SYNTHESIS OF SOME PYRENE ANNELATED MACROCYCLIC SYSTEMS

by

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We accept this dissertation as conforming
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ABSTRACT

The synthesis of *trans*-10b,10c-dimethyl-10b,10c-dihydrodibenzo-[*cd,lm*]perylene has been achieved in 22 steps starting from mesitylene. Wittig rearrangement of dithiacyclophanes carrying electron-withdrawing substituents *ortho*- or *para*- to the bridge was found to be influenced markedly by temperature. Wittig rearrangement at elevated temperatures, or alternatively Stevens or Benzyne-Stevens, followed by sulfoxide-thermolysis or sulfone-basic elimination led to the corresponding pyrene in disappointingly low yields, compounded by solubility problems. The desired tetrahydropyrene, however, could be synthesized from the pyrolysis of the bridge sulfone, obtained by the oxidation of the dithiacyclophane, and conversion of the resulting *meta*-cyclophane to the intermediate tetrahydropyrene in fairly good yields. In addition, using the intermediate 1,3-bis(bromomethyl)-2-methyl-4,5,9,10-tetrahydropyrene, highly annelated *trans*-14c,14d-dimethyl-14c,14d-dihydrobenzo[*rst*]-dinaphtho[8,1,2-*cde*:2',1',8'-*klm*]pentaphene and *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*rst*]naphtho[8,1,2:*cde*]pentaphene have also been obtained. The first examples of benzannelated *cis*-dihydropyrenes were also synthesized. Access to a benzannelated system carrying a saturated bridge has been made possible by means of partial dehydrogenation of a saturated system.

The aromatic character of *trans*-10b,10c-dimethyl-10b,10c-dihydrodibenzo[*cd,lm*]perylene has been substantiated by the classical concept of electrophilic aromatic substitution as well as by its diatropic nature.

Qualitative predictions have been made to assess the diatropicity of the compounds synthesized as compared to the parent compound *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene using an empirically-arrived at linear relationship between the chemical shift shielding of the protons embedded in the π-electron cloud of a series of benzannelated dihydropyrenes and the average deviation of the π-SCF bond order of the macrocyclic ring from the Hückel [14]annulene value of 0.642. The chemical shifts determined agree with those calculated to < 0.5 ppm, both in the *trans*- as well as in the *cis*- series. The strength of the macrocyclic ring current is greatly influenced by the bond localization that may result from monobenz- or higher ring annelation. The compounds made are all diatropic and this suggests that mere increase in the degree of annelation does not lead to bond localization in a macrocyclic ring.

EXAMINERS:

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TO

MOM AND DAD

CHAPTER ONE

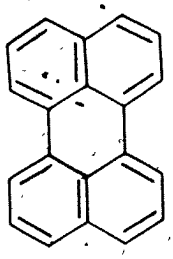
INTRODUCTION

1.1 *Prologue*

Changes in the meaning of words is a process that goes on ceaselessly, inexorably and imperceptibly. When first used at the beginning of the nineteenth century, the generic name *aromatic* was given originally to a structurally diverse collection of compounds which had one common property, a fragrant odor.

The definition of aromaticity has always been one of the most difficult and yet one of the most fascinating problems in chemistry. The discovery of benzene by Faraday[1] in 1825 and its subsequent synthesis by Mitscherlich[2] in 1833 were the early signposts heralding the advent of *aromatic* chemistry. Aside from their very considerable commercial importance, hydrocarbons[3], be they saturated or unsaturated, have really captured the imagination of theoreticians and experimentalists alike in recent years. Kekulé's[4] intuitive assignment of the structure of benzene led to an unprecedented expansion in both experimental and theoretical aromatic chemistry and the interplay of the two fields provided the necessary fillip to considerable progress in this area. The changing emotional content with which the word *aromatic* has been endowed is indeed a fine reflection of the technological revolution in the tooling of chemistry with the widespread introduction of, for example, spectroscopy and chromatography in many and varied forms. The advent of high-speed electronic computers influenced the interpretive and predictive powers to a degree that cannot be over-emphasized.

Whereas there remains a fundamental and as yet unresolved problem in defining the term *aromatic character* comprehensively, qualitatively there has never been real disagreement. In 1925, Armit and Robinson[5] recognized and reenunciated Bamberger's hexacentric theory suggesting that the aromatic properties of the benzene ring are related to the presence of a closed loop of electrons. The remarkable flowering of molecular orbital theory, particularly developed by Hückel,[6] and its application to benzene deprived the concept of aromatic sextet[3a] of its primacy by predicting relative electron stability to be general for *planar, monocyclic, fully conjugated systems possessing a closed shell of (4n+2)π-electrons*. While Hückel's (4n+2)π-electrons postulate remains the centerpiece of any discussion of aromaticity, the theoretical concepts of the Hückel rule were weakened by the bond alternation[7] concept; for example, in a (4n+2)π-electron system with 'n' sufficiently large, bond alternation rather than delocalization sets in. The inadequacy of the Hückel rule becomes evident when one looks at the π-electron system in perylene 1 and dibenzo(*e*,*l*)pyrene 2, both of which are (4n)π-electron



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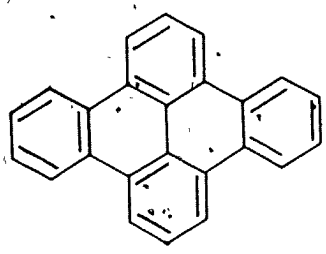


2

systems but very stable, aromatic compounds. In order to broaden Hückel's rule, the periphery modification of Platt[8], the polycyclic version of Volpin[9] and Randić's[10] enumeration of conjugated π-electron

circuits have evolved over a number of years.

The major stimulus for the progress of aromatic chemistry was the development of wave-mechanics in the 1920's. Following Hückel's simple but elegant solution to the problem of benzene by separation of the π-electrons from σ-electrons, it was just a matter of time before one advanced from simpler resonance-Linear Combination of Atomic Orbital (LCAO) theories to π-Self Consistent Field-Hückel Molecular Orbital (π-SCF-HMO) methods[11].

1:2 *Criteria for aromaticity*

The oldest of all definitions of aromaticity is that aromatic molecules have the appearance of being unsaturated but nevertheless behave chemically unlike alkenes or alkynes. It was recognized that benzene, naphthalene, anthracene and related compounds possessed the common traits of stability to oxidation, reluctance to undergo hydrogenation or halogen addition reactions but a proneness to electrophilic substitution. Thus substitution, rather than addition, is considered to be a guide to the aromaticity of the reactant. However, the fact that a molecule does not undergo electrophilic substitution does not necessarily mean it is not aromatic, but merely that other energetically more favorable pathways are readily available to the molecule under consideration.

The delocalization of π-electrons lowers the energy content of the aromatic molecule relative to the hypothetical bond-localized structure. The best available aromaticity values are from Dewar's resonance energy[11] calculations. However, resonance energy calculated from bond energies[12],

Kékulé's structures[13] or graphical methods[14] are also available. To get an estimate of the resonance energy one can determine the heats of combustion or hydrogenation which are measurable quantities. But the use of resonance as a criterion for aromaticity is not always satisfactory since the values obtained are sensitive to the initial choice of model compounds. Steric interaction and angle strain in larger rings can complicate stability measurements.

Extensive π-electron delocalization in an aromatic system requires the planar molecule to have similar bond lengths, around the periphery. In a linear polyene such delocalization does not occur and results in unequal bond lengths as shown (Figure 1). The actual physical confirmation of such equivalence of bond lengths e.g. in benzene can be

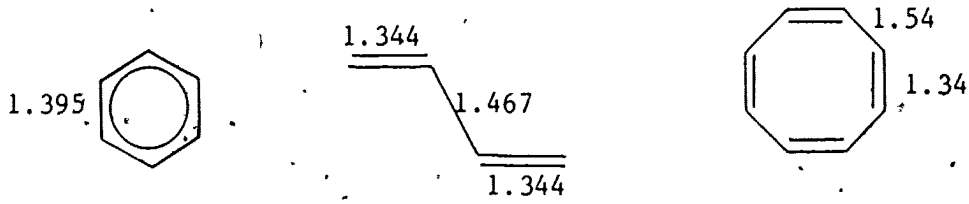
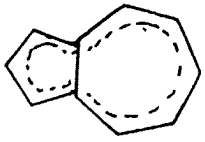


Fig. 1. Bond lengths (°A) in benzene, 1,3-butadiene and cyclooctatetraene.

obtained by electron and neutron diffraction[15], spectroscopic[16] and X-ray crystallographic[17] methods. In azulene 3, a molecule widely regarded as aromatic, the peripheral bond lengths[10] are all nearly equal, whereas the transannular bond is slightly longer. Extension of this definition to a heterocycle, e.g. pyridine is again a problem.

An X-ray analysis[18] of 1,6-methano[10]annulene-2-carboxylic acid 4 indicated that the perimeter is not quite planar, but that the bonds are typical benzenoid aromatic bonds, their lengths varying only between

1.38 and 1.42 °A. The structure reported for [18]annulene 5 in the



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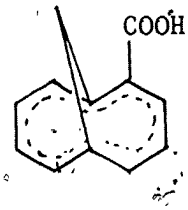

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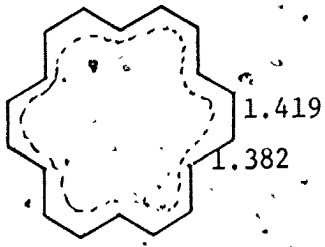

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solid state indicated only a small deviation from planarity, but two types of bonds of different lengths[19]. However, such studies involve preparation of suitable crystals, and besides, they entail lengthy procedures requiring specialized apparatus and technical skill and hence cannot be considered for routine use.

It has been suggested that the position of the ultra-violet or visible maximum gives an indication of the aromaticity of the molecule[20]. The electronic spectrum of the (4n) and (4n+2) series of cyclic conjugated systems is not so clear. All large ring polyenes are colored compounds with absorptions in the ultra-violet and visible regions. The electronic spectrum, however, is not simply a property of the ground state of the molecule, but depends upon the differences in the energy between the ground state and the excited state. Within a group of molecules, the electronic spectrum is often an excellent indicator of the way in which the system has been perturbed, but it does not appear to be a useful general criterion for aromaticity. With the advent of magnetic techniques, most notably ^{1}Hmr spectroscopy,[21,22,23] one can determine experimentally, whether or not a compound has a closed ring of π-electrons and on this basis *aromaticity* can be defined as *the ability to sustain an induced ring current (diamagnetic current) of π-electrons*. A compound

which exhibits this ability is called diatropic. Although this definition is not without its flaws,[24] it is the one most commonly accepted today. Theoretical[25] and experimental[26,27] methods have been developed using gas-phase microwave spectra to measure the magnetic susceptibility anisotropy in any molecule which has a microwave spectrum. The large anisotropy in benzene compared to cyclohexa-1,3-diene was interpreted as strong evidence for the existence of a substantial ring current in aromatic compounds. The availability of more reliable values for the Pascal constants of the susceptibilities of the component parts has led to more accurate estimates of the susceptibilities of model systems and Dauben[28] and co-workers have used diamagnetic susceptibility exaltation as a measure of aromaticity. Although attractive, such a determination requires a calculated estimate of the expected susceptibility in the absence of exaltation, a problem reminiscent of resonance energy estimation.

One of the predictions of the Hückel theory is that the π-electrons of the aromatic ring will be in a doughnut-shaped cloud above and below the plane of the ring. Presumably, the center or cavity of this π-electron cloud should be empty space. The effect of an applied magnetic field perpendicular to the plane of the ring is to induce a circulation of electrons, as shown in fig. 2. This electron current, called a diamagnetic ring current, generates an induced field, the effect of which is to oppose the applied field inside the ring and to reinforce it outside the ring. Therefore, the protons outside the ring are deshielded[21] and resonate at low field compared to protons not under the influence of an induced ring current. In conjugated systems exhibiting a diamagnetic ring

current, protons within the ring are shielded and appear at high field.

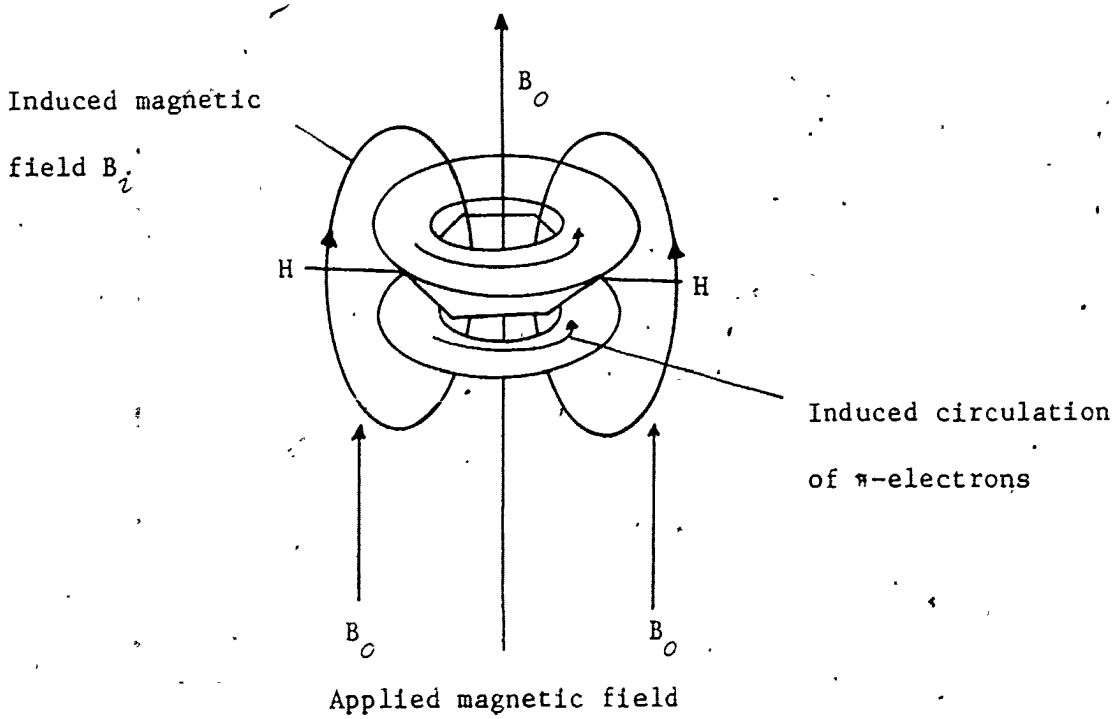


Fig. 2 An *aromatic* hydrogen atom and the ring current effect.

In contrast to the (4n+2) systems, (4n)π-electron systems exhibit a resultant paramagnetic ring current so that the inner protons are deshielded while the outer ones are shielded. These (4n) systems are called anti-aromatic or more correctly, paratropic. However, as in the case of a diamagnetic ring current, non-planarity and bond length alternation partly inhibit the paramagnetic ring current. Cyclic conjugated polyenes in which the protons appear at the usual position as expected for a system without significant delocalization are called non-aromatic or atropic.

It must be said, however, that not a single one of these criteria

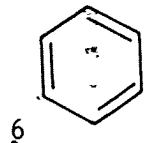
can always be counted on to classify a compound as aromatic; all have their exceptional cases, and none, when violated are good enough by themselves to rule out aromaticity. It has even been proposed[29] that the use of the word *aromatic* be discontinued altogether.

What does the word *aromaticity* convey ? Simply stated - " When I use a word,' Humpty Dumpty[30] said, in rather a scornful tone, " it means just what I choose it to mean- neither more nor less."

" The question is," said Alice, " whether you *can* make words mean so many different things."

