6H, $-CH_3$) and 1.62 (bs, 2H, $-CH_2OH$, exchanged with D_2O); ir(KBr), 3240(bs), 1440(bs), 1000 (s), 800(s), 790(s), 760(s), 750(s) and 730(s)cm^{-1}; ms peaks at m/e (relative intensity) 318(M^+, 100), 300($M-H_2O$, 63), 285($M-H_2O$, CH_3, 69), 282($M-2H_2O$, 86), 270(84), 269(88), 267(85), 255(76) and many smaller peaks.

Anal. calcd. for $C_{22}H_{22}O_2$: C 82.98, H 6.97.

Found: C 82.38, H 6.95.

5. 3,3"-Bis(bromomethyl)-2,2"-dimethyl-o-terphenyl (28)

A solution of PBr_3 (20 mL, 0.20 mol) in dry benzene (200 mL) was added dropwise over 3h to a vigorously stirred solution of diol (27) (13g, 41 mmol) in dry benzene (400 mL) and 5 drops pyridine at RT. After 12h, the mixture was washed with ice water (200 mL). The organic layer was washed successively with water, $NaHCO_3$ soln., water, dried and evaporated. The resulting brown oil was separated over a column (1.0m × 4cm) of silica gel using pentane-dichloromethane (7:3) as eluent to yield the product (28), 13.5g (74%). A portion was recrystalised from cyclohexane to yield white crystals of (28), mp 129-130°C; pmr, δ, (60MHz),

7.50-6.75 (m, 10 H, Ar-H), 4.35 (s, 4H, $-CH_2Br$) and 2.07 (s, 6H, $-CH_3$); ir (KBr), 1450(s), 1380(m), 1265(m), 1210(s), 1190(m), 800(s), 760(s) and 725(s)cm^{-1}; ms peaks at m/e (relative intensity) 444(M^+, $C_{22}H_{20}{}^{79}Br_2$, 41, correct isotope pattern), 365(M-Br, 48), 364(M-HBr, 100), and many smaller peaks.

Anal. calcd. for $C_{22}H_{20}Br_2$: C 59.88, H 4.54.

Found: C 59.99, H 4.51.

6. Anti-9,21-dimethylbenzo(10,11-a)-2-thia[2,3]metacyclophane (29) and dimer (30) (possibly 9,21,30,42-tetramethyl-2,23-dithia[3,3]-3,3"-o-terphenylophane).

A solution of bis-bromide (28) (6.0 g, 0.0135 mole) in dry benzene (250 mL) was added through one dropping funnel at the same rate as a solution prepared by dissolving powdered $Na_2S \cdot 9H_2O$(3.57 g, 0.0149 mol) in N_2 purged H_2O(80 mL) and then adding N_2 purged 100% EtOH(170 mL) in a second addition funnel, to vigorously stirred, 95% EtOH(700 mL) under N_2, over 7h. The mixture was stirred for a further 12h and then evaporated. The residue was extracted with CH_2Cl_2(300 mL) and H_2O(300 mL). The CH_2Cl_2 layer was dried and evaporated. The residue was pre-

absorbed onto silica gel and chromatographed over a column (1.0 m × 4 cm) of silica gel using pentane-dichloromethane (7:3) as eluant to yield firstly anti-isomer (29), 2.03 g(48%) and secondly dimer (30), 1.75 g(20%). A portion of (29) was recrystallized from cyclohexane to yield white crystals, mp 201-202°C; pmr,δ, (60MHz), 7.75-7.00(m, 10H, ArH), 3.80 and 3.55 (AB quartet, 4H, J_{AB} = 13Hz, -S-C$\overset{H_A}{\underset{H_B}{<}}$-) and 0.94(s,6H,-$CH_3$); ^{13}Cmr, ppm 141.8, 139.5, 138.9, 134.5 (quaternary aromatic C), 130.6, 129.7, 129.0, 128.0, 126.0(aromatic -CH), 30.7(-CH_2-) and 17.4(internal -CH_3); ir(KBr), 1450(s), 1425(s), 795(s), 755(s), 755(s) and 730(s)cm^{-1}; ms peaks at m/e (relative intensity) 316(M^+, 100), 284(M-S, 43), 283(M-HS, 100), 282(M-H_2S,43), 269(M-S, CH_3, 70), 267(M-H_2S, CH_3, 50), and many smaller peaks.

Anal. calcd. for $C_{22}H_{20}S$: C 83.50, H 6.37.

Found: C 83.02,H 6.64.

A portion of (30) was recrystallized from benzene to yield white crystals, mp 251-253°C; pmr, δ, (90MHz), 7.5-6.7(m, ArH), 3.25(s, -CH_2-S-) and 2.1-1.4(8s, unequal, $\overset{-CH_2-}{-CH_3}$); ir(KBr),1465(s), 1430(s), 805(m), 795(m), 765(s), 745(m), 730(m) and 720(m)cm^{-1}; ms, molecular ion at m/e 632.

Anal. calcd. for $C_{44}H_{40}S_2$: C 83.50, H 6.37 .

Found: C 83.24, H 5.95.