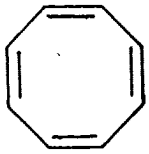
1.3 *Annulenes to Benzannulenes.*

A very large part of current activity in the whole sphere of aromatic chemistry is concerned with synthesis. Hückel's $(4n+2)\pi$-electron rule spurred the synthesis of higher homologs of benzene (monocyclic polyenes termed annulene by Sondheimer[31]). At first sight [10]-annulene 8 should be the first cyclic polyene after benzene to exhibit diatropicity. Of the three geometrically possible isomers of [10]-annulene, steric interaction of the two internal hydrogen atoms occurs[32,33] in 8A whereas 8C is affected by angle strain. Mislow[32] suggested that [30]annulene 12 would be the smallest planar macrocyclic system in which bond angle strain and non-bonded interaction would be sufficiently reduced to allow synthesis. Other authors contended that [18]annulene 5 should be capable of existence in a planar form. The [18]annulene 5 was the first macrocyclic annulene to be prepared by Sondheimer and his co-workers[31], which was diatropic compared to the non-aromatic [8]annulene cyclooctatetraene 7 as seen from the chemical shift of the protons (see Table 1) and could be acetylated and nitrated



6

[6]annulene



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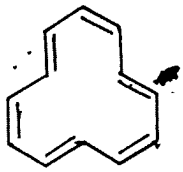
[8]annulene



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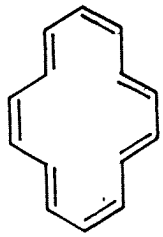
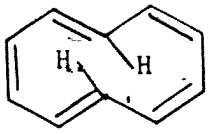
[12]annulene

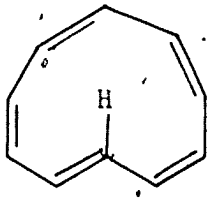


10

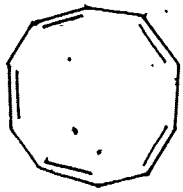
[14]annulene



8A

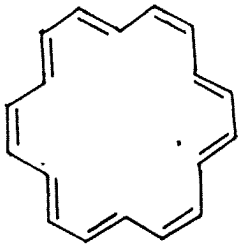


8B



8C

[10]annulene



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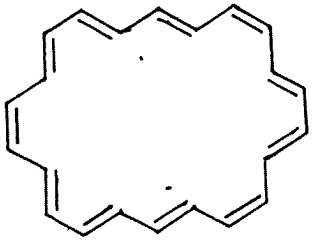
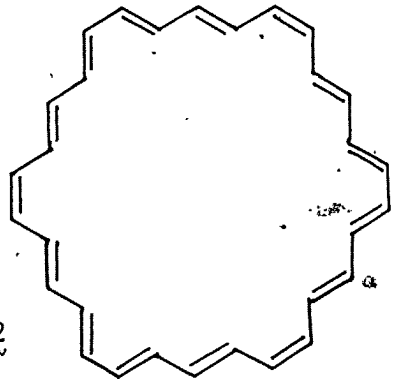
[18]annulene



11

[22]annulene



12

[30]annulene

under specific conditions. The all *cis* 8C and mono *trans* 8B have been prepared [34] at - 80 °C and are non-planar. Whereas [14]- and [22]-annulene(10 and 11 respectively) have been prepared[35,36] and are diatropic, [26]annulene itself is yet to be synthesized and the ^{1}Hmr of [30]annulene 12 could not be obtained.[37] The (4n+2)annulenes possessing 14 to 22 carbon atoms are all diatropic systems but unlike benzene, they are fluxional

Table 1. Comparison of chemical shifts (δ) for inner and outer protons in (4n+2)annulenes and [8]annulene,cyclooctatetraene.*

Annulene	Inner H	Outer H	Ref.
[6]-6	-	7.24	38
[8]-7	..... 5.70	.....	39
[10]-8B	..... 5.84	.....	34b,d
[10]-8C	..... 8.66	.....	34b,d
[12]-9	8.0	6.00	34g,h
[14]-10	0.0	7.60	35
[18]-5	-2.99	9.28	31,35
[22]-11	-0.40, -1.20	9.65-9.30, 9.10-8.85	36
[30]-12	No ^{1}Hmr obtained		37

* Spectra run at different temperatures. Spin-spin splitting patterns and coupling constants wherever applicable are not given.

molecules which undergo conformational changes with low inversion barriers, as shown in Table 2.

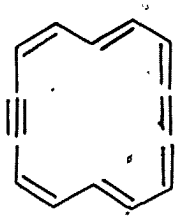
The replacement of one or more of the alkenic linkages in annulene by alkynic linkages leads to what are known as dehydroannulenes. The triple bond contributes only two π-electrons to the ring π system, with the remaining two π-electrons occupying an orthogonal orbital. Thus the dehydroannulenes will be of the same Hückel type as the corresponding annulenes. Sondheimer[42] and co-workers have prepared a number of

Table 2. Inversion barriers to proton exchange in the annulenes

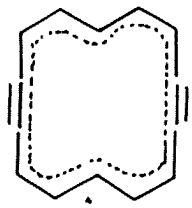
Annulene	$\Delta G^{\neq}$ (KJmol^{-1})	Ref.
[12]-9	23.0	35c
[14]-10	42.43, 45.2	35c, 40
[16]	36.20, 36.0	35c, 40
[18]-5	61.50, 56.1	35c, 40
[20]	41.0	41
[22]-11	53.6	40
[24]	46.0	40

dehydroannulenes. The dehydroannulenes have magnetic properties similar to the annulenes but the triple bond imposes some conformational integrity making the σ-framework more rigid. Consequently the fluxional behaviour is damped and non-averaged ^{1}Hmr spectra are often obtained at room temperature for the (4n+2)dehydroannulenes unlike the spectra of some (4n+2)annulenes which have been found to be temperature-dependant. In addition to monodehydroannulenes, di-[42c], tri-[43], tetra-[43], and penta-[31] dehydroannulenes have also been synthesized.

A novel example is 1,8-bisdehydro[14]annulene 13

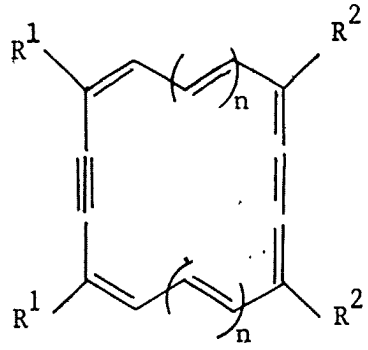


13



13a

Unlike some of the (4n+2)dehydroannulenes, 13 can be written as two equivalent Kekulé structures as in the case of benzene. It can be readily nitrated, acetylated and sulfonated under conditions[42] which decompose [14]annulene. Nakagawa and co-workers[44] have devised a general synthesis of dehydroannulenes which proceeds in good yields. The 'acetylene-cumulene' bisdehydro(4n+2)annulenes 14 (n=1-5) containing 14, 18, 22, 26 and 30 carbon atoms as well as the tetrakisdehydro-annulene 15 (n=1,2) can be made similarly, are clearly symmetrical, delocalized systems and exhibit a much stronger ring current than the corresponding 'acetylene' dehydro(4n+2)annulenes. The substituents R^1, R^2- other than hydrogen- can be identical or different.



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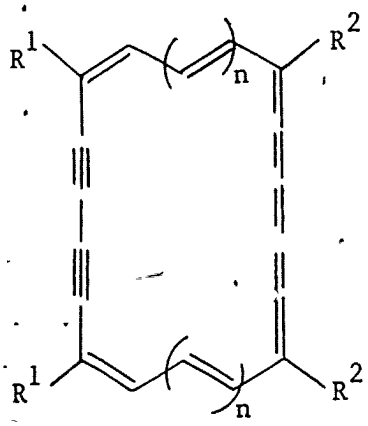


15

The ^{1}Hmr spectra of 15 (n=1) when R^1= Ph, R^2= Bu^t and R^1= Bu^t, R^2= Ph are identical implying symmetrical delocalized systems. The ^{1}Hmr spectra of these compounds suggest that all are diatropic. Although the diatropicity decreases with increasing ring size, it is pertinent to note that bisdehydro[30]annulene 14 (n=5) is definitely diatropic , in spite of being a 30-carbon ring system, whereas in an

usual [30]annulene, bond alternation is believed to set in making it non-aromatic(see Table 3).

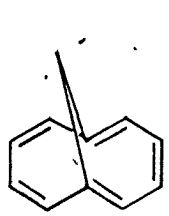
Table 3. ^{1}Hmr δ values of some tetra-t-butyl-dehydroannulenes[44b]

	Outer H	Inner H	Δδ (Outer-Inner)	Ref.
Dehydro-annulene 14				
[14] n=1	9.42	-4.39	13.81	47
[18] n=2	9.57[a]	-3.64	13.21	48
[22] n=3	8.99[a]	0.82	8.17	49
[26] n=4	8.10[a]	∿2.00	6.10	50
[30] n=5	7.50	3.50	4.00	51
Tetrakis-dehydro 15				
[18] n=1	9.98	-4.92	14.90	45
[22] n=2	9.90[a]	-3.44	13.34	46

[a]Average δ value taken in this case

We have seen that the introduction of alkynic feature in an annulene tends to impart some measure of stability to the annulene perimeter. In those annulenes in which the internal hydrogen atoms impose such strain that the compound is not very planar or only marginally stable, an elegant way of overcoming or minimizing some of the strain is by replacing those

atoms by a single bridging atom leading to a rigid, planar annulene perimeter in which all the peripheral bonds are equivalent. As discussed by Haddon,[60] these criteria are best met in some of the bridged annulenes, e.g. 20, 25 and 28 synthesized by Vogel[52] and Boekelheide[61]. Vogel *et al.* succeeded in preparing the bridged [10]annulene 16 and its



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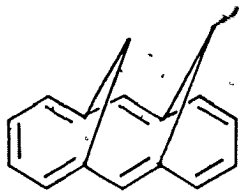

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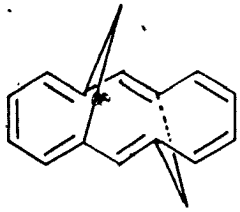

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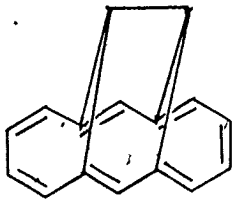
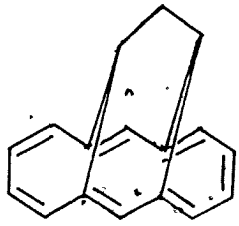


19[57]



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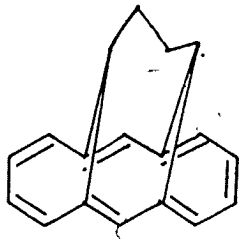

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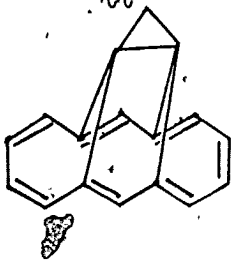

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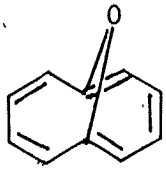
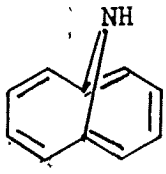


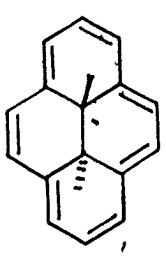
23[58]



24[58,59]

aromatic nature was confirmed on the basis of its ^{1}Hmr, stability and susceptibility to electrophilic substitution. Such bridging is feasible with atoms other than carbon; the epoxide 23 and amine 24 are well-

defined aromatic compounds similar in their behaviour to 1,6-methano-[10]annulene 16. A number of bridged [14]annulenes have also been synthesized. Bridging in the annulene leads to a more stable structure with the resulting molecules having fewer non-bonded interactions and these compounds can be considered macrocyclic systems provided the bridge is looked upon as a minor perturbation of the whole system. Boekelheide and Phillips prepared *trans*-15,16-dimethyl-15,16-dihydropyrene[61] 25 which is a [14]annulene bridged by a two-carbon unit and is diatropic, nearly planar[62] with almost equal bond lengths and can be subjected to electrophilic substitution.[63] Incidentally, the protons of the internal methyl groups appear at δ -4.25. The diethyl- and di- n-propyl homologs of 25 have also been shown to be aromatic and have been used to map the magnetic field inside the ring.[61a, 63d] Eventually the parent compound 26 was reported by Mitchell and Boekelheide[64]; the inner protons appear at δ -5.49, indicating that it is the most diatropic of all known [14]annulene systems. The importance of planarity becomes evident when one notes that the internal methyl protons of the *cis* compound 27 appear at δ -2.06 indicating a reduced diamagnetic ring current compared to 25. Whereas the monocyclic [18]annulene has its



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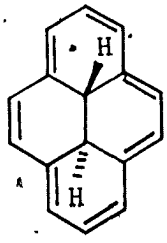

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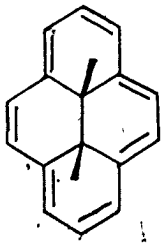

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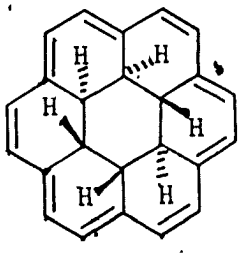
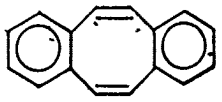


28

internal protons at δ -2.99 at - 70 °C, in the bridged [18]annulene 28

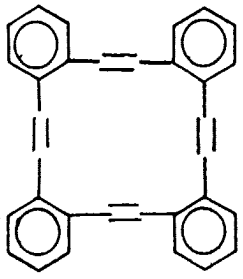
two of the six internal protons[65] appear at δ -7.88, the highest value for any of the known (4n+2) uncharged systems.

Synthetically the easiest way to stabilize an annulene is to annelate the system with benzene rings, e.g., dibenzocyclooctatetraene 29

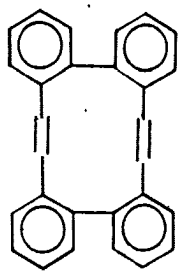


29

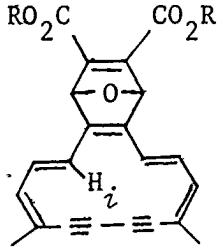
was fully characterized[66] before cyclooctatetraene 7 itself. The phenomenon, whereby in fused systems some rings give up part of their aromaticity to adjacent rings, is called annelation. The effect on NMR data when annulenes are benzannelated has been reviewed[67] recently. Tetrabenz[16]annulene[68] 30 and tetrabenz[12]annulene[69] 31 were among



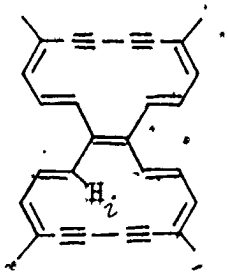
30[68]



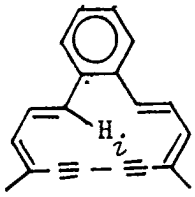
31[69]



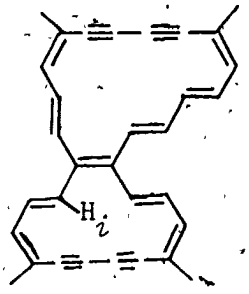
32[70a]



33[70c]

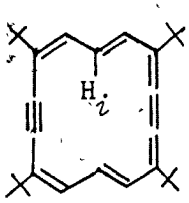


34[70b]

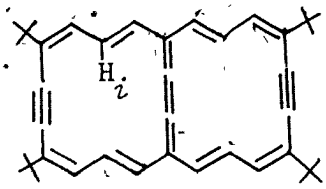


35[75]

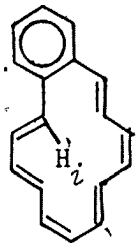
the earliest examples to be made and both are non-planar [4n]annulenes, whereby one cannot comment on the effect of the benzene ring on the macrocyclic ring system.



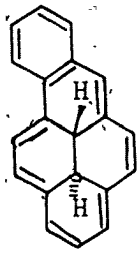
36[76]



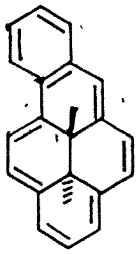
37[76]



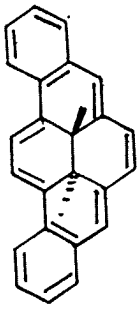
38[77]



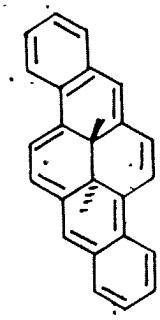
39[74]



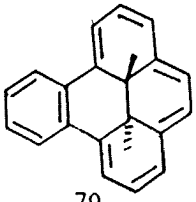
40[78]



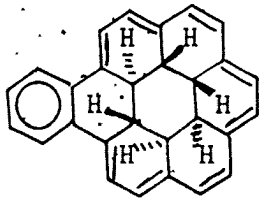
41[78]



42[78]



43[79]



44[72]

A considerable amount of effort has been devoted to the synthesis and study of benzannulenes and annelated dehydroannulenes of both the (4n) and (4n+2) electron series, especially by Sondheimer,[70] Staab,[71] Boekelheide,[72] Nakagawa,[73] and Mitchell[74] and in all cases the diatropicity or paratropicity of the macrocyclic ring is reduced (Table 4). The effect of annelating 32 [70a] by another macrocycle to give 33[70c] is much less compared to that observed in the benzannelated product 34.[70b] Examination of the inner protons of the 14-membered ring shows that in the case of 35,[75] the 16-membered ring makes a paratropic contribution, the inner protons being at higher field than in 33. In the bridged

Table 4. ^{1}Hmr δ values for inner protons or methyl groups of some annulenes and their annelated derivatives.

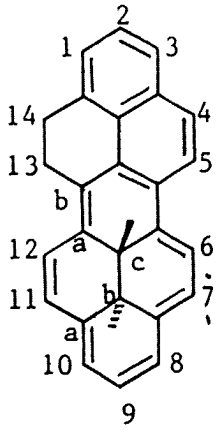
Annulene	Inner proton or methyl group	Ref.
[14]-10	0.0	35
-32	-2.12	70a
-33	3.82	70b
-34	4.99	70c
-35	1.42	75
-36	-4.39	76
-37	-2.85	76
-38	5.2 - 4.2	77
-26	-5.49	64
-39	-1.35	74
-25	-4.25	61
-40	-1.60	78
-41	0.02	78
-42	-3.58	78
-43	-1.85	79
[18]-44	-1.1, -2.6	72
-28	-7.88	65

macrocycle 37 [76] the internal protons appear at δ -2.85 compared to δ -4.39 seen in the parent 36.[76] This suggests that 37 behaves more like two [14]annulenes systems fused together rather than a [26]annulene moiety in which the bridge is just a minor perturbation.

While benzannelation stabilizes 38, it induces greater bond-localization of the annulene perimeter compared to the parent [14]annulene 10. Introduction of an ethano-bridge in 10 to form 26 helps hold the molecule

in a planar configuration, thereby enhancing its diatropicity. Benzannelation of 26 to form 39 results in the internal protons shifting from δ -5.49 in 26 to -1.35 in 39, a definite reduction in diatropicity of the macrocyclic ring. While benzannelated dimethyldihydropyrene 40 is less diatropic than the parent dimethyldihydropyrene 25, the dibenzannelated *cisoid*-dimethyldihydropyrene 41 is even less so. However in 42, which is also a dibenzannelated derivative of 25, but *transoid* - unlike 41, the internal methyl groups appear at higher field (δ -3.58) suggesting that the degree to which the ring current (or diatropicity in this case) is quenched is influenced not only by the extent but also by the mode of annelation. Benzannelation of 28 to 44 results in the signal due to the internal protons moving from δ -7.88 in 28 to -1.1 in 44.

We thus became interested in the feasibility of making diatropic



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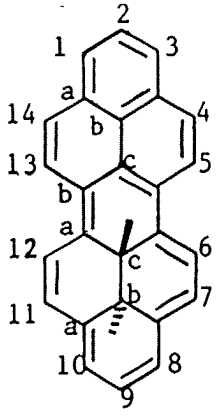
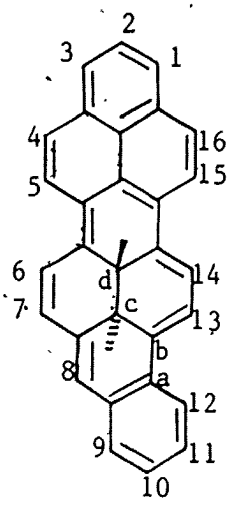


46

45 : *trans*-10b,10c-Dimethyl-10b,10c,13,14-tetrahydrodibenzo[*cd*,*lm*]-perylene.

46 : *trans*-10b,10c-Dimethyl-10b,10c-dihydrodibenzo[*cd*,*lm*]perylene.



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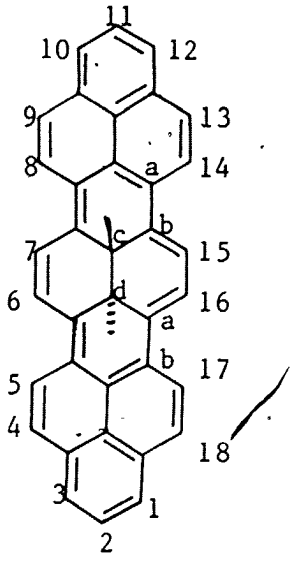


48

47 : *trans*-12c,12d-Dimethyl-12c,12d-dihydrobenzo[*rst*]naphtho-[8,1,2-*cde*]pentaphene.

48 : *trans*-14c,14d-Dimethyl-14c,14d-dihydrobenzo[*rst*]dinaphtho-[8,1,2-*cde*:2',1',8'-*klm*]pentaphene.

(relatively symmetrical) highly annelated derivatives of 25. We were also interested in seeing whether there existed any correlation between the ring current deshielding and the degree of bond localization in such annulenes. With this in mind we decided to synthesize the compounds 45, 46, 47 and 48.

CHAPTER TWO

PREDICTED RELATIVE DIATROPICITY

2.1 *From Kekulé structure to Quantum Chemistry*

The Kekulé structures of benzene, while admittedly unsatisfactory, were generally used by chemists as late as 1945. The currently accepted structure of benzene is the result of an extension of the structural theory; this extension is the concept of *resonance*. Hückel determined[6a] the energy levels for the π-orbitals of benzene by a Linear Combination of Atomic Orbitals (LCAO) method, introducing a series of simplifying approximations which constitute the framework of the Hückel Molecular Orbital (HMO) method. One of the basic assumptions is that the σ-electrons and π-electrons in bonds act independently. In order to overcome the weakness inherent in Hückel's use of one-electron Hamiltonians coupled with the neglect of electronic interaction, Pople,[80] Pariser and Parr[81] proposed the use of many-electron Hamiltonians wherein electronic interactions were taken into account. This self-consistent-field(SCF) approach is known as the Pople-Pariser-Parr (PPP) approximation and has been used to calculate a variety of molecular properties.

A property that bears some relation to structural features is the *ortho* H-H coupling constant in ^{1}Hmr spectrum.[82a] A linear relation exists between the *ortho*-coupling constants, J, of fused benzenoid hydrocarbons and the π-bond order, P, as given by the equation

$$J = 12.7\ P - 1.1\ Hz \quad \text{------} \quad (1)$$

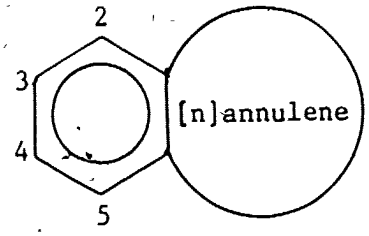
The π-bond order, P, of the appropriate C-C bond can be calculated using simple molecular orbital theory. The calculated values of the coupling constant J compared to the experimentally observed values for some

hydrocarbons are indicated in Table 5.

Table 5. *ortho* Coupling constants in some Polycyclic Aromatic Hydrocarbons.[83]

Compound	C—C bond	P π-bond order	J_{exp}	J_{cal}
Benzene	1,2	0.667	8.0	7.4
Naphthalene	1,2	0.725	8.1	8.1
	2,3	0.603	6.4	6.6
Anthracene	1,2	0.738	8.3	8.3
	2,3	0.586	6.5	6.3
Pyrene	1,2	0.670	7.6	7.4

On the basis of PPP-SCF calculations, Günther *et al.*[84] have shown how the ratio of π-bond order, $Q = P_{23}/P_{34}$, in the six membered ring of benzannulene 49 may be used to determine the electronic ground state properties of [n] annulene. Estimates of bond order 'P' can be made



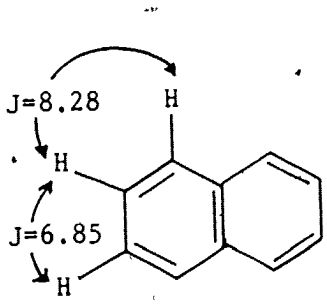
49

from vicinal H—H coupling constants $^3J(H,H)$. For benzenoid hydrocarbons,

one makes use of the equation (2).

$$P_{\mu,\nu}\ (SCF) = 0.104\ {}^{3}J_{\mu,\nu} - 0.120 \qquad \text{---} \qquad (2)$$

The value of 'Q' is used as a guide to the diatropicity of the ring. For delocalized [4n+2]annulenes the ratio (Q) of P_{23}/P_{34} is > 1.10 and for delocalized [4n]annulenes it is < 1.04, whereas the localized systems of either type exhibit values between 1.04 and 1.10. Thus naphthalene 50 has a Q-value of 1.252, benzocycloheptatriene 51 of 1.076, benzotropylium cation 52 of 1.223, benzocyclooctatetraene 53 of 1.072 and benzocyclooctatetraenyl dianion 54 of 1.584.



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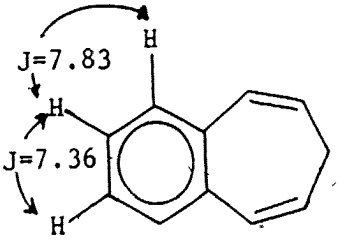
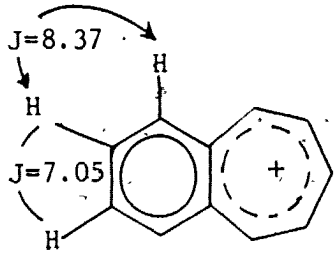
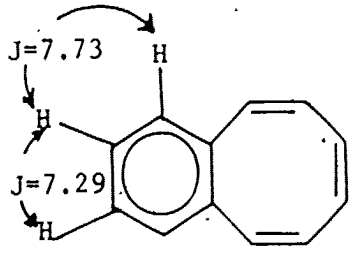


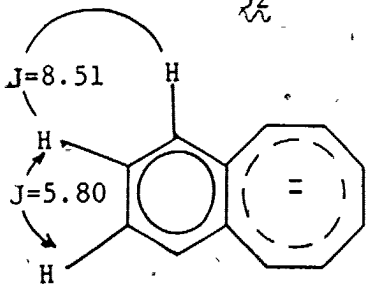
51[82b]



52[82b]



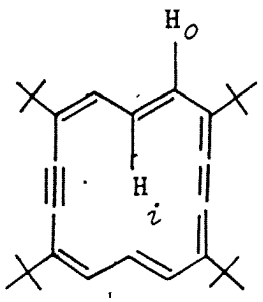
53[82b]



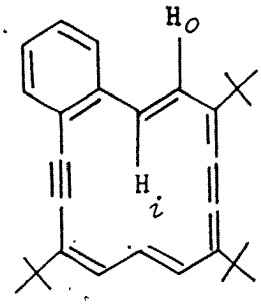
54[82b]

A series of annelated systems have been prepared by Nakagawa[44b] and it was suggested that the difference in chemical shifts of the inner and outer protons, i.e. $\Delta\delta = |\delta_i - \delta_o|$ where δ_i and δ_o are the shifts of the inner and outer protons respectively, is an indication of the magnitude of the diamagnetic ring current. A cursory glance at Table 6 indicates

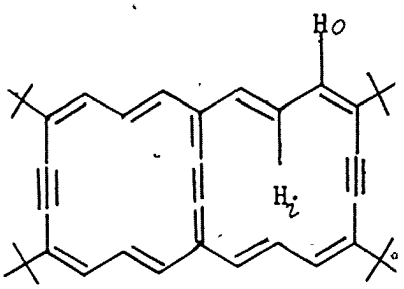
the effect benzannelation has on diatropicity. Whereas annelation by one



36



55



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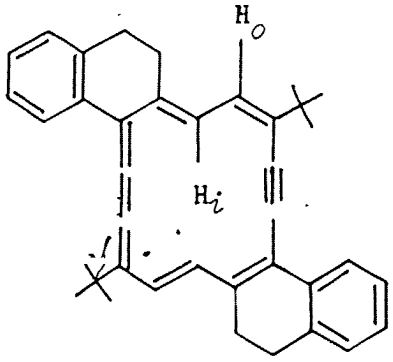

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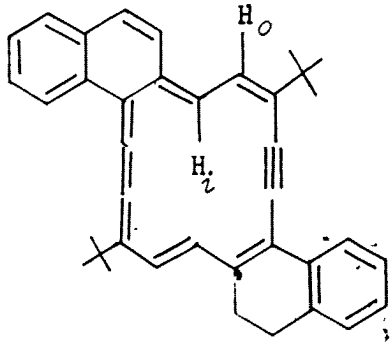
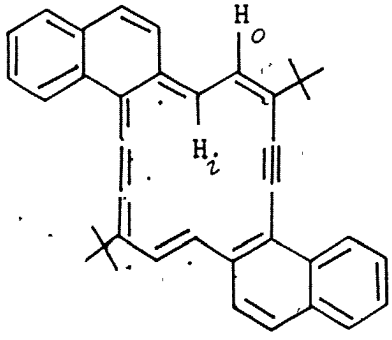


57



58

Table 6. ^{1}Hmr δ values of inner and outer protons and the percentage of ring current in some annulenes and annelated systems.[67]

Compound	δ_i *inner*	δ_o *outer*	$\Delta\delta = (\delta_i - \delta_o)$	% RC
36	-4.39	9.42	13.81	100
55	0.81-0.71	8.97-8.30	7.6-8.2	57
37	-2.85	10.16-9.61	∿12.80	93
56	-3.47	9.52	12.99	(∿100)
57	-1.22-1.53	9.80-9.17	10.6-11.0	78
58	-3.45	10.22	13.67	100

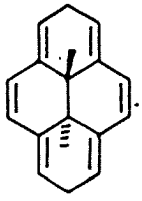
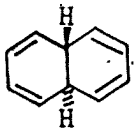
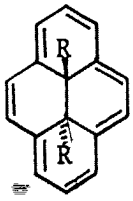
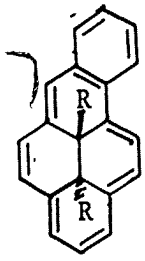
$$\% \text{ RC} = \frac{\Delta\delta \text{ (annulene)}}{\Delta\delta \text{ (parent)}}$$

benzene ring in 55 reduces the diatropicity considerably compared to the parent 36, annulenoannelation in 37 does not cause bond localization to the same extent. The mononaphthannelated compound 57 is less diatropic than the parent but the fusion of two naphthalene rings as in 58 increases the diatropicity over that of the bisdihydronaphthalene analog 56. This can be accounted for by a comparison of the Kekulé structures. Whereas 58 has two equivalent Kekulé structures (as in benzene) they are not equivalent in case of 56. Thus, when fusion

occurs such that the resulting Kekulé structures are symmetrical and identical, i.e. that no bond localizing effects are caused, then the resulting annulenes are strongly diatropic.

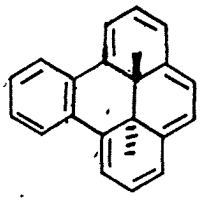
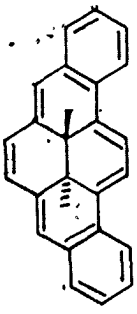
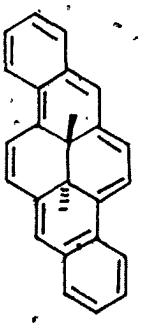
Turning our attention to the ethano-bridged [14]annulene, we can have both the internal hydrogens or the internal methyl groups in the shielding region of the π-electron cloud. A series of such annulenes along with some of their mono- and dibenzannelated analogs have been made, thanks to Boekelheide[63,85] and Mitchell[74] and the chemical shifts, along with the percentage of ring current retained on annelation, are shown in Table 7. Here, however, instead of comparing δ_i and δ_o a model non-aromatic system is used as the standard, e.g., for the internal hydrogen case we use 9,10-dihydronaphthalene 60 as the model and for the internal methyl situation we consider *trans*-15,16-dimethyl-2,7,15,16-tetrahydropyrene 59 as the standard. As seen monobenzannelation of 26 to 39 reduces the ring current to about 50 %. Similarly, monobenzannelation of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (i.e., *trans*-15,16-dimethyldihydropyrene) 25 to give 40 or 43 also quenches the ring current to about 50 %. However, the effect on dibenzannelating a substrate depends on the way the annelation is effected. An explanation on the basis of equivalent Kekulé structure has been advanced by Mitchell[78], e.g., let us consider 41 and 42. Whereas 42 can be written as two pairs of equivalent Kekulé structures 42A and 42B, those for 41 are not equivalent, are probably of different energies (dominated by two benzene rings) and thus would be predicted to be less diatropic. In the Kekulé structure contributing to 42, we see that the bond arrowed is a double bond in two out of a possible four Kekulé

Table 7. Calculation of % RC of some benzannelated bridged [14]annulenes.

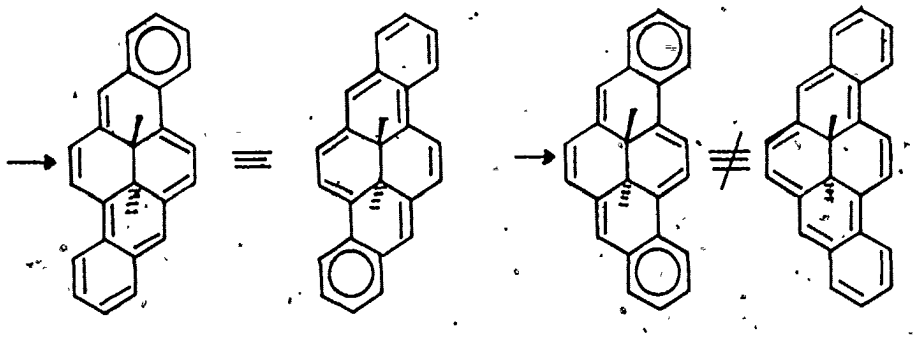
Compound	δ	$\Delta\delta=\lvert\delta_{compd}-\delta_{model}\rvert$	% RC	Ref.
 Model 59	0.97	-	-	63a, 85a,b
 Model 60	2.86	-	-	34b
 26 (R=H)	-5.49	8.35	100	63a, 85a
25 (R= Me)	-4.25	-5.22	100	85b
 39 (R=H)	-1.35	-4.21	50	74
40 (R= Me)	-1.60	-2.53	48	78

contd...

Table 7. (contd..)

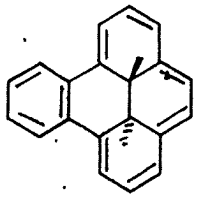
Compound	δ	$\Delta\delta=\lvert\delta_{compd}-\delta_{model}\rvert$	% RC	Ref.
 43	-1.85	-2.82	54	79
 41	0.02	-0.95	18	78
 42	-3.58	-4.55	87	78

structures. In 41 , however, it is so only in four out of the five possible Kekulé contributors. In other words, bond localization is more predominant in 41 than in 42 leading to a marked reduction in the

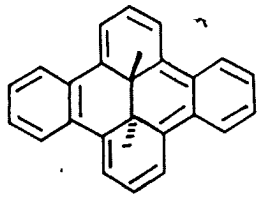


42A 42B 41A 41B

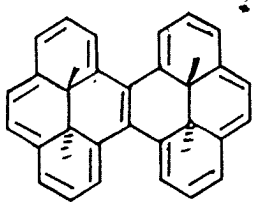
diatropicity of 41. Hess and Schaad have attempted to derive a qualitative correlation of HMO bond orders[86] and the chemical shifts for 25, 40, 41 and 42. In order to avoid any local structural effects of the annelating benzene ring(s), they excluded from the calculations those bonds that were common to two rings and concentrated on the annulene perimeter bonds shown in heavy lines in 25. An inherent shortcoming of such a choice is the virtual exclusion of compounds where those bonds are part of another ring as in 43 and in the yet to be synthesized 61 and 62.