7. Wittig rearrangement of thiacyclophane (29)

A solution of lithium di-isopropylamide prepared from n-BuLi (3.3 mmole in hexane (1.65 mL)) and diisopropylamine (0.66 mL, 3.3 mmol)in dry THF (25 mL) was added dropwise over 10 min. under N_2 to a solution of the thiacyclophane (29) (0.52 g, 1.65 mmol) in dry THF (25 mL). The reaction mixture became dark brown, and after 10 min. methyl iodide (0.31 mL, 5.0 mmol) such that the dark color disappeared. After a further 10 min. H_2O(150 mL) and CH_2Cl_2(300 mL) were added, and then the organic layer was washed with H_2O(150 mL), dil HCl solution (150 mL), H_2O (200 mL), dried and evaporated. The resulting brown crystals were chromatographed over a column (0.2 m × 4 cm) of silica gel using pentane-dichloromethane (8.5 : 1.5) as eluant to yield the product (31), 0.445 g(80%). A portion of (31) was recrystallized from cyclohexane to give colourless crystals, mp 165-166°C; pmr, δ, (60MHz), 8.0-7.1(m, 10H, Ar$\underline{H}$), 3.88(dd, 1H, J_{XB}=11Hz, J_{XA}=3Hz,-C$\underline{H}$S-), 3.28(dd, 1H, J_{AB}=11Hz, J_{AX}=3Hz, -SC$\underline{H}_A$-$\underline{H}_B$-), 2.60(t, 1H, J_{BA}=11Hz, J_{BX}=11Hz, -SC$\underline{H}_A$-$\underline{H}_B$-), 2.28(s,3H, -SC$\underline{H}_3$) and 0.80(s, 6H, Ar-C$\underline{H}_3$); ir(KBr), 1450(m), 1420(s), 1375(m), 800(m), 760(s) and 725(s)cm^{-1}; ms peaks at m/e (relative intensity) 330(M^+, 41), 315(4), 285(17), 267(100) and 252(76).

Anal. calcd. for $C_{23}H_{22}S$: C 83.59, H 6.71.

Found: C 83.91, H 6.60.

8. Anti-sulphonium salt (32)

The anti-cyclophane (31) (0.183 g, 0.55 mmol) in CH_2Cl_2 (5 mL) was added slowly to a stirred suspension of $(MeO)_2CHBF_4$[62] (0.25 g, 1.5 eq) in CH_2Cl_2 (5 mL) at -30°C under N_2, which was then stirred without further cooling for 3h. Ethyl acetate (2 mL) was added and after stirring for 12h the white precipitate was collected by filtration and dried to give the sulphonium salt (32), 0.22 g(80%), as a white powder. The compound decomposed at 287°C.

9. trans-12c,12d-Dimethyl-12c,12d-dihydrobenzo[e]pyrene (20)

Potassium t-butoxide (78 mg, 0.69 mmol) was added to a suspension of the sulphonium salt (32) (0.20 g, 0.46 mmol) in dry THF (10 mL) at RT under N_2. The reaction mixture was then heated under reflux for 0.5h, cooled, and extracted with CH_2Cl_2 (50 mL) and aq 1N HCl (50 mL). The organic layer was washed with H_2O(3 × 100 mL), dried and evaporated. The residue was

dissolved in a few mL of pentane and chromatographed on silica gel (0.2m × 4 cm) using pentane as eluant to yield the product (20), 0.098 g (75%), as dark red crystals from hexane mp 136-138°C; pmr(60MHz), δ, 8.70(see text 2H, H-9,12), 8.18(d,2H, J=7Hz, H-1,8), 7.62-6.94(m, 8H, H-2, 3, 4, 5, 6, 7, 10, 11), and -1.85(s, 6H, Ar-C$\underline{H}_3$); ^{13}Cmr, ppm, 138.1, 134.7, 128.9 (quaternary aromatic C), 125.7, 124.5, 122.7, 122.1, 117.0(aromatic -$\underline{C}$H), 35.2 (internal bridge C) and 16.8(internal methyl C); ir(KBr), 1650(s, broad), 1380(m), 1360(m), 1330(m), 840(s), 825(m), 755(m) and 740(s)cm^{-1}; uv(cyclohexane)λ_{max}(logε_{max}), 634nm(2.27), 531(3.57), 502(3.64), 390(4.41), 372(4.22), 354(3.91), 338(4.24), 322(4.11), 304(4.14), 259(3.89), 253(3.96), 247(3.98) and 242(3.99); ms peaks at m/e(relative intensity) 282(M^+, 52), 267(M-CH_3, 96) and 252(M-2CH_3, 100).

Anal. calcd. for $C_{22}H_{18}$: C 93.58, H 6.42.

Found: C 93.37, 94.02, H 6.04, 6.14.

10. Reaction of (31) with lithium-ammonia

The Wittig rearrangement product (31) (0.5 g, 1.5 mmol) in dry THF (20 mL) was added to a blue solution of lithium (0.1g,

15 mmol) in liq. ammonia (100 mL) at about -70°C. After 5 min., solid NH_4Cl was added to the reaction mixture until the blue colour disappeared. The NH_3 was allowed to evaporate, and then H_2O, aq HCl and CH_2Cl_2 were added. The organic layer was washed, dried and evaporated to yield a residue which was shown to contain (37) by pmr and ms, but from which (37) was unable to be separated pure either by chromatography (SiO_2, Al_2O_3) or recrystallisation.

11. Anti-8,20-dimethylbenzo(9,10-a)[2,2]metacyclophane (37)

A mixture of (31) (0.5 g, 1.5 mmol), W-7 Raney Nickel[63] (9 g, 100 fold excess) and 100% ethanol (50 mL) were refluxed for 12h. After cooling, the catalyst was removed by filtration and the solvent evaporated to yield (37), 0.42 g(85%) as the sole product. A small sample was recrystallized from cyclohexane and gave colorless crystals, mp. 156-157°C; pmr, δ, (90MHz), 7.80-7.25(m, 6H, Ar$\underline{H}$), 7.03(s, 4H, Ar$\underline{H}$), 3.15-2.40(m, 4H, Ar-C$\underline{H}_2$-) and 0.67(s, 6H, Ar-C$\underline{H}_3$); ir(KBr), 1455(m), 1425(m), 805(m), 790(m), 765(s), 755(s) and 730(s)cm^{-1}; uv(cyclohexane)λ_{max}($\log\varepsilon_{max}$),285nm (3.50), 250(4.61), 233(4.56), 211(4.66) and 197sh(4.57); ms peaks

at m/e (relative intensity) 284(M^+, 28), 269(M-CH_3, 100), 254(M-$2CH_3$, 38), 253(38) and 252(37).

Anal. calcd. for $C_{22}H_{20}$: C 92.96, H 7.04.

Found: C 92.90, H 6.92.

12. Benzyne induced Stevens rearrangement of (29).

A solution of anthranilic acid (68 mg, 0.50 mmol) in 1,2-dichloroethane (20 mL) was added dropwise over 1.5h under N_2 to a refluxing solution of thiacyclophane (29) (126 mg, 0.399 mmol) and isoamyl nitrite (210 mg, 2.16 mmol) in 1,2-dichloroethane (20 mL). After a further 15 min reflux the reaction mixture was concentrated under reduced pressure, and the residue taken up in pentane-benzene (1:1) and transferred to a silica gel column. Elution with pentane-benzene (1:1) gave pale yellow crystals of (39) 138 mg(86%), which on recrystallisation from cyclohexane gave (39) as white crystals, mp 161-163°C; pmr, δ, (60MHz), 8.0-6.9(m, 10H, Ar-H), 4.23(dd, 1H, J_{XB}=11Hz, J_{XA}=3Hz, Ar-CH_XS-), 3.25(dd, 1H, J_{AB}=11Hz, J_{AX}=3Hz, Ar—C$^{H_A}_{H_B}$-), 2.60(t, 1H, J_{BA}=J_{BX}=11Hz, Ar-C$^{H_A}_{H_B}$-), 0.72 and 0.67 (s, 3H each, Ar-CH_3); ir(KBr), 1590(m), 1575(m), 1485(m), 1450(m),

1440(m), 1420(m), 1090(m), 1030(m), 800(m), 770(s), 755(s), 735(s), 730(s) and 690(m)cm^{-1}; ms peaks at m/e (relative intensity) 392(M^+, 23), 283(M^+-S, 100), 268(45), 267(M^+-SH, CH_3, 90), 253(69) and 252(96).

Anal. calcd. for $C_{28}H_{24}S$: C 85.72, H 6.12.

Found : C 85.71, H 5.87.

13. Raney Nickel reduction of (39) to cyclophane (37)

A mixture of (37) (0.1 g, 0.126 mmol), W-7 Raney Nickel (1.55 g, 100 fold excess) and 100% ethanol (10 mL) were refluxed for 12h. After cooling, the catalyst was removed by filtration and the solvent evaporated. The residue was recystallised to give white crystals of (37), 0.085 g(96%), identical (mp, nmr) to the previously obtained sample.

14. Attempted dehydrogenation of (37) to dihydropyrene (20)

Treatment of (37) with Pd/C in refluxing benzene for 12h, or DDQ in refluxing toluene for 12h or irradiation with uv light in benzene or cyclohexane in the presence or absence of DDQ did not give any detectable (20).

15. Oxidation of Wittig rearrangement product (31) to its sulphone (43).

Hydrogen peroxide (30%)(10 mL) was added to a warm solution of (31) (0.4 g, 1.2 mmol) in acetic acid (20 mL) and benzene (40 mL). The reaction mixture refluxed for 5h and then evaporated. The residue was chromatographed in dichloromethane on a column of silica gel (10 × 2 cm) to yield the sulphone (43), 0.41 g(93%). A portion of (43) was recrystallized from benzene to give white crystals, mp 227-229°C; δ, (90MHz), 8.1-7.0(m, 10H, Ar-H), 3.85(dd, 1H, J_{XA}=3Hz, J_{XB}= 12Hz,-CH_XSO_2), 3.72(dd, 1H, J_{AB}=12Hz, J_{AX}=3Hz,-$CHSO_2Me$-CH_A-), 3.02(s, 3H,-SO_2-CH_3), 2.88(t,1H, J_{BA}=J_{BX}=12Hz, -HCH_B-Ar) and 0.72, 0.70(s, 3H each, Ar-CH_3); ms peaks at m/e (relative intensity) 362(M^+, 40), 283(M-SO_2CH_3, 100), 268(70), 267(97), 253(96) and 252(98); ir(KBr)1315(m), 1295(s), 1140(s), 760(s) and 730(s)cm^{-1}.

Anal. calcd. for $C_{23}H_{22}SO_2$: M = 362.1341

Found: (Mass spec.) M = 362.1369.