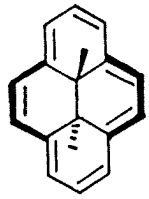
43[79]



61



62[87]



25

A plot of standard deviation (S) of the bond order against the observed chemical shifts of the internal methyl protons of 15,16-dimethyldihydropyrene 25 and its benzannelated derivatives 40, 41 and 42 establishes a linear relationship between the two (see Fig. 3). Application of this technique to Nakagawa's compounds 55, 57 and 58 leads to an excellent correlation between the standard deviation of HMO bond order and the difference in the chemical shift $\Delta\delta$ |outer - inner protons|.

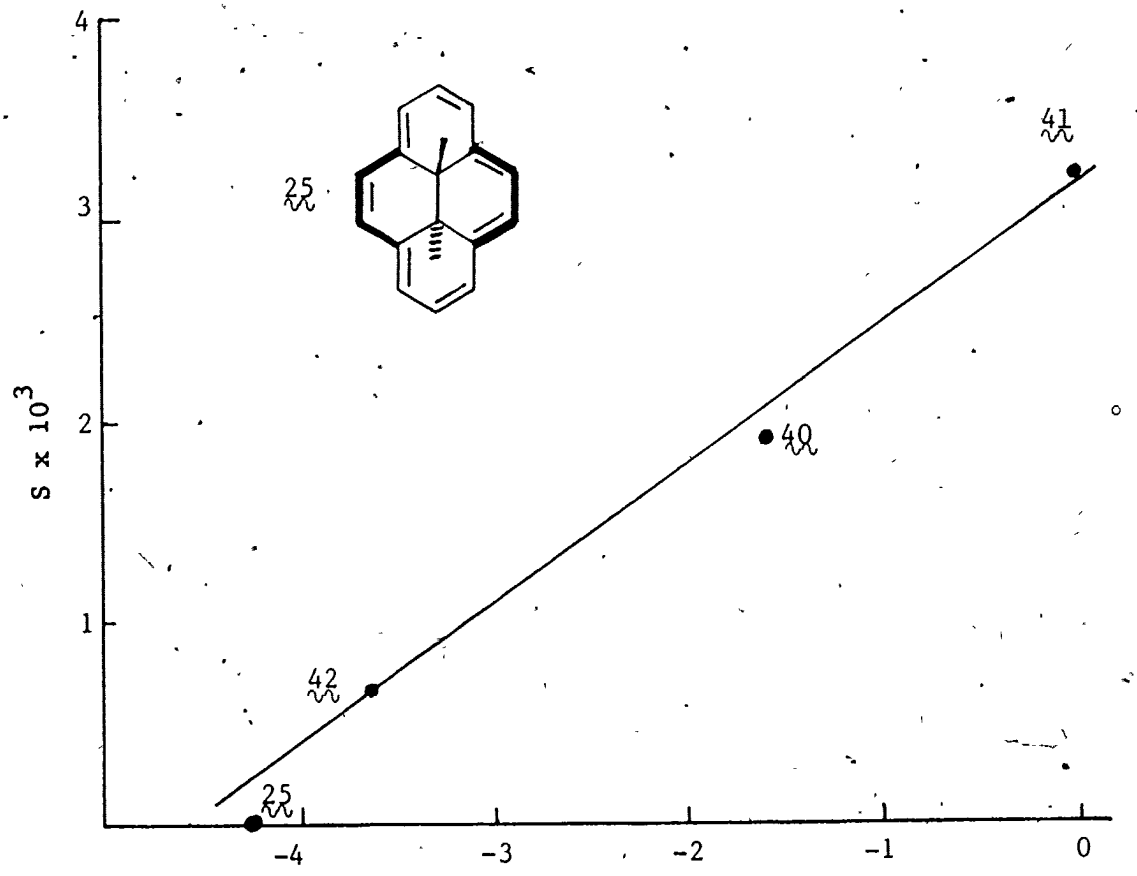


Fig. 3. A plot of standard deviation (S) of HMO bond orders versus the observed chemical shift of the internal methyl protons of 15,16-dimethyldihydropyrene and some of its benzannelated derivatives.[67]

2.2 *Standard π-SCF-HMO Bond Order Deviation -Chemical Shift Correlation.*

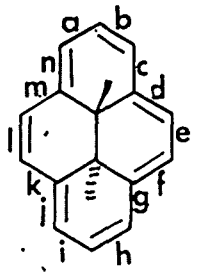
The use of HMO calculations, as seen above, has limitations because they do not differentiate between isomeric compounds 40 and 43. As stated earlier, the HMO approximations tend to ignore the electron

repulsion integral, $\gamma_{\mu,\nu}$, completely and so underestimate the amount of bond localization in a benzannulene as compared to results obtained by the use of π-SCF method. On the foundations laid by Pauling[88] and London,[89] progress has been made in theoretical calculations of the nuclear magnetic resonance spectra of aromatic hydrocarbons.[90] Although the correlation of resonance energies and ring currents has been established[91] and bond fixation does influence [60] resonance energies, it is obvious that for the practising chemist it would be ideal to have a formal (even if empirically derived) relationship between the degree of bond localization and the strength of the annulene ring current shown by the molecule under consideration.

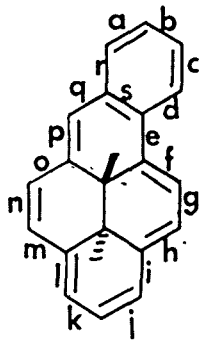
In order to obviate the deficiencies of using only selected HMO bond orders resorted to by Hess and Schaad, we[92] opted to use π-SCF bond order calculations throughout and excluded those bonds that were common to two rings. The bond orders were calculated using Pople-Pariser-Parr (PPP)-π-electron method, with parameters[93] similar to those used by Günther.[84]

In order to use this as a predictive tool, molecules 25, 40, 41, 42 and 43, whose chemical shifts are known, were chosen as the standard compounds. Table 8[94] presents both the HMO as well as the π-SCF bond orders for the compounds used as standards. The bond orders for 25 obtained by both the PPP-SCF-π-electron method and the HMO technique are fairly close to each other.

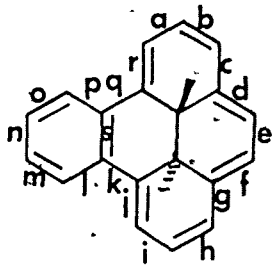
Considering the 'ideal' or perfectly delocalized Hückel bond order as 0.642 for a [14]annulene, the sum (ΔP_μ) of the moduli of the deviation of bond order is given for the macroring of the standards chosen, bearing



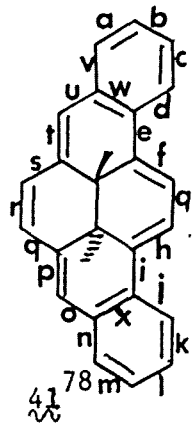
25[63a,85a]



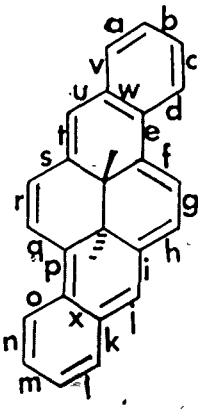
40[78]



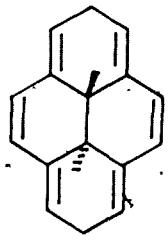
43[79]



41[78]



42[78]



59[63a, 85a]

in mind that we exclude bonds common to the annulene and the benzannelating ring, e.g., 's' in 40 and 43 or 'w','x' in 41 and 42. This exclusion is not unreasonable and is resorted to in an attempt to minimize the structural effects[95] due to the ring fusion at different sites; besides, the bonds involved are common to 6π and 14π-systems which may have opposing ring currents. The individual bond order difference was taken as the absolute difference between the π-SCF bond order and the HMO bond order and the summation taken over all 'm', where 'm' is the number of bonds involved in the calculation, e.g., m = 14 in case of 25 but m = 13 for 40 and 43.

Thus $\Delta P_\mu = \sum_m |(P_\mu - 642)|$

The average deviation Δr was plotted against $\Delta\delta$ where

$$\Delta\delta = \delta_{CH_3}(59) - \delta_{CH_3}(\text{annulene}).$$

i.e., $\Delta\delta$ is the shielding of the internal methyl protons of the annulene compared to those of the non-conjugated model 59 used by Boekelheide.[63a] A reasonably good linear relationship was found between $\Delta\delta$ and Δr (see Fig. 4).

A least squares fit gave the equation

$$\Delta\delta = 5.533 - 0.02752\ \Delta r \quad --- \quad (3)$$

with a correlation coefficient, $\rho = 0.9902$. Using eqn. (3), the values of $\Delta\delta$ were calculated ($\Delta\delta_{calc}$ in Table 8) and results in a reasonably good agreement.

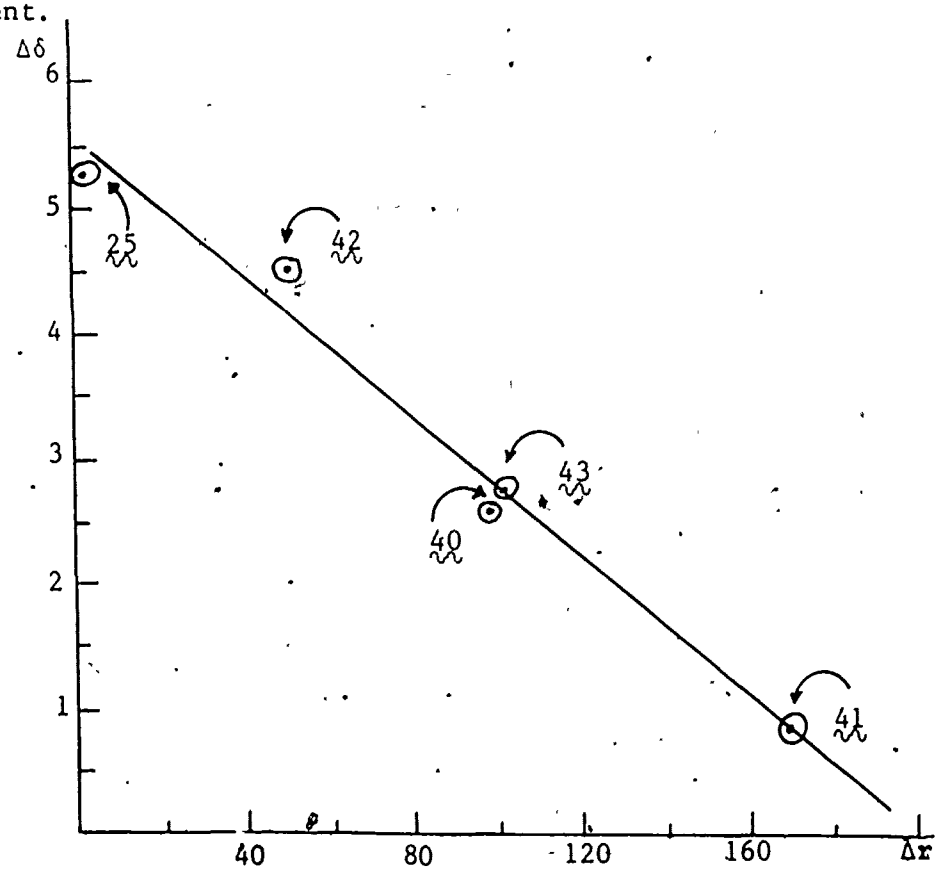


Fig. 4: Plot of chemical shift shielding ($\Delta\delta$) versus average bond order deviation (Δr) for known annulenes 25, 40, 41 and 43.

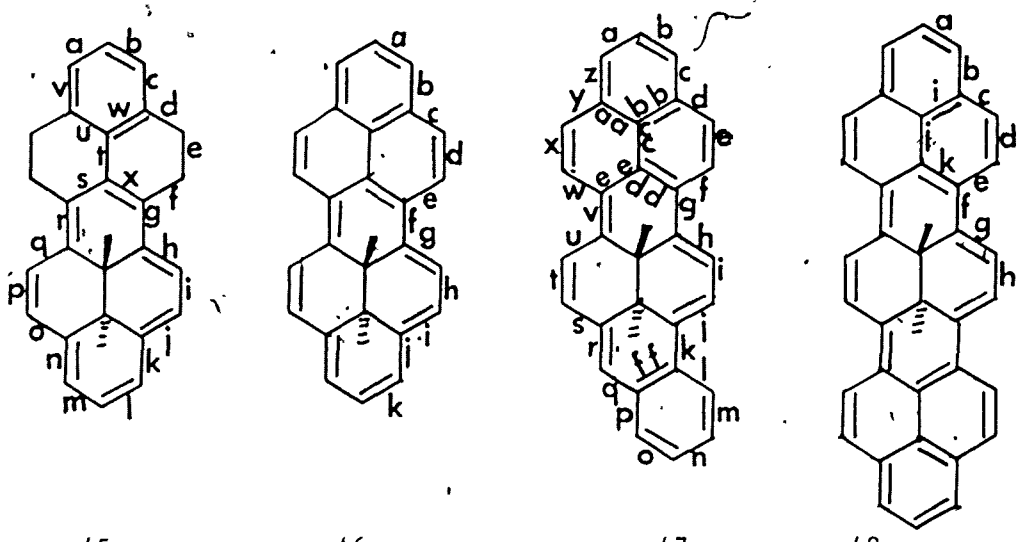
Table 8. Hückel M.O. bond orders (x 10^3) ($\bar{P}_\mu$) and π-SCF bond orders (x 10^3) (P_μ) for compounds 22, 40, 41, 42 and 43.

COMPOUND:	22		40		41		42		43	
BOND (μ)	$\bar{P}_\mu$	P_μ	$\bar{P}_\mu$	P_μ	$\bar{P}_\mu$	P_μ	$\bar{P}_\mu$	P_μ	$\bar{P}_\mu$	P_μ
a	642	647	708	713	698	696	716	735	597	550
b	642	639	611	612	621	629	602	586	676	729
c	642	636	708	711	697	694	716	734	611	553
d	642	650	571	574	583	596	561	545	669	713
e	642	636	529	481	503	438	550	543	614	567
f	642	639	704	745	735	794	674	672	669	715
g	642	647	597	552	557	489	629	635	611	553
h	642	647	676	719	735	794	629	621	676	729
i	642	639	611	558	503	438	674	680	597	550
j	642	636	669	717	583	596	550	545	704	748
k	642	650	614	573	697	694	561	545	529	477
l	642	636	669	712	621	629	716	735	571	580
m	642	639	611	553	698	696	602	586	708	707
n	642	647	676	731	581	595	716	734	611	617
o			597	538	507	443	561	545	708	707
p			704	752	726	792	550	543	571	580
q			529	484	571	488	674	672	529	477
r			571	575	706	780	629	635	704	748
s			502	538	571	488	629	621	502	537
t					726	792	674	680		
u					507	443	550	545		
v					581	595	561	545		
w					513	554	490	508		
x					513	554	490	508		
y										
z										
$\Delta P_\mu = \sum_\mu \lvert(P_\mu - 642)\rvert$		72		1279		2009		584		1303
$n = \sum_\mu$		14		13		12		12		13
$\Delta\tau = \Delta P_\mu / n$		5.143		98.385		167.417		48.667		100.231
$\delta = \delta_{CH_3}$ (annulene)		-4.25		-1.60		+0.02		-3.58		-1.85
$\Delta\delta = 0.97 - \delta$		5.22		2.57		0.95		4.55		2.82
$\Delta\delta_{calc}$ (eqn. 3)		5.39		2.83		0.93		4.19		2.77

2.3 *Predicted Relative Diatropicity for 45, 46, 47 and 48.*

Having established a formal relationship between standard bond order deviation and chemical shift on a quantitative footing for known compounds, we calculated chemical shifts for the compounds 45, 46, 47 and 48 using similar calculations and these are indicated in Table 9. The calculated chemical shifts for the internal methyl protons are shown in fig. 5.

Fig. 5 : Calculated chemical shifts of the internal methyl protons of 45, 46, 47 and 48.



	45	46	47	48
$\delta_{(CH_3)}$ Calc.	-2.75	-3.97	-1.73	-2.99

To confirm the validity of the calculated chemical shifts and hence that of eqn. (3), we had to devise an effective scheme to synthesize compounds 45, 46, 47 and 48.

Table 9. π-SCF bond orders (x 10^3), P_μ, and ring current shielding calculations for compounds 45, 46, 47 and 48.

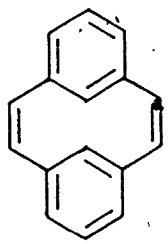
COMPOUND	45	46	47	48
BOND (μ)	P_μ	P_μ	P_μ	P_μ
a	610	670	652	670
b	720	603	687	601
c	567	474	583	477
d	488	793	495	788
e	783	490	773	497
f	503	570	518	559
g	520	667	495	683
h	714	629	749	605
i	583	646	532	
j	692	632	757	
k	[illegible]	648	473	
l	[illegible]	531	579	
m	599	525	708	
n	686	518	614	
o	583		711	
p	702		576	
q	574		483	
r	711		746	
s	541		547	
t	457		710	
u	575		588	
v	716		636	
w	558		468	
x	561		808	
y			454	
z			621	
aa			526	
bb			534	
cc			527	
dd			560	
ee			472	
ff			538	
ΔP_μ	854	260	1134	570
m	13	12	11	10
Δr	65.692	21.667	103.091	57
$\Delta\delta_{calc}$	3.72	4.94	2.70	3.96

CHAPTER THREE

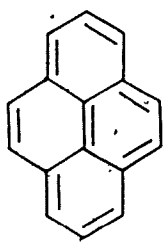
AN APPROACH TO THE SYSTEM

3.1 *Possible synthetic routes*

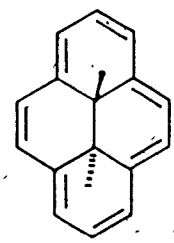
The target molecules which we attempted to synthesize are characterized by one common feature, i.e. a dihydropyrene moiety. A dimethyldihydropyrene skeleton is difficult to envisage and synthesize. Although Pellegrin[96] has claimed the synthesis of [2,2]metacyclophane-1,9-diene 26A, subsequent attempts to repeat his preparation have been unsuccessful.[97] Methylation, using methyl iodide, of the dianion derived from pyrene 63 could conceivably lead to the formation of 25. Although



26A



63

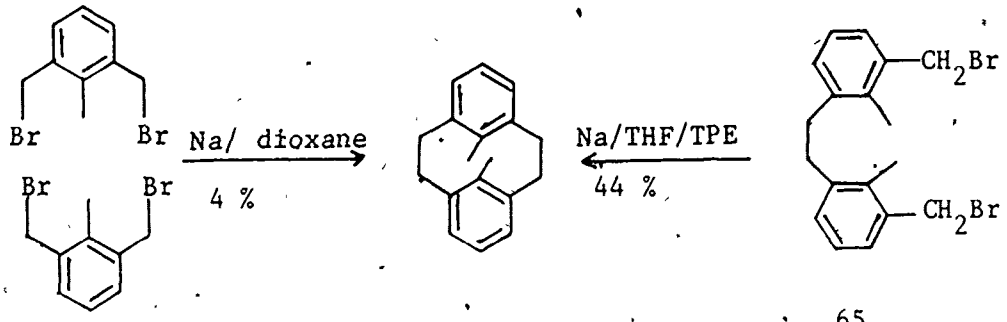


25

Neunhoffer and Woggon[98] have claimed that treatment of 63 with sodium followed by acidification gives 15,16-dihydropyrene 26, alkylation[97] of the dianion of pyrene with methyl iodide did not give the desired dimethyldihydropyrene 25.

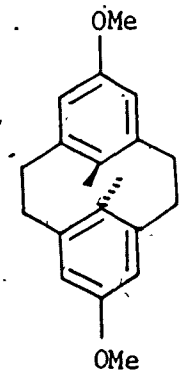
The first successful synthesis of a 15,16-dihydropyrene derivative resulted from an approach centered around the synthesis of [2,2]metacyclophanes. Of the methods investigated up until the early 70's for the synthesis of cyclophanes, the Wurtz[99] reaction along with the

Müller-Röscheisen[99c] modification (addition of TPE) was a favored route. The modest yields, severity of conditions narrowing the choice of compounds and its restriction to the synthesis of symmetrical cyclophanes limit its use.



64 66 65 (TPE = Tetraphenylethylene)

The synthesis of 15,16-dimethyldihydropyrene 25 itself was finally accomplished by Boekelheide and Phillips.[61c,63a] In order to circumvent the problem of introducing the necessary side-chain unsaturation, they altered the synthetic pathway to introduce the transannular linkage at an early stage. This they achieved by preparing 5,13-dimethoxy-8,16-dimethyl[2,2]metacyclophane 67 by the stepwise Wurtz synthesis of suitably substituted bromides and oxidizing 67 using chromic acid in acetone to yield 68 with the transannular bond in place. The bis-dienone 68 was



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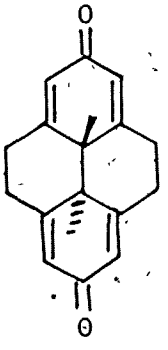


68

converted to 15,16-dimethyldihydropyrene 25 in three steps as follows:

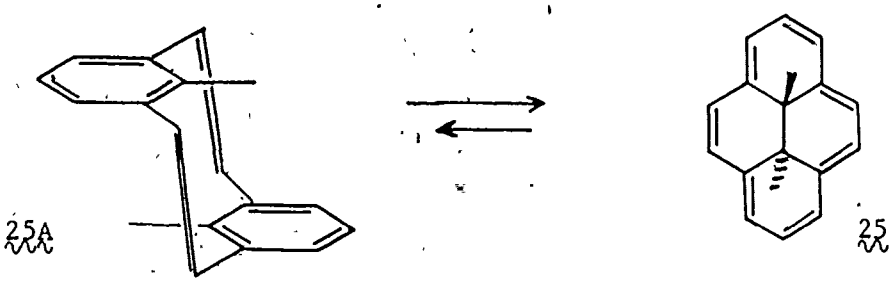
i) Oxidation with N-bromosuccinimide or by air oxidation in an alkaline solution to *trans*-15,16-dimethyldihydropyrene-2,7-quinone,

ii) Lithium aluminum hydride-aluminum chloride reduction to *trans*-15,16-dimethyl-2,7,15,16-tetrahydropyrene and

iii) Catalytic dehydrogenation (Pd-C) or dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to 25.

Boekelheide *et al.* also reported the conversion[100] by visible light of 15,16-dimethyldihydropyrene 25 to its valence tautomer having the meta-cyclophane-diene structure 25A. In the dark 25A reverts back to the more stable 25. Besides, the interconversions could be carried out repeatedly without any deterioration of the sample. However, this method of generating the transannular linkage by oxidation with chromic acid required the methoxy groups para- to the carbon atoms to be linked and hence was not suitable as a general method for synthesizing suitably substituted dialkyldihydropyrenes.

Earlier attempts were aimed at the synthesis of 25 indirectly through generating the cyclophane-diene 25A, possibly by introducing unsaturation

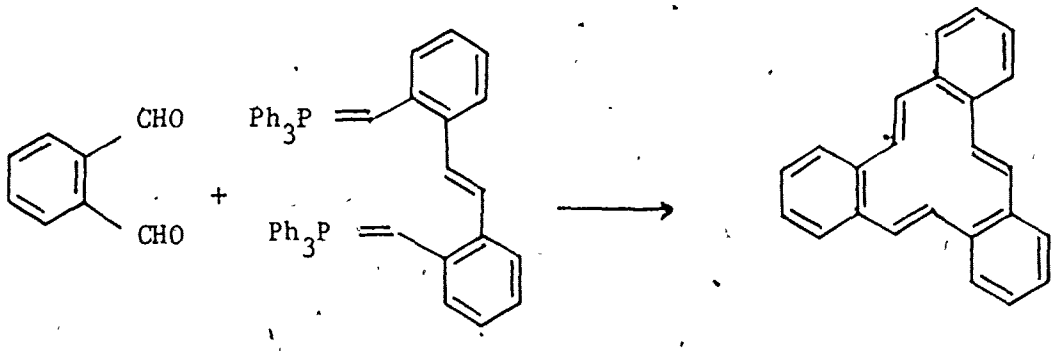


25A 25

in 66. Even though the elegant studies of Dewhirst and Cram[101] have

shown that [2,2]paracyclophane can be converted to the corresponding mono- and diolefins, attempts to introduce unsaturation into the bridging ethano groups of metacyclophane were unsuccessful and it was not possible to obtain [2,2]metacyclophane-1,9-diene 25A, the valence tautomer of *trans*-15,16-dimethyldihydropyrene 25. So the spotlight shifted to preparing the dienes without having to go through the metacyclophanes.

The bis-Wittig[102a] reaction used for synthesizing benzannelated systems, e.g., an annelated [12]annulene[102b] 70 fails however when applied to generate the [10]membered ring system of the metacyclophane-diene

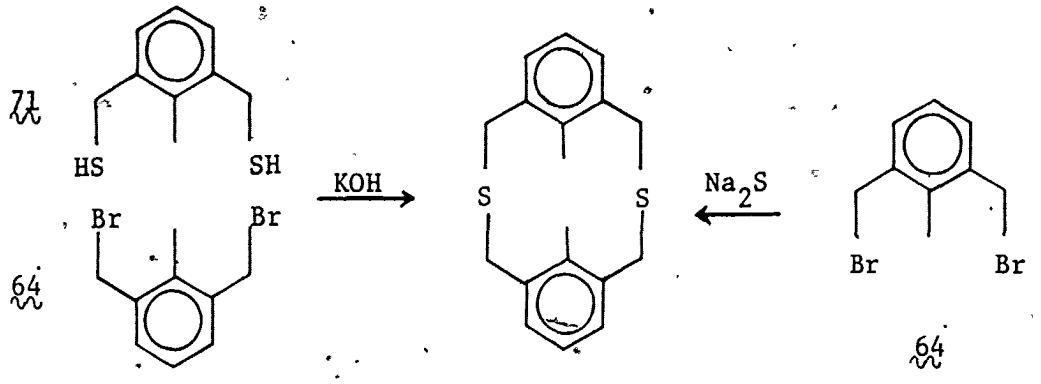


69 70

skeleton. It is quite useful for synthesizing some [10]annulene systems, however.

Perkins[102c] condensation and the Ramberg-Backlund[102d] reaction, which have been employed for the generation of larger cyclic diene systems, fail when applied to creating the cyclophane-diene system. Through the sagacity of sulfur chemists, the carbon-carbon bonds were linked through a sulfur atom which could then be extruded. The self-coupling of 64 with sodium sulfide[61c,103] gives dithiacyclophane 72 and 72A. A recent review by Mitchell[104] has highlighted the utility of

thiacyclophanes as a precursor to both cyclophanes and the synthesis of a variety of novel, highly conjugated compounds. Improved yields[85a,105] of dithiacyclophanes and synthesis of unsymmetrical dithiacyclophanes were achieved by the dropwise addition of a dilute solution of a mixture

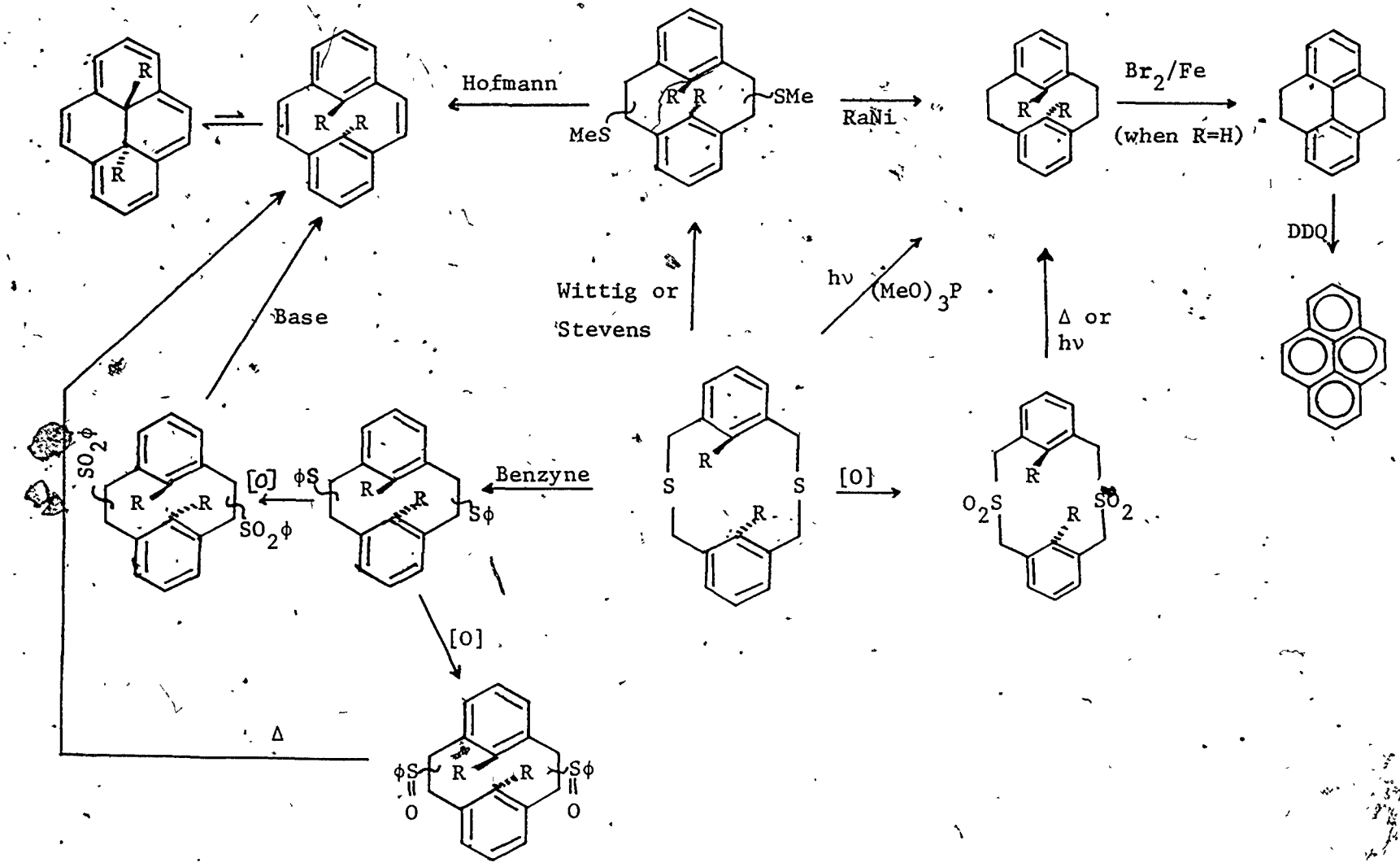


72 (*Anti*) +

72A (*Syn*)

of dithiol 71 and dibromide 64 in benzene into a solution of alcoholic potassium hydroxide. The attractiveness of the thiol-bromide coupling lies in its ease of operation, high yields as well as its applicability to obtain unsymmetrical dithiacyclophanes. Unlike the Wurtz coupling, these methods ultimately lead to both *anti*- as well as *syn*-[2,2]metacyclophane. Extrusion of sulfur has been accomplished in a variety of ways to yield either the metacyclophane or dimethyldihydropyrene (see Scheme 1).

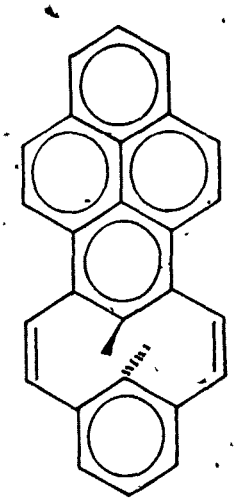
The concept of making dithiacyclophanes followed by oxidation and sulfur dioxide extrusion to yield the *anti*-[2,2]metacyclophanes was worked out by Vögtle.[106] These metacyclophanes, as mentioned earlier, cannot be converted to dimethyldihydropyrenes. The thiacyclophane could



Scheme 1. Dithiacyclophane-Sulfur extrusion scheme

be subjected to Stevens[64,85a,103,107] or Wittig[105] rearrangement, followed by a Hofmann elimination step to yield the diene 25A, which valence tautomerizes to *trans*-15,16-dimethyldihydropyrene. Other variations include photolyses of sulfones[108,109] and sulfides[110] or Raney Nickel desulfurization to give metacyclophanes; however, Benzyne-Stevens rearrangement[111] followed by basic elimination[112] of the sulfone or thermolyses of sulfoxide,[111] as shown in Scheme 1 leads to the diene system. Treatment of metacyclophane (R = H) with bromine/iron leads to a tetrahydropyrene system, which could then be oxidized to the pyrene using DDQ.