16. Elimination of sulphone (is) to give dihydropyrene (20)

Potassium t-butoxide (77 mg, 0.69 mmol) was added to a solution of the sulphone (43) (50 mg, 0.14 mmol) in THF (10 mL) under N_2 at about 30°C, and the reaction mixture was then heated under reflux for 2h. After cooling H_2O and CH_2Cl_2 were added. The organic layer was washed, dried and evaporated. The residue was pre-absorbed on silical gel and filtered through a short column of silica gel (10 × 2 cm) in pentane to give the product (20), 19 mg(47%), identical to the previously obtained sample.

17. Oxidation of the phenylsulphide (39) to its sulphone (42).

Hydrogen peroxide (30%)(38 mL) was added to a warm solution of sulphide(39)(1.5 g, 3.8 mmol) in acetic acid (75 mL) and benzene (150 mL). The reaction mixture was refluxed for 5h, cooled and evaporated. The residue was filtered through a short column of silica gel (10 × 2.5 cm) in dichloromethane and gave 1.3 g(80%) of (42) as white crystals from benzene, mp 238-239°C; pmr, δ, (60MHz), 8.2-6.9(m, 10H, Ar-H), 3.92(dd, 1H, J_{XB}=12Hz, J_{XA}=3Hz, $-CH_xSO_2\phi-$), 3.70(dd, 1H, J_{AB}=12Hz, J_{AX}=3Hz, H_A,page30), 2.95(t, 1H, $J_{BX}=J_{BA}$=12Hz,H_B, page30), 0.67 and 0.47(s, 3H each Ar-CH_3); ir(KBr), 1450(s), 1420(m), 1320(s), 1310(m), 1295(s),

1155(s), 1145(s), 1085(s), 800(m), 780(m), 770(s), 735(s), 720(s), 700(m), 690(m), 665(m), 640(m) and 630(m)cm^{-1}; ms peaks at m/e (relative intensity) 424(M^+, 18), 360(M-SO_2,8) and 283(M-$SO_2\phi$, 100).

Anal. calcd. for $C_{28}H_{24}O_2S$: C 79.25, H 5.66.

Found: C 78.96, H 5.37.

18. Basic elimination of phenyl sulphone (42) to dihydropyrene(20)

Potassium t-butoxide (26 mg, 0.24 mmol) was added to a refluxing solution of the sulphone(42) (20 mg, 0.047 mmol) in THF (5 mL) under N_2. After 1h, the reaction was cooled and CH_2Cl_2, H_2O and aq HCl were added. The organic layer was washed, dried and evaporated. The residue was pre-absorbed on silica gel and chromatographed on a column of silica gel (10 × 2.5 cm) in pentane to yield (20) 47%, as the only product, identical to previously obtained samples.

19. Anti-9,20-dimethylbenzo(10,11-a)-2-thia[2,3]metacyclophane 2,2-dioxide (46)

The thiacyclophane (29) (0.1 g, 0.29 mmol) in benzene (20 mL), acetic acid (10 mL) and 30% H_2O_2 (5 mL) was heated under reflux for 5h. After cooling, aq $NaHCO_3$ was added, then the organic layer was washed dried and evaporated. The residue was filtered in dichloromethane through a column of silica gel (10 × 2.5 cm) to give the sulphone (46) in quantitative yield. A portion of (46) was recrystallized from benzene as white crystals, mp 310-312°C; pmr, δ, (90MHz), 7.7-6.8(m, 10H, Ar-H), 4.45(d, 2H, J=14 Hz, Ar-CH_2-), 4.16(d, 2H, J=14Hz, Ar-CH_2-) and 0.95(s, 6H, Ar-CH_3); ir(KBr), 1450(m), 1425(m), 1315(s), 1270(m), 1115(s), 820(s), 750(s) and 720(s)cm^{-1}; ms peaks at m/e (relative intensity) CI 349(MH^+, 100) and 284(MH^+-SO_2, 15).

Anal. calcd. for $C_{22}H_{20}SO_2$: C 75.86, H 5.75.
Found: C 75.95, H 5.73.

20. Attempted conversion of sulphone (46) to dihydropyrene (20) with butyl lithium.

BuLi(1.0 mL, 0.59 mmol) was added to a solution of sulphone (46) (0.1 g, 0.29 mmol) in THF (10 mL). This solution was then introduced via syringe into a refluxing slurry of lithium aluminium hydride (0.1 g) in dioxane (20 mL). After 6h, the reaction mixture

was cooled and extracted with CH_2Cl_2 and H_2O. The organic layer was washed with H_2O, dil HCl, dried and evaporated. The residue contained the reduced suphide(8) and unreacted starting material (46) by TLC.

21. 2-Nitro-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo(e)pyrene (55)

Powered cupric nitrate trihydrate (0.17 g, 0.94 mmol) was added to a solution of (20) (0.15 g, 0.53 mmol) in acetic anhydride (50 mL) at 0°. After 40 min., ice-H_2O (50 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was washed with satd. aq $NaHCO_3$, H_2O, dried and evaporated. The residue was preabsorbed onto silica gel and chromatographed on a column (0.5 m × 4 cm) of silica gel using CH_2Cl_2-pentane (2:8) as eluant to yield a blue solution of mono-nitro product (55), which on evaporation yielded 61 mg (35%). Recrystallisation from cyclohexane gave dark blue crystals, mp 163-164°C; pmr, δ, (60MHz), 9.2-7.3(m, 11H, Ar$\underline{H}$), and -1.85(s, 6H, Ar-C$\underline{H}_3$); ir(KBr), 1485(m), 1325(m), 1285(s, broad), 1065(m), 875(m), 860(m), 815(m), 800(m), 740(s), 730(s), 725(s), 720(s) and

715(s)cm^{-1}; uv(cyclohexane)$\lambda_{max}(\log\varepsilon_{max})$ 592nm(3.74), 550sh (3.70), 386(4.09), 342(4.20), 324(4.19), 307(4.22), 258(4.69) and 232(4.87); ms peaks at m/e (relative intensity) 327(M^+, 38), 312(M-CH_3, 63), 297(M-2CH_3, 23), 266(M-CH_3, NO_2, 100), 250(39) and 239(23).

Anal. calcd. for $C_{22}H_{11}NO_2$: C 80.73, H 3.36, N 4.28.
Found: C 80.50, H 5.17, N 4.13.

22. Nitration of (20) to produce mainly dinitro derivative (56)

Powered cupric nitrate trihydrate (0.2 g, 1.1 mmol) was added to a solution of (20)(0.2 g, 0.71 mmol) in acetic anhydride (40 mL) at RT. After stirring for 30 min. the color of the solution had changed from purple to green. The mixture was stirred at RT for 2h before adding ice (70 g) and ether (140 mL). When the reaction of the acetic anhydride with the water was complete, the ether layer was separated, washed with water (3 × 200 mL), dried and evaporated. The residue was chromatographed in pentane-dichloromethane (8:2) on a column (40 × 4 cm) of silica gel to yield the product (56) as a mixture of isomers (green-blue solution), 50 mg(20%), which on recrystallisation from benzene yielded dark blue crystals, decomp. at 197°C; pmr, δ, (90MHz), 9.09(d, 2H,

J=1.5Hz, H-1,8), 9.2-8.6(n, 2H, H-9,12), 8.71(d, 2H, J=1.5Hz, H-3,6), 7.92(s, 2H, H-4, 5), 8.1-7.7(m, 2H, H-10, 11) and -1.60(s, 6H, $-CH_3$); ^{13}Cmr, ppm, 131.3, 128.6, 125.5, 123.9, 111.5 (aromatic-$\underline{C}H$), 36.6(internal bridge C) and 18.4(internal $-\underline{C}H_3$)-note the quaternary aromatic C could not be clearly observed; ir(KBr), 1500(s), 1320(s), 1300(s), 1085(m), 885(m), 755(m) and 735(m)cm^{-1}; uv(cyclohexane)$\lambda_{max}(\log\varepsilon_{max})$,631nm(3.64), 589(3.70), 530sh(3.53), 419(4.00), 398(3.85), 338(3.31), 322(4.09), 275sh(3.67), 259(3.74), 253(3.75), 247(3.77), 237(3.80) and 213 (4.14); ms peaks at m/e (relative intensity) CI 373(MH^+, 100), 268(MH-CH_3, 31), 327(MH-NO_2, 9), 312(MH-CH_3 and NO_2, 20) and 281(MH-$2NO_2$, 12).

Anal. calcd. for $C_{22}H_{10}N_2O_4$: M = 372.111.

Found (Mass spec) M= 372.124.

23. Nitration of (20) to produce mainly a trinitro derivative.

The pyrene (20) (0.35 g, 1.2 mmol) was added to a preformed solution of powered cupric nitrate trihydrate (0.6 g, 5.4 mmol) in acetic anhydride (50 mL) at RT. After 20 min. the color of the solution had changed to dark green. Then ice water (50 mL) and CH_2Cl_2(50 mL) were added to the reaction mixture, and the

organic layer was washed with aq $NaHCO_3$, H_2O, dried and evaporated. The residue was preabsorbed onto silica gel (20 g) and chromatographed in CH_2Cl_2-pentane (4:6) on a column (60 × 4 cm) of silica gel to yield the product (57) 95 mg(18%), light green solution which on recrystallization from benzene yield dark green crystals, decomp. at 198°C; pmr, δ, (60MHz) 9.7-7.85(m, 9H, ArH), -1.50 and -1.55(s, 3H each, $-CH_3$); ir (KBr), 1530(s), 1510(s), 1315(b,s), 1100(b,s), 895(m), 870(m), 815(m), 780(m), 765(m), 755(m), 735(m) and 685(m)cm^{-1}; uv(cyclohexane)$\lambda_{max}(\log\varepsilon_{max})$, 682nm, sh(3.04), 612(3.61), 580sh(3.57), 424(3.85), 325(3.84) and 222(3.78); ms peaks at m/e (relative intensity) CI, 418(MH^+, 100).

Anal. calcd. for $C_{22}H_{15}N_3O_6$: M = 417.0961.
Found. (Mass spec) M = 417.0961.

24. 2-Acetyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene (58)

Acetic anhydride (4 mL) and boron trifluoride etherate (30 drops) were added to a solution of (20) (0.25 g, 0.87 mmol) in CH_2Cl_2 (50 mL) at RT. After 3 min., the reaction mixture