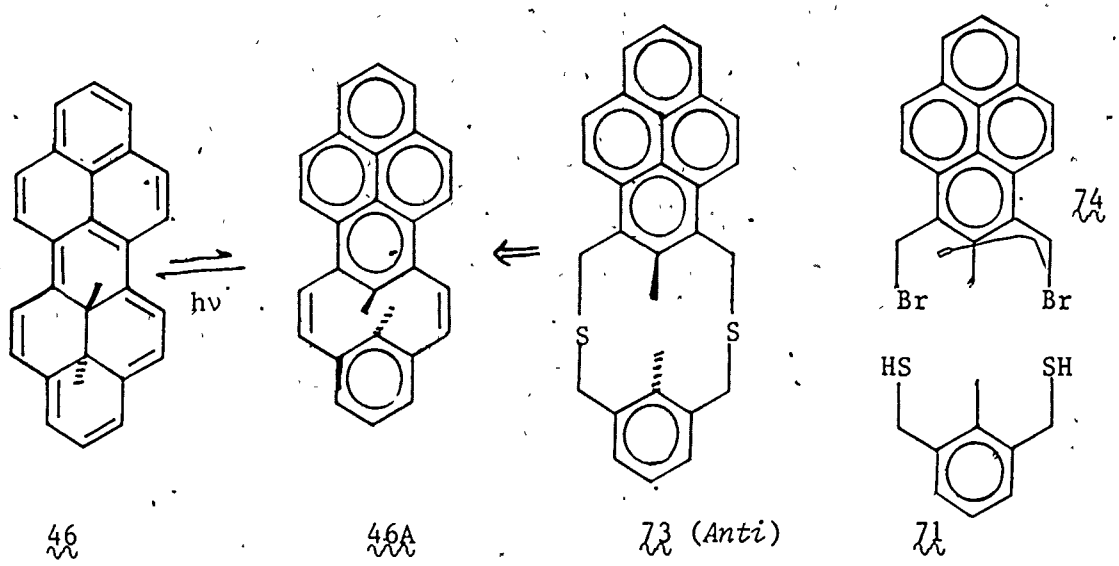
46A



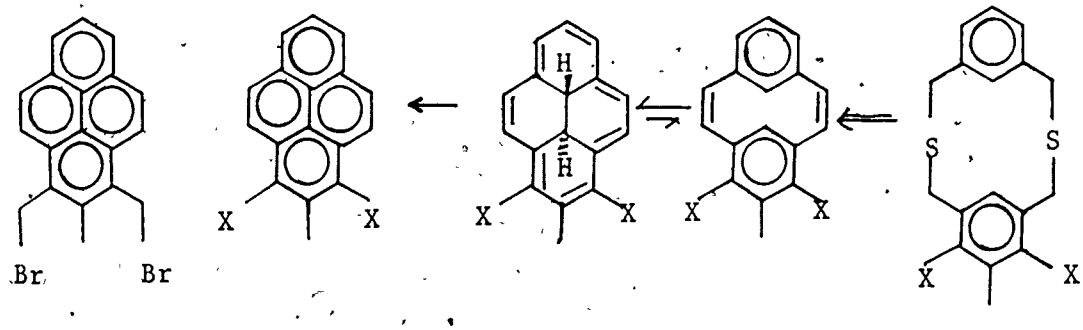
As the metacyclophane-diene 46A can be transformed to 46, we proposed the synthesis of 46A as an intermediate.

3.2 *Desired intermediates in the synthetic pathway*

On the basis of earlier examples, the diene 46A could be obtained from dithiacyclophane 73, which could be prepared by the coupling of



46 46A 73 (*Anti*) 74 71



74 75 76 77 78

75, X= Br
75A, X= CN
75B, X= CHO
75C, X= CH_2OH
75D, X= CH_2SH

76, X= Br
76A, X=CN

77, X= Br
77A, X= CN

78, X= Br
78A, X= CN

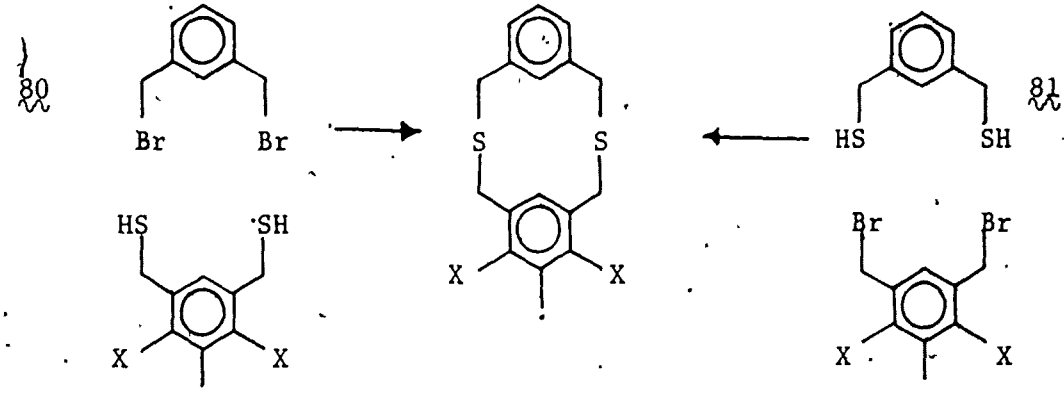
the bromide 74 and dithiol 71. So retrosynthetically, the synthesis of the appropriately substituted pyrene 75, which could be modified to 74, becomes crucial. A diene such as 77 could be prepared from the dithiacyclophane 78 by using some of the methods indicated in Scheme 1. In effect, if we started with a dibromide and a dithiol, carrying suitable functionalities receptive to modification, it would be feasible to make the pyrene 75 and hence the required bromide 74.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 *General routes to key intermediates* 78 *or* 78A.

The dithiacyclophane 78 or 78A could be accessed from the alcoholic potassium hydroxide coupling of the dithiol 79/79A and *m*-xylylene dibromide 80 or by the coupling of the dithiol 81 and the dibromide 82/82A. As 80 is commercially available, it was more practical to convert the bromide 80 to the corresponding dithiol 81 rather than transform the laboriously prepared dibromide 82 to the corresponding dithiol 79.



79, X = Br 78, X = Br 82, X = Br

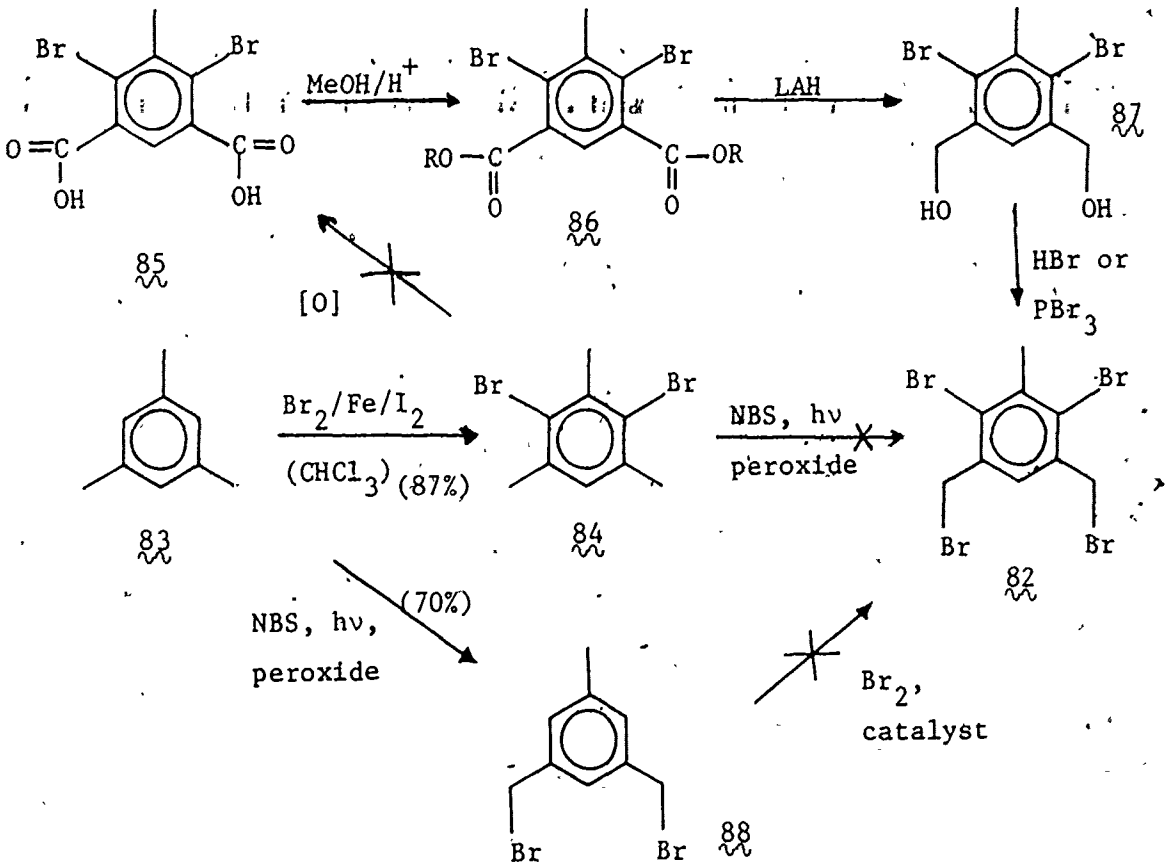
79A, X = CN 78A, X = CN 82A, X = CN

Thus the synthesis of 82/82A has been attempted by a variety of methods.

4.1.1 *Synthesis of the required bromide* 82/82A.

An approach to the synthesis of 82 is illustrated in Scheme 2. 2,4-Dibromomesitylene 84 was prepared earlier[115] using nitric acid as a solvent for bromination; instead we brominated mesitylene 83 in

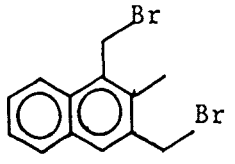
chloroform using bromine, in the presence of iron powder and iodine as catalyst, to obtain 2,4-dibromomesitylene 84 as colorless crystals (87% yield), mp 62-64 °C [lit.[115] mp 62 °C]. Its ^{1}Hmr spectrum indicated two different types of methyl groups. It was expected that free radical bromination of 2,4-dibromomesitylene 84 would lead to the desired bromide 82, the hindered methyl group on the carbon atom between the



Scheme 2

two bromine substituents being spared in the process. Unfortunately, however, when the reaction was carried out in refluxing carbon tetrachloride by adding N-bromosuccinimide in portions in the presence of catalytic amounts of benzoyl peroxide, a complex mixture of products was obtained, from which the desired bromide 82 could not be isolated

either by column chromatography or crystallization. This is not unlike the results[116] obtained in the free radical bromination of 89 with N-bromosuccinimide wherein the second bromine atom enters the hindered



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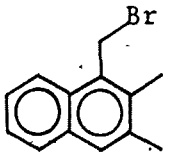

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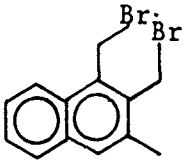


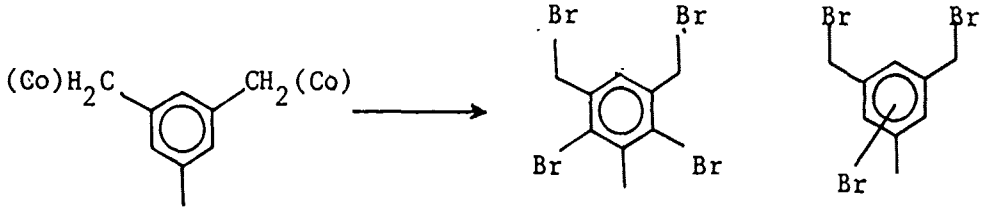
90

methyl to give 90 as the major product, whereas only 15% of the desired bromide 91 was obtained. Use of methyl formate[117] as a solvent to improve the selectivity did not prove beneficial and bromination of 84 using bromine at elevated temperatures[118] (125 °C and 210 °C) led to a mixture of bromides. In order to follow the acid-ester-alcohol route (85--86--87), selective oxidation of the methyl groups of 84 was tried. Nitric acid [119a] oxidation gave low yields and was not selective. Purple benzene[119b] oxidation, on the other hand, was tried and proved to be totally ineffective. An alternative route which involved obtaining 82 from bromide 88 by electrophilic aromatic substitution was next tried. Mesitylene 83 was brominated using N-bromosuccinimide in refluxing carbon tetrachloride in the presence of benzoyl peroxide as catalyst to give 3,5-bis(bromomethyl)toluene 88[120] (70% yield). Bromination of 88 in chloroform using bromine was attempted under several* different reaction conditions in an effort to obtain the bromide 82. In all cases

* (a) Fe powder, 3 h, (b) Fe powder, reflux, 24 h, (c) I_2 crystals, 3 h, (d) I_2 powder, reflux, 24 h, (e) $AlBr_3$, 3 h, (f) $AlBr_3$, reflux, 24 h, (g) $FeBr_3$, 3 h and (h) $FeBr_3$, reflux, 24 h.

the desired bromide 82 could not be isolated from the resulting mixture. Changing to the polar solvent N,N-dimethylformamide(DMF)[121,63f] with N-bromosuccinimide (NBS) as the source of bromine, did not result in pure 82 either at room temperature or at reflux condition.

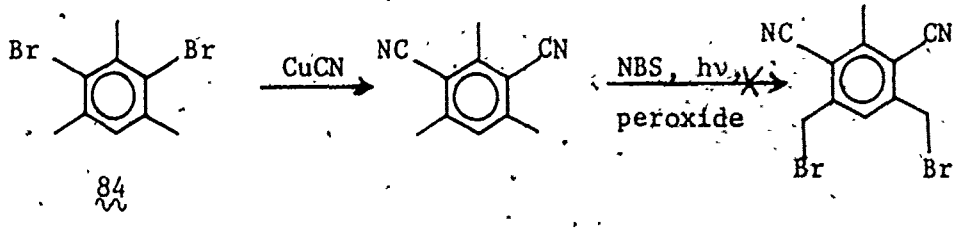
Although some bromomethyl compounds have been obtained by the reaction of benzylcobaloximes[122] with halogens in acetic acid, in the



92 82 (70%) 93 (<30%)

case of 92 it leads to both 82 and 93 separation of which, on the basis of our earlier trials, might be rather difficult.

In an effort to explore whether the presence of a cyano group might somehow influence the entry of bromine in the molecule, 2,4-dibromomesitylene 84 was treated (see Scheme 3) with excess of copper (I) cyanide in N-methyl-2-pyrrolidinone under refluxing condition to yield 2,4,6-trimethylisophthalonitrile 84A (83% yield), mp 144-146 °C[lit.[123] mp 142 °C]. The dinitrile 84A showed the characteristic -CN stretch

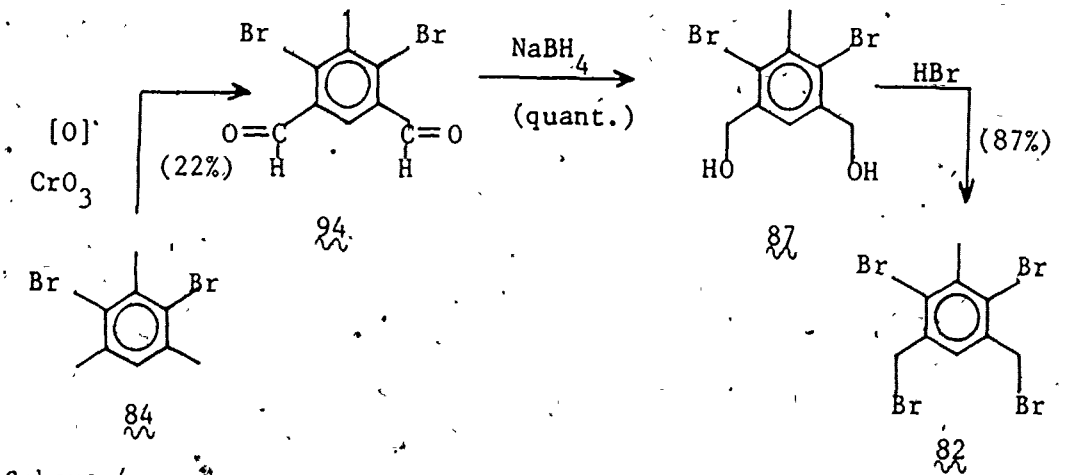


84 84A 82A

Scheme 3

at 2228 cm^{-1} in its ir spectrum. Treatment of 84A with NBS in refluxing carbon tetrachloride using benzoyl peroxide as the initiator gave a mixture of at least four compounds, from which pure 82A could not be isolated. Methyl formate as solvent gave mostly unconverted starting material.

A slightly modified approach was chosen (see Scheme 4), where the alkyl groups were selectively oxidized to an aldehyde functionality. Benzylic methyl and methylene groups can be converted to carbonyl functions by treatment with ceric ammonium nitrate in acidic media (acetic acid, nitric acid or perchloric acid)[124]. The reaction normally stops at the monocarbonyl stage. However, a second methyl group may undergo oxidation under more drastic conditions. Although



Scheme 4

Ce^{IV} oxidation of 84 gave some aldehydes, it was not feasible to isolate the dialdehyde 94 from the resulting mixture.