(black in color) was poured into ether (250 mL) and sat. sodium carbonate solution. The organic layer was washed with sat. aq. sodium carbonate (200 mL) and water (200 mL), dried and evaporated. The residue was dissolved in pentane (30 mL) and chromatographed on a column (0.5 × 4 cm) of silica gel using firstly pentane to elute any unchanged pyrene (20) and then pentane-ether (9.5:0.5) to give the acetyl compound (58). The recovered pyrene (20) was re-acetylated, and this process was repeated 2 times until almost of the starting material had been converted. The yield of product was then 0.22 g(76%). A portion of (58) was recrystallized from cyclohexane to yield dark purple crystals, mp 140-142°C; pmr, δ, (60MHz) 9.2-7.1(m, 11H, Ar-H), 2.80(s, 3H, -C-CH_3) and -1.67(s, 6H, Ar-CH_3); ir(KBr), 1660(s), 1590(s), 1400(s), 1360(m), 1335(m), 1280(s), 1250(m), 1215(s), 1180(m), 940(m), 885(m), 870(m), 860(m), 825(m), 745(s), 730(s) and 625(m)cm^{-1}; uv(cyclohexane)λ_{max}($\log\varepsilon_{max}$) 538nm(3.72), 397(4.08), 379(4.06), 337(4.21), 318(4.26), 305(4.30) and 231(4.87); ms peaks at m/e (relative intensity) 324(M^+, 45), 309(M-CH_3, 54), 294(M-$2CH_3$, 16), 279(M-$3CH_3$, 20), 267(M, $2CH_3$, CO+H, 100), 266 (M-$2CH_3$, CO, 52) and other small peaks.

Anal. calcd. for $C_{24}H_{20}O$: C 88.88, H 6.17.

Found: C 88.82, H 6.02.

25. Methylation of sulphone (43)

A solution of lithium diisopropylamide (prepared from iPr_2NH(0.12 mL, 0.62 mmol) and n-BuLi(0.62 mmol) in dry THF (5 mL)) was added quickly via syringe to a solution of sulphone (43)(0.15 g, 0.41 mmol) in dry THF (20 mL) at 78°C under N_2. The reaction mixture turned a dark brown color. After 30 min., methyl iodide (0.076 mL, 1.2 mmol) was added to the reaction mixture, which was then allowed to warm to RT, before adding H_2O(10 mL) , and CH_2Cl_2(20 mL). The organic layer was washed with H_2O(20 mL), dil aq HCl (20 mL), H_2O(20 mL), dried and evaporated. The residue was filtered through a column (10 × 2 cm) of silica gel in dichloromethane and gave the ethyl sulphone (69), 0.107 g (69%) as white crystals from benzene, mp 198-200°C; pmr, δ, (90MHz), 8.15-6.96(m, 10H, Ar-H), 4.0-3.5(m, 2H, Ar-CHS-CH-Ar), 3.21(q,J=7Hz, 2H, $-SO_2-CH_2-CH_3$), 2.90(t, 1H, J=12Hz, Ar-CH-SO_2), 1.34(t,J=7Hz, $-CH_2-CH_3$), 0.70 (s, 6H, Ar-CH_3); ms peaks at m/e (relative intensity) 376(M^+, 14), 283(M-SO_2Et, 100), 268(32), 267(50), 253(73) and 252(81).

Anal. calcd. for $C_{24}H_{24}SO_2$: M= 376.1497.

Found: (Mass spec.) M= 376.1477.

When 5eq of lithium diisopropylamide were used in the above reaction there was obtained the bis methylated product, the

isopropyl sulphone (70), 0.105 g(65%), which on recrystallisation from benzene funished white crystals, mp 242-244°C; pmr, δ,(90MHz), 8.1-7.0(m, 10H, Ar-H), 4.0-3.3(m, 3H, $ArCH(SO_2CH)-CH-$) 2.90(t, 1H, J=12Hz, ArCHS-CH-Ar), 1.47 and 1.23(d, 3H each, J=7Hz, $-CH(CH_3)_2$) and 0.70(s, 6H, Ar-CH_3); ms peaks at m/e (relative intensity)390(M^+, 15) 283(M-SO_2CHMe_2, 100), 268(35), 267(40), 253(67) and 252(55).

Anal. calcd. for $C_{25}H_{26}SO_2$: M = 390.1653.

Found: (Mass spec.) M = 390.1681.

26. Methylation of phenyl sulphone (42).

A solution of lithium diisopropylamide (prepared from i-Pr_2NH(6.1 mL, 31 mmol) and n-BuLi (31 mmol in hexave 15 mL)) in dry THF (20 mL) was added to a solution of sulphone (42) (1.2 g, 3.1 mmol) in dry THF (100 mL) at -78°C under N_2. After 1h, excess methyl iodide was added, and then the reaction was allowed to warm to RT before adding H_2O(50 mL) and CH_2Cl_2(50 mL). The organic layer was washed with dil HCl(30 mL) and H_2O(50 mL), dried and evaporated. The residue was chromatographed in CH_2Cl_2 through a column (20 × 2.5 cm) of silica gel and gave the product (71), 1.1 g(89%). A portion was recrystallised from benzene to

yield (71) as white crystals, which decomposed at 218°C; pmr, δ, (90MHz), 8.1-7.0(m, 15H, Ar-H), 3.67 and 2.62(d, 1H each, J=15Hz, $-CH_2Ar$), 1.70(s, 3H, $-\underset{SO_2\phi}{C}CH_3$), 1.23 and 0.72(s, 3H each, $Ar-CH_3$); ir(KBr), 1460(m), 1450(m),1410(m), 1290(s), 1140(s), 770(m), 760(m), 735(s), 695(m) and 635(m)cm^{-1}; ms peaks at m/e (relative intensity) 438(M^+, trace), 297($M^+-SO_2\phi$, 100), 282($M^+-SO_2\phi$, CH_3, 30), 281(65), 268(20), 267(62), 266(71), 253(21) and 252(39).

Anal. calcd. for $C_{29}H_{26}SO_2$: C 79.45, H 5.94.
Found: C 79.11, H 5.78.

27. Trans-4,12c,12d-trimethyl-12d,12d-dihydrobenzo(e)pyrene(66) and anti-8,20-dimethyl-1-methylenebenzo(9,10-a)[2,2]metacyclophane(72)

Potassium t-butoxide (0.55 g, 4.9 mmol) was added to a refluxing solution of sulphone (71) (0.2 g, 0.49 mmol) in dry THF (10 mL) under N_2 and then heating under reflux was continued for 1h. After cooling, CH_2Cl_2(20 mL) and H_2O(10 mL) were added to the reaction mixture. The organic layer was washed with dil HCl(10 mL) and H_2O(10 mL), dried and evaporated. The purple residue was pre-absorbed onto Al_2O_3(activity III) and chromatographed in pentane on a foil wrapped column (40 × 2.5cm) of Al_2O_3(III) to yield firstly the cyclophane (72), 0.011g (9%) and then pyrene(66)

0.099 g (77%). A portion of (25) was recrystallized from pentane as purple crystals, mp 158-159°C; pmr, δ, (90MHz) 9.0-8.7(m, 2H, H-9, 12), 8.35 and 8.30(d, 1H each, J=7Hz, H-1 and 8), 8.0-7.0 (m, 7H, Ar$\underline{H}$), 2.61(s, 3H, outer Ar-C$\underline{H}_3$), -1.90 and -1.95(s, 3H each inner Ar-C$\underline{H}_3$); ir (KBr), 1360(m), 1335(m), 870(m) and 750(s)cm^{-1}; uv(cyclohexane), $\lambda_{max}(\log\varepsilon_{max})$ 640nm(2.30), 532sh (3.53), 507(3.58), 393(4.46), 374(4.29), 357sh(4.01), 340(4.28), 325(4.14), 307(4.12), 243(3.94) and 235(3.97); ms peaks at $\underline{m}/\underline{e}$ (relative intensity) 296(M^+, 22), 281(M-CH_3, 89) and 266(M-2CH_3, 100).

Anal. calcd. for $C_{23}H_{20}$: C 93.24, H 6.76.

Found: C 92.69, H 6.80.

A portion of (72) recrystallized from pentane gave white crystals, mp 143-145°C with some softening from 135°C; pmr, δ, (90MHz), 7.8-6.8(m, 10H, Ar-$\underline{H}$), 5.28 and 4.96(bs, 1H each, =C$\underline{H}_2$) 3.46(superimposed dd) t, 2H, J=14Hz Ar-C$\underline{H}_2$-), 0.76 and 0.67 (3H each, Ar-C$\underline{H}_3$); ir(KBr), 1420(m), 895(m), 800(m), 765(m), 760(s) and 730(s)cm^{-1}; uv(cyclohexane), $\lambda_{max}(\log\varepsilon_{max})$ 290nm, sh(4.83), 248(4.86) and 245(4.86); ms peaks at $\underline{m}/\underline{e}$ (relative intensity) 296(M^+, 19), 281(M-CH_3, 97) and 266(M-2CH_3, 100).

Anal. calcd. for $C_{23}H_{20}$: M = 296.1565.

Found: (Mass spec.) M= 296.1572.

28. General procedure for photoisomerisation of dihydropyrenes (36), (63), (64) & (65).

A solution of the pyrene (15 mg-25 mg) in C_6D_6 (ca 1 g) was irradiated by visible light (from a slide projector) in an nmr tube for 0.5h, when it was fully converted to the colourless open cyclophane-ene form. It was then immediately placed in the probe of the nmr spectrometer, which had been previously set at the desired temperature. The reversion to the closed pyrene form was followed by recording the internal methyl peaks (including integration) for both forms at suitable time intervals. If necessary the samples were kept in a constant temperature bath out of the nmr probe. The chemical shifts for anti-8,20-dimethylbenzo(9,10-a)[2,2]metacyclophane-1-ene (36), and its derivatives were also obtained in this way: (90MHz)

Parent-(36): δ, 8.1-6.9(m, 10H, Ar$\underline{H}$), 6.63(s, 2H, H-1,2) and 1.41 (s, 6H, Ar$C\underline{H}_3$)

5-acetyl-(63): δ, 7.85-6.73(m, 9H, Ar$\underline{H}$), 6.49(s, 2H, H-1, 2), 2.52 (s, 3H, -C-$C\underline{H}_3$), and 1.42 & 1.37(s, 3H each, Ar$C\underline{H}_3$)

5-nitro-(64): δ, 7.8-6.7(m, 9H, Ar$\underline{H}$), 6.48 & 6.46(s, 2H, H-1, 2) and 1.41(s, 6H, Ar$C\underline{H}_3$)

1-Methyl-(65): δ, 7.7-6.4(m, 10H, Ar$\underline{H}$), 6.22(bs, 1H, H-2), 2.21 (s, 3H, 1-Methyl) and 1.29 & 1.25(s, 3H each, Ar$C\underline{H}_3$).

The ^{13}Cmr spectrum (ppm) of (36) showed quaternary aromatic carbons at 143.1, 142.2, 140.3, 137.1, aromatic -CH carbons at 131.7, 131.0, 128.6, 128.2, bridge carbons at 125.4 and internal methyl carbons at 19.5.