A solution of p-nitrotoluene in a mixture of glacial acetic acid-acetic anhydride-sulfuric acid is oxidized using chromium trioxide to the aldehyde (protected as the diacetate) which can be hydrolysed

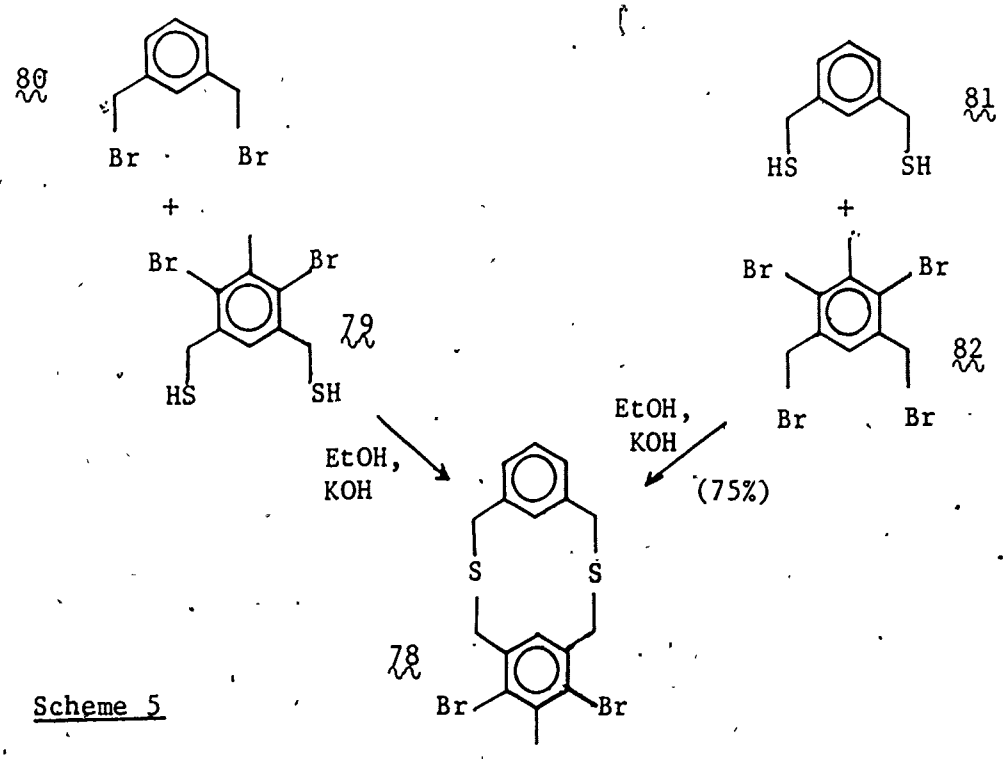
to the aldehyde by refluxing in alcohol- dilute sulfuric acid medium. A similar oxidation of dibromide 84 in glacial acetic acid-acetic anhydride-sulfuric acid, kept cold using an ice-salt bath, by the gradual addition of chromium trioxide so that the temperature does not rise above 15 °C, followed by acid hydrolysis gave the dialdehyde 94. Recrystallization from carbon tetrachloride gave the pure dialdehyde 94, mp 172-174 °C; the structure of 94 was evident from the aldehydic protons present at δ 10.43, the C=O stretch seen at 1686 cm^{-1} and a molecular ion at m/e 306 (correct 1:2:1 isotope pattern) in its ^{1}Hmr, ir and mass spectra respectively. As well, the aldehydic carbons appeared around δ 190.8 in its ^{13}Cmr spectra. Subsequent reduction of the dialdehyde 94 with sodium borohydride in tetrahydrofuran gave the dialcohol 87 in quantitative yield, mp 192-194 °C (methanol-benzene). Absence of the carbonyl stretch at 1686 cm^{-1} (seen in the case of 94) and the appearance of the -OH absorption at 3330 cm^{-1} in its ir spectrum indicated the structure of the dialcohol as 87, confirmed by a satisfactory elemental analysis coupled with the molecular ion at m/e 310 (correct 1:2:1 isotope pattern) in its mass spectrum. No ^{1}Hmr spectrum could be obtained for the dialcohol 87 because of its near insolubility in most organic solvents. Alcohol 87 on refluxing for 22 h with hydrobromic acid (48%)[125] containing a small amount of conc.sulfuric acid gave 87% yield of the bromide 82, mp 120-122 °C. The methylene protons were seen at δ 4.56 in the ^{1}Hmr spectrum and the compound also gave the correct molecular ion at m/e 436 in its mass spectrum and CHN analysis. Although such an alcohol to bromide conversion can be effected using phosphorous tribromide, it was far more convenient to use hydrobromic acid for scaling- up experiments,

especially because of the difficulty of drying the alcohol and the large volumes of dry ether or benzene required in the phosphorous tribromide process.

The next objective was to convert 2,6-dibromo-3,5-bis(bromomethyl)-toluene 82 into the dithiacyclophane 78.

4.1.2 *Synthesis of 5,7-dibromo-6-methyl-2,11-dithia[3,3]-metacyclophane* 78.

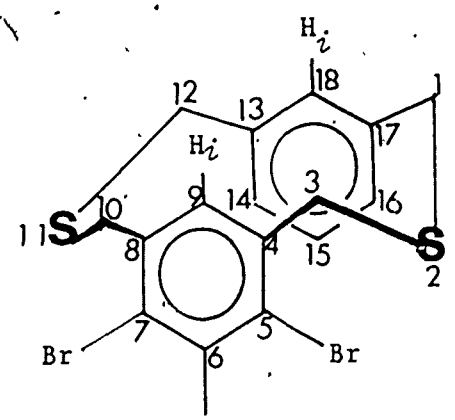
The coupling of m-xylylene dithiol[85a] 81 and the dibromide 82 under high dilution conditions using potassium hydroxide in ethanol-benzene yielded, after chromatography over silica gel, 75% yield of the dithiacyclophane[126] 78, mp 172-173 °C (see Scheme 5). The structure of



Scheme 5

78 was established on the basis of the base peak molecular ion at m/e

444 in its mass spectrum. The ^{1}Hmr spectrum of 78 showed the methylene protons as two singlets which remained unchanged when the sample was cooled to - 90 °C. It was assigned the *syn*-stereochemistry 78 (see below) on the basis of its ^{1}Hmr spectrum by comparison with the known *syn*-cyclophane 95 (see Table 10) since the 9- and 18- aryl protons of



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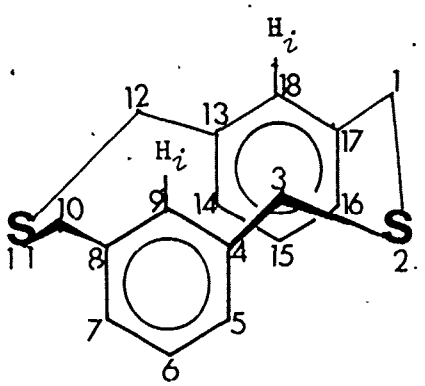

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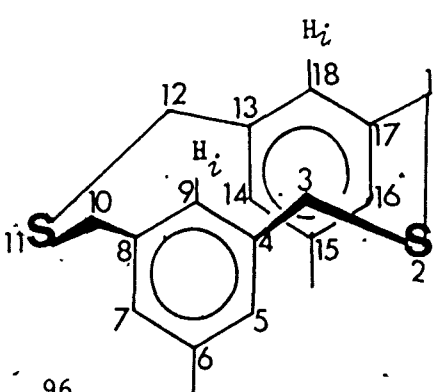

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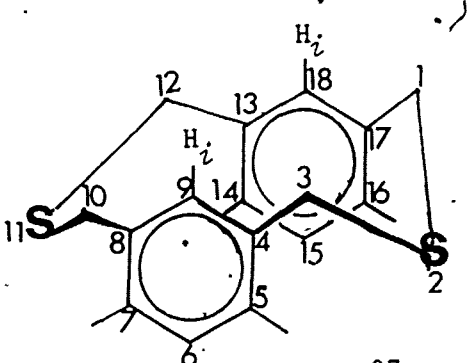

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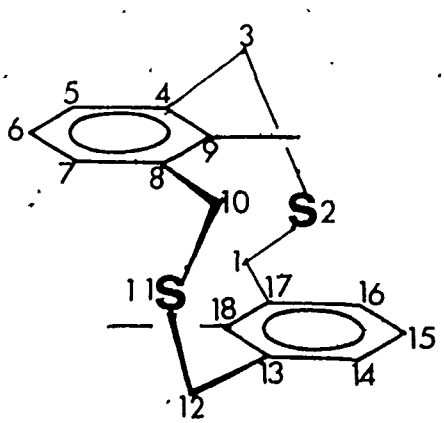

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Table. 10. ^{1}Hmr data (δ) for selected derivatives of 95.

Compound	H_i	H_{ar}	Ref.
95	6.82	6.91	127
96	6.58	6.66	120b
97	6.50	6.58	128
78	7.28 (H-18) 6.62 (H- 9)	7.0 - 6.9	This work

78 appear at δ 6.62 and 7.28 (those for 95 appear at δ 6.82),[127] whereas if 78 existed as the *anti*-isomer, the 9- and the 18- aryl protons might be expected to be shielded by the opposite benzene ring to *ca.* δ 5.0. The consequence of face to face stacking of benzene rings[85a] is seen in the shielding of the 14, 15 and 16- aryl protons of 78 which appear at δ 7.0 - 6.9.

Table 11. ^{13}Cmr data (δ) for some selected dithiacyclophanes

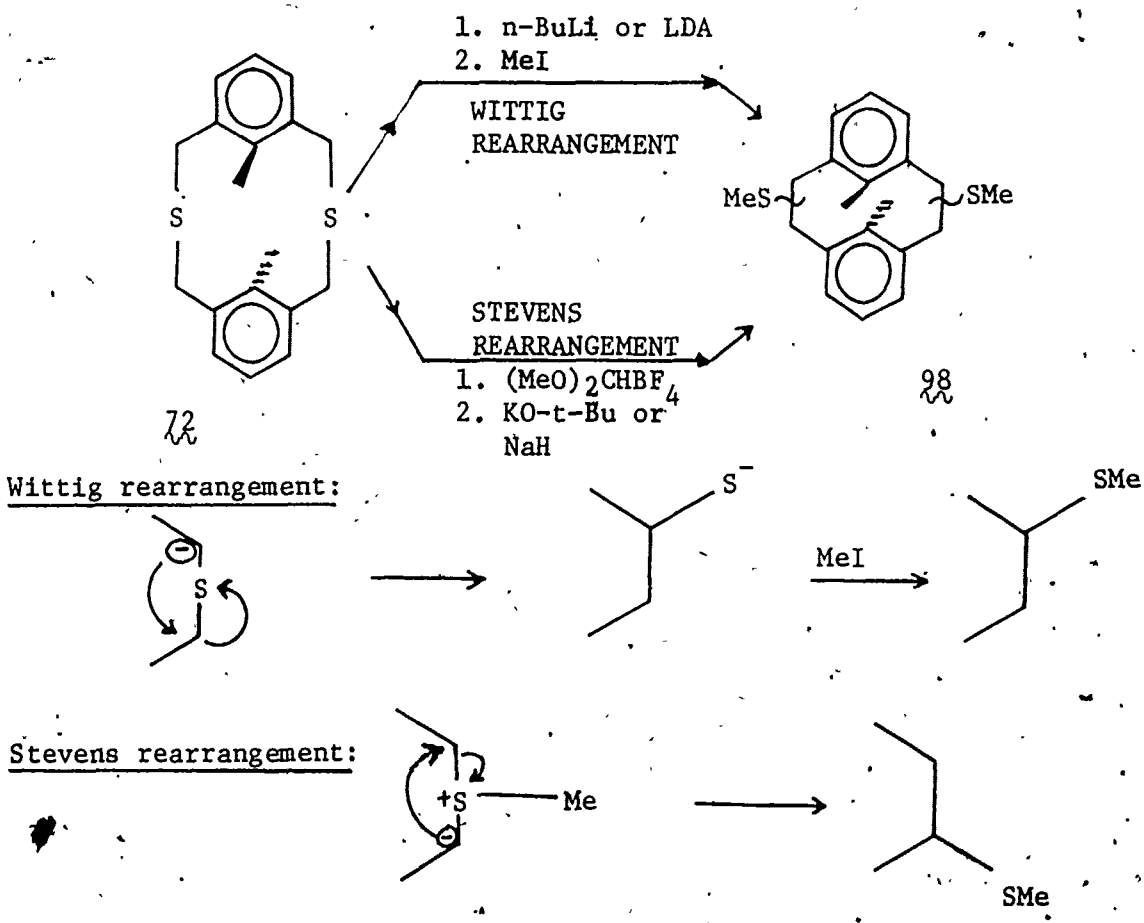
Compound	Solvent	C_{13}	C_{14}	C_{15}	C_9, C_{16}	C_1, C_3	Ref.
95	CD_2Cl_2	137.7	127.3	128.7	132.1	38.3	127
72	CD_2Cl_2	136.1	130.6	125.8	139.4	32.0	*a
78	$CDCl_3$	135.3	127.3	128.3	131.1 135.3	38.2 38.6	This work.

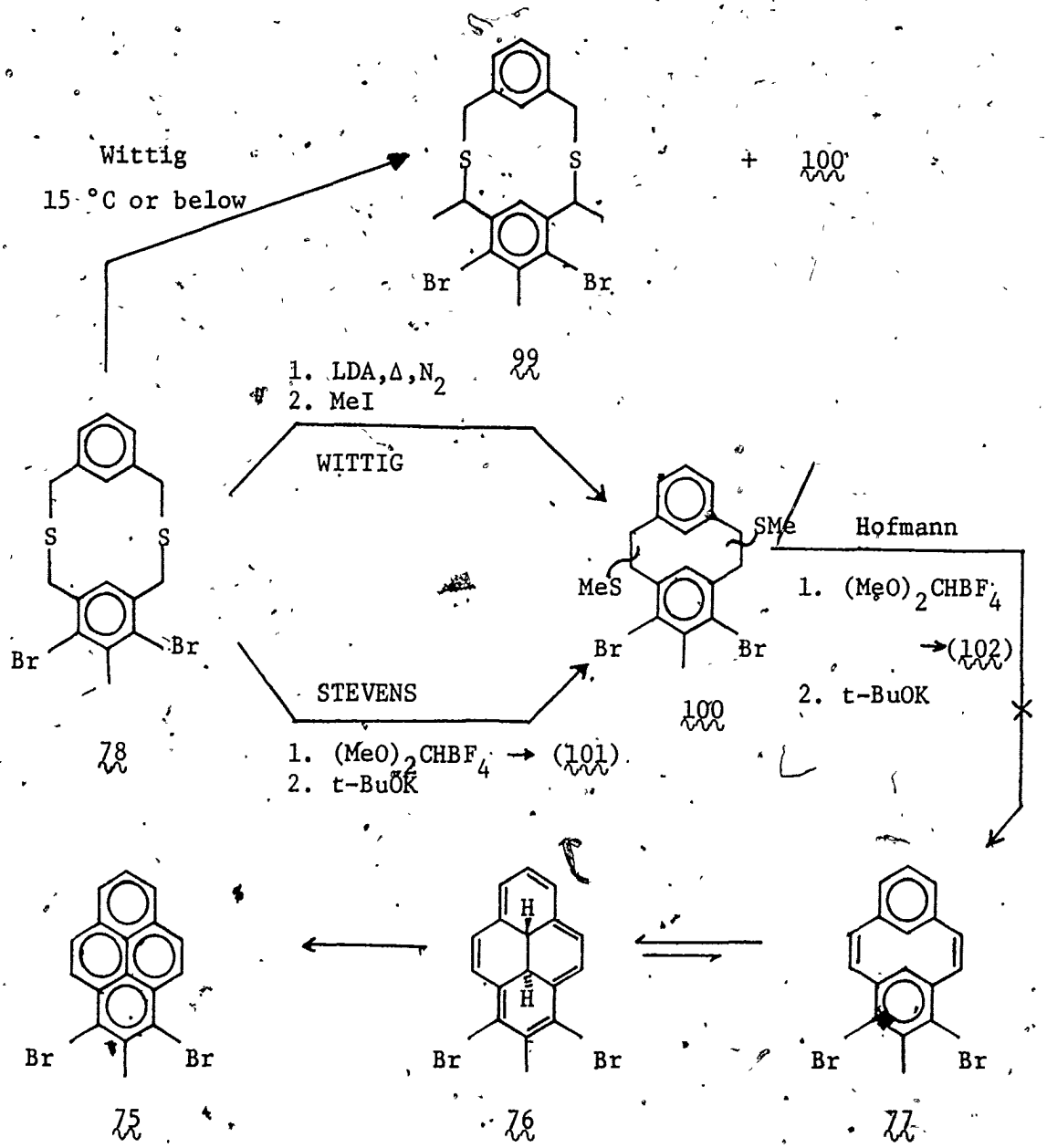
*a : Private communication from Mr. W. Anker, Department of Chemistry, University of Victoria.

Further confirmation of the assigned structure is provided by the ^{13}Cmr spectrum of 78 which shows the bridge carbons at *ca.* δ 38 similar to those of *syn*-95, whereas those of the *anti*-isomer 72 are at *ca.* δ 32, shielded by the benzene rings below (see Table 11).

4.1.3 *Attempted conversion of dithiacyclophane 78 to dibromo-pyrene 75 or dicyanopyrene 75A.*

Among the methods available for the extrusion of sulfur from dithiacyclophanes, two of the most widely used approaches in our group are the Wittig[105] and the Stevens[103] rearrangement.



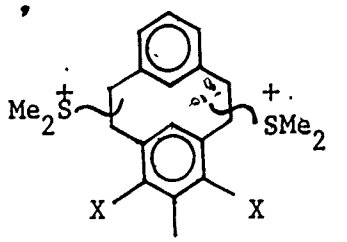


Scheme 6

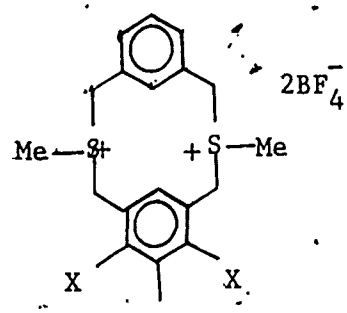
Wittig rearrangement of dithiacyclophane 78 in dry THF using lithium diisopropylamide or n-BuLi, both at 0 °C and at 15 °C (room temperature), followed by the addition of methyl iodide gave the alkylated dithiacyclophane 99 as the major product, along with some of the desired 100. (see

Scheme 6). This appeared rather unusual as Wittig rearrangements of dithiacyclophanes are usually carried out at room temperature or at 0 °C. When the rearrangement was carried out at 22 °C and methyl iodide added, the desired cyclophane 100 was obtained as a mixture of stereoisomers in 56% yield. It seems that the rearrangement of the first-formed anion at or below 15 °C is rather sluggish, probably because the bromine atoms which are ortho- or para- to the site of the negative charge can stabilize this anion by inductive electron withdrawl. Rearrangement at still lower temperatures (- 5 °C, - 40 °C and - 78 °C) led essentially to bridge alkylation rather than sulfur extrusion. It was also discovered that when the reaction was scaled-up, after the addition of LDA was complete, the reaction mixture was heated under reflux for 0.5 h, cooled and then methyl iodide was added, it gave 77% yield of 100 after chromatography. Attempts to isolate a pure isomer of 100 by recrystallization from various solvents failed. The characteristic $-SCH_3$ protons of 100 appeared as sharp singlets at δ 1.88 and 1.85 in the ^{1}Hmr spectrum and the compound had the correct molecular weight as indicated by m/e at 472.