29. Wittig rearrangement of dimer (30) and reduction to cyclophane (76)

A solution of lithium diisopropylamide (prepared from diisopropylamine (0.63 mL, 3.2 mmol)) and n-BuLi(1.6 mL, 3.2 mmol) in dry THF (20 mL) was added dropwise over 1h under N_2 to a solution of the thia-cyclophane (30) (0.5 g, 0.79 mmol) in dry THF (50 mL). After 30 min., the reaction mixture was quenched with methyl iodide (0.3 mL, 4.5 mmol). After a further 30 min. H_2O (30 mL) and CH_2Cl_2(100 mL) were added. The organic layer was washed successively with H_2O(50 mL), dil HCl solution (50 mL), H_2O (50 mL), dried and evaporated. The residue (0.43 g, 82%) was directly reduced to the cyclophane (76) by addition of W-7 Raney Nickel (10 g, 100 eq.) and ethanol (50 mL) and heating under reflux for 12h. After cooling, the catalyst was removed by filtration and the filtrate concentrated. The residue was pre-absorbed on silica gel and chromatographed in pentane: dichloromethane (9:1) on a column (20 × 2.5) of silica

gel to give the product (76) 0.17 g(46%), which on recrystallization from cyclohexane gave white crystals, mp 245-246°C; pmr, δ, (90MHz), 7.6-6.6(m, 20H, Ar-H), 3.1-2.3(m, 8H, Ar-CH_2-) and 1.90(broad singlet, 12H, Ar-CH_3); ir (KBr), 1470(m), 1435(m), 800(m), 765(s), 755(s) and 730(s)cm^{-1}; uv(cyclohexane) λ_{max} ($\log\varepsilon_{max}$) 215nm(5.06), tail: 270(3.91), 300(2.98), 300(2.5), 350 (terminates); ms peaks at m/e (relative intensity) 568(M^+, 100).

Anal. calcd. for $C_{44}H_{40}$: C 92.96, H 7.04.

Found: C 92.78, H 7.10.

30. Attempted coupling to give dibenzometacyclophane (77)

(a) di-Grignard reagent of 3,3"-dichloro-2,2"-dimethyl-o-terphenyl (22): A solution of (22) (3.0 g, 9.2 mmol) in dry THF (50 mL) was added dropwise over 30 min. to "active" Mg[64] (1.84 mmol) in THF. When the addition was complete the reaction mixture was heated under reflux for 3h, cooled and filtered.

(b) The Grignard reaction: A solution of o-dibromobenzene (2.2 g, 9.3 mmol) in dry THF (50 mL) was added dropwise over 10 min. at -70°C under N_2 to the stirred filtrate of (a) above containing the Grignard reagent. The reaction mixture was then allowed to warm to room temperature over 1h before heating under reflux for 12h. After cooling, and addition of ice-water

(30 mL), and CH_2Cl_2 (50 mL) the organic layer was separated, washed with 10% of HCl (300 mL), H_2O(2 × 100 mL), dried and evaporated. The resulting brown oil was preabsorbed onto silica gel (10 g) and chromatographed on a column (30 × 2.5cm) of silica gel using pentane as eluant to yield 45 mg(18%) of 2,2"-dimethyl-o-terphenyl (79), as an oil. The compound could only be crystallised from pentane, with difficulty to give crystals mp 84-86°C, pmr, δ, (60MHz), 7.15(s, 4H, ArH), 7.1-6.7(m, 8H, ArH) and 1.87(s, 6H, $ArCH_3$); ms peaks at m/e 258(M^+, 100), 243(M-CH_3,62) and 228(M-$2CH_3$, 35).

Anal. calcd. for $C_{20}H_{18}$: M = 258.1409.

Found: (Mass spec.) M = 258.1417.

31. Methylation of sulphone (46)

A solution of lithium diisopropylamide (prepared from diisopropylamine (0.72 mL, 3.6 mmol) and n-BuLi (1.8 mL, 3.6 mmol)) in dry THF (5 mL) was added quickly to a solution of the sulphone (46) (0.125g, 0.36 mmol) in dry THF 940 mL) under N_2 at -78°C. After 1h, the reaction mixture was quenched with methyl iodide (0.62 mL, 10 mmol) and stirred for 40 min. before addition of H_2O (20 mL) and CH_2Cl_2 (100 mL). The organic layer was washed with H_2O (30 mL), dil HCl solution (50 mL), H_2O (50 mL),

dried and evaporated. The residue was filtered in dichloromethane through a column (10 × 2 cm) of silica gel to give the product (80), 0.1 g(74%), which on recrystallization from benzene yielded white crystals, mp(dec) 240°C; pmr, δ, (90MHz), 7.7-6.8(m, 10H, Ar-H), 4.30(q, J=7Hz, 2H, Ar-$\overset{CH_3}{\overset{|}{C}}$H-$SO_2$-), 1.74(d, J=7Hz, 6H, -$\overset{SO_2}{\overset{|}{C}}$H-$CH_3$) and 0.98(s, 6H, Ar-$CH_3$); ir(KBr), 1460(s), 1430(m), 1385(m), 1300(s), 1250(m), 1215(s), 1130(s), 1095(s), 1060(s), 1035(m), 820(s), 810(s), 770(s), 730(s) and 630(s)cm^{-1}; ms peaks at m/e (relative intensity) CI:377(MH^+, 84) and 312 ($M-SO_2$, H, 100).

Anal. calcd. for $C_{24}H_{24}O_2S$: C 75.86, H 5.75

Found: C 76.01, H 5.95.

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