Alternatively, treatment of 78 with dimethoxycarbonium fluoroborate gave the Stevens salt 101, mp 190-191 °C, as a white powder



102 (102, X = Br)
(102A, X = CN)



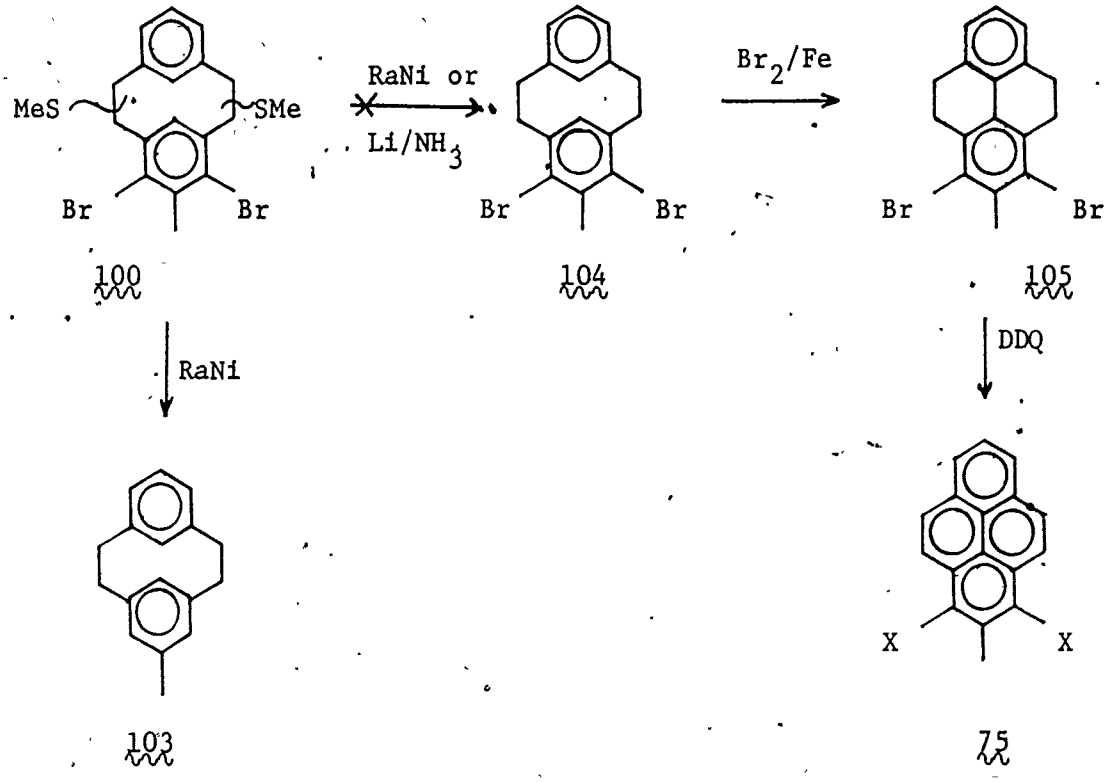
101 (101, X = Br)
(101A, X = CN)

(86% yield). Stevens rearrangement of salt 101 with potassium t-butoxide in dry tetrahydrofuran gave a mixture of stereoisomers of the cyclophane 100 in 86% yield. It was not possible to crystallize a single isomer from this mixture. The peak at m/e 472 in the mass spectrum along with the signal of the $-SCH_3$ protons at δ 2.2 and 1.1 suggested 100 as the correct structure. Conversion of 100 to the bis(sulfonium)salt 102 proceeded in poor yield (22%) and subsequent treatment of 102 with potassium t-butoxide both at reflux and room temperature did not give a product that could be positively identified. Hence this approach was slightly modified to get to compound 75.

Although in the early stages of cyclophane chemistry effective methods to convert a cyclophane, e.g., 104 to tetrahydropyrene 105 were not well exploited, it has been accomplished in excellent yields by a transannular reaction with pyridinium-hydrobromide perbromide[114] ($Py.HBr_3$) or with $Fe\text{-}Br_2$.[113] The substituted pyrene 75 could be obtained by dehydrogenation of tetrahydropyrene 105 with DDQ[113] in boiling benzene or toluene (see Scheme 7).

Desulfurization[129] of 100 using Raney Nickel, which contains enough hydrogen for this reaction, is an ideal way of cleaving the C-S bond to generate the metacyclophane 104. However, when we attempted to cleave the C-S linkage using W-7 Raney Nickel[130] catalyst, the ^1Hmr spectrum of the product and its mass spectrum suggested it to be mainly 103 along with some Birch reduction product. Thus hydrogenolysis of the aryl halide[131] had occured along with desulfurization. Use of $Li\text{-}NH_3$ or Al(Hg)[131c] to effect a reductive

C-S bond fission failed to give 104. So this approach to the pyrene skeleton was abandoned for the moment.



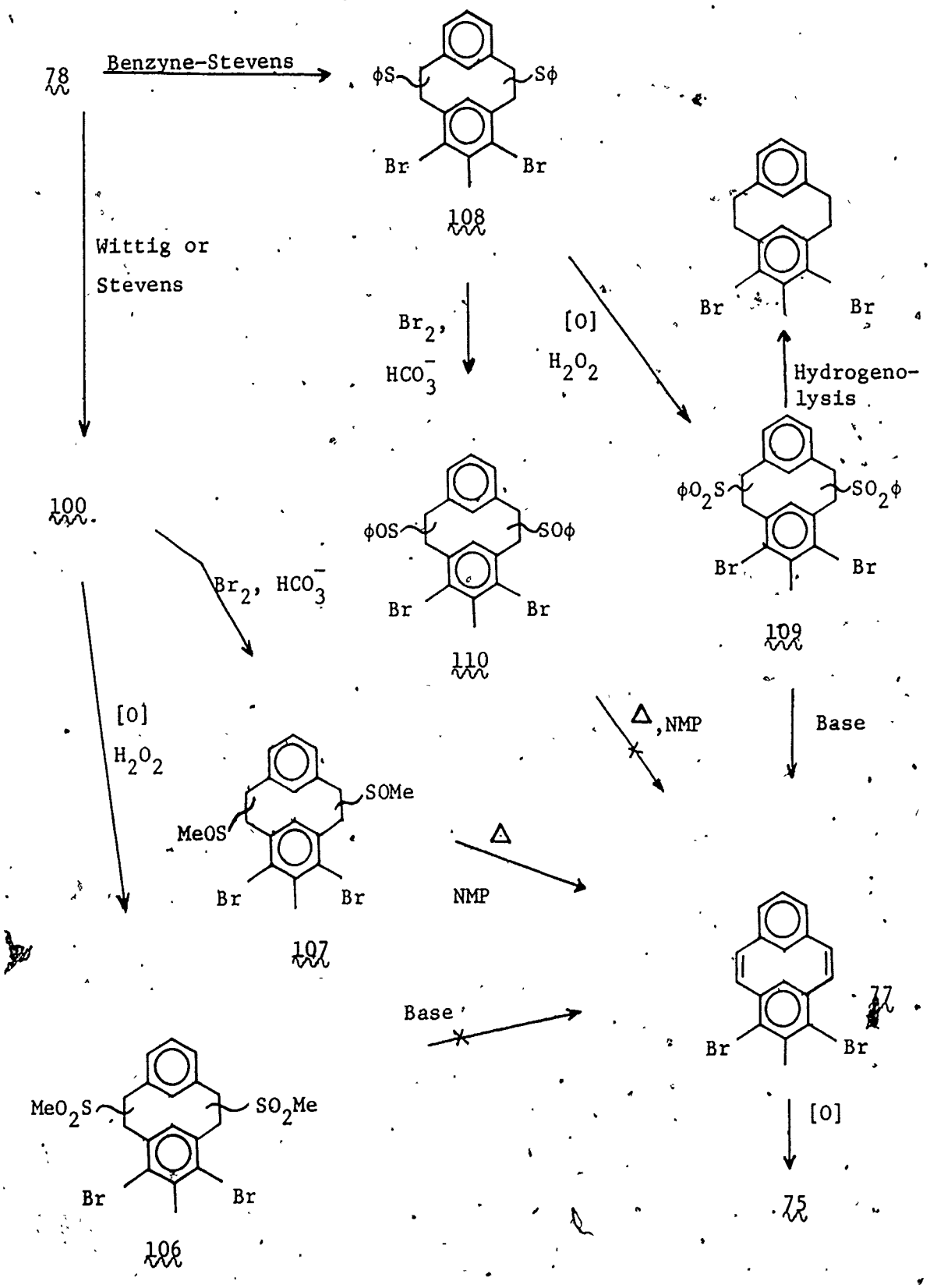
75 , X = Br 75C, X = CH_2OH

75A , X = CN 75D, X = CH_2SH

75B , X = CHO

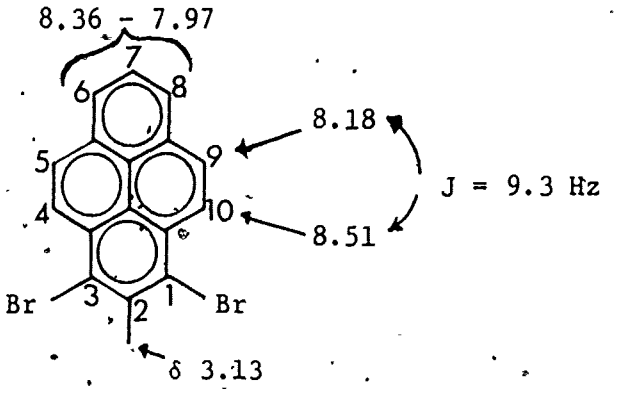
Scheme 7

As both Hofmann elimination and desulfurization of 100 to yield the metacyclophane diene(or the pyrene) and the metacyclophane 104 respectively failed, an alternative route to construct the pyrene 75 was attempted. Sulfinic acid elimination[112] from sulfones to generate the alkene system has had some success. Thus the rearranged product. 100 was oxidized to the sulfone 106 by heating a solution of 100 in


78
Benzyne-Stevens
108
Wittig or
Stevens
100
Br2,
HCO3−
[O]
H2O2
Hydrogeno-
lysis
109
110
Br2, HCO3−
[O]
H2O2
Δ, NMP
Base
107
Δ
NMP
Base
77
[O]
75
106

Scheme 8

benzene-acetic acid (1:1) and hydrogen peroxide (30%) for 5 h (see Scheme 8). This gave the sulfone 106 as a mixture of stereoisomers, mp 120-141 °C. As in the case of 100, a pure isomer of 106 could not be obtained by recrystallization process. The elimination of methanesulfinic acid ($MeSO_2H$) from 106 was attempted using potassium t-butoxide in refluxing tetrahydrofuran. This did not give any product that could be assigned the structure 75 or 77. Use of potassium carbonate in DMF[132] did not prove to be any more useful. Thermal elimination of benzenesulfenic acid (PhSOH) to generate the C=C bond has been reported by Boekelheide.[133] We thus investigated such an elimination on the sulfoxide 107. The selective oxidation of a sulfide to the corresponding sulfoxide without generation of the sulfones has been explored rather extensively recently using bromine/potassium bicarbonate[134a] or titanium (III) chloride/hydrogen peroxide[134b] as oxidants. Thus oxidation of 100 with bromine in aqueous bicarbonate solution gave 77% yield of the sulfoxide 107 as a buff colored product. While the ^{1}Hmr spectrum clearly indicated a mixture of stereoisomers with the $-SOCH_3$ protons appearing as singlets at δ 2.77 and 2.74, its ir spectrum showed the characteristic S=O stretch at 1040 cm^{-1} and a peak at 505 corresponding to MH^+ confirmed the structure as 107. In an effort to convert the sulfoxide 107 to the diene 77 and hence finally to 75, a solution of 107 in N-methyl-2-pyrrolidinone was heated to reflux for 20 h and gave 65% yield of 1,3-dibromo-2-methylpyrene 75 as a yellow product, mp 238-240 °C. The compound 75 proved to be highly insoluble in most organic solvents. ^{1}Hmr of the compound, along with the peak at m/e corresponding to MH^+, confirmed the structure of 75.



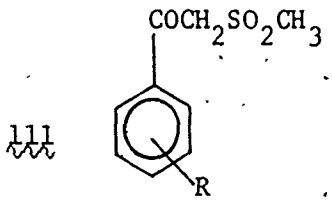
75

Neither pyrolysis of 107 at 500 °C nor thermolysis in sulfolane or chlorobenzene proved effective to prepare 75. As an alternative, the dithiacyclophane 78 was converted to 108 via a Benzyne-Stevens rearrangement by adding a solution of anthranilic acid in 1,2-dichloroethane to a refluxing mixture of the dithiacyclophane 78 and isoamyl nitrite in 1,2-dichloroethane. The Benzyne-Stevens rearranged[133] product 108 (73% yield) was a pale yellow semi-solid which gave a small peak at m/e 597 corresponding to MH^+. While many methods are available to oxidize sulfides to sulfones, including the chemoselective oxidation using potassium hydrogen persulfate[135], it was more convenient to use hydrogen peroxide-acetic acid as in the earlier case. This gave sulfone 109 (90% yield), which on recrystallization from benzene gave colorless crystals, mp 308-311 °C and showed the strong absorption due to sulfones at 1325 and 1160 cm^{-1}. Various base eliminations* of benzene sulfinic acid from 109 were attempted using

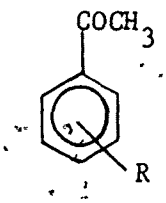
* Other trials include (a) t-BuOK-diglyme, reflux, (b) t-BuOK-DMF, reflux, (c) DBU- t-BuOK-THF, reflux and (d) NaH-DMF, reflux.

potassium t-butoxide, both with and without added 1,8-diazabicyclo-[5,4,0]undec-7-ene (DBU), in refluxing tetrahydrofuran; this did not yield the diene 77 or the pyrene 75.

The reductive elimination of methanesulfonyl group has been achieved by the use of chromous (II) sulfate[136] which was found suitable as a selective reducing agent in the case of compounds carrying halogen group bound on the aryl ring. Corey *et al.*[131c] have used aluminum amalgam for the reduction of β-ketosulfoxides, β-ketosulfones and β-ketosulfonamides.



111



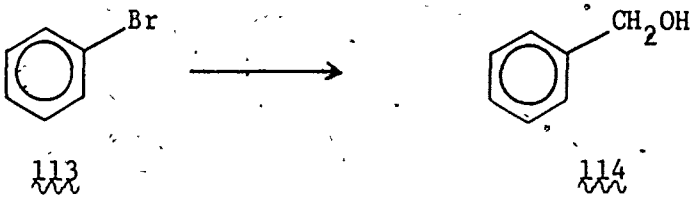
112

R = 2-OH, 3-OH, 4-OH, 2-Cl, 3-Cl, 4-Cl, 2-OMe, 3-OMe, 4-OMe etc.

Hydrogenolysis of phenyl sulfone 109 using chromous sulfate gave the metacyclophane 104, as confirmed by mass spectrum, but in disappointingly low yields (15-20%). Use of aluminum amalgam returned unconverted starting material. To see whether the elimination of benzenesulfenic acid (PhSOH) was any easier, phenyl sulfide 108 was treated with bromine in the presence of aqueous potassium bicarbonate to get the sulfoxide 110 in 71% yield, mp 243-246 °C; this was confirmed by the MH^+ peak at m/e 629 in its mass spectrum. No identifiable products were obtained by thermolyzing 110 in N-methyl-2-pyrrolidinone.

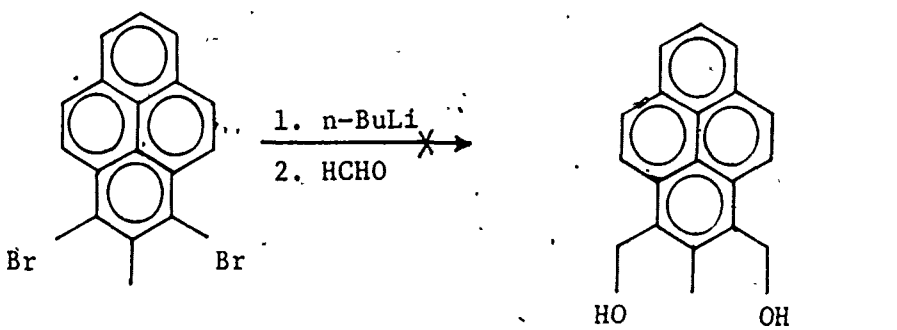
Bromobenzene 113 can be easily converted to benzyl alcohol 114

via its organo-lithium compound.[137]



113 114

Treatment of 75 in dry tetrahydrofuran with n-BuLi, followed by addi-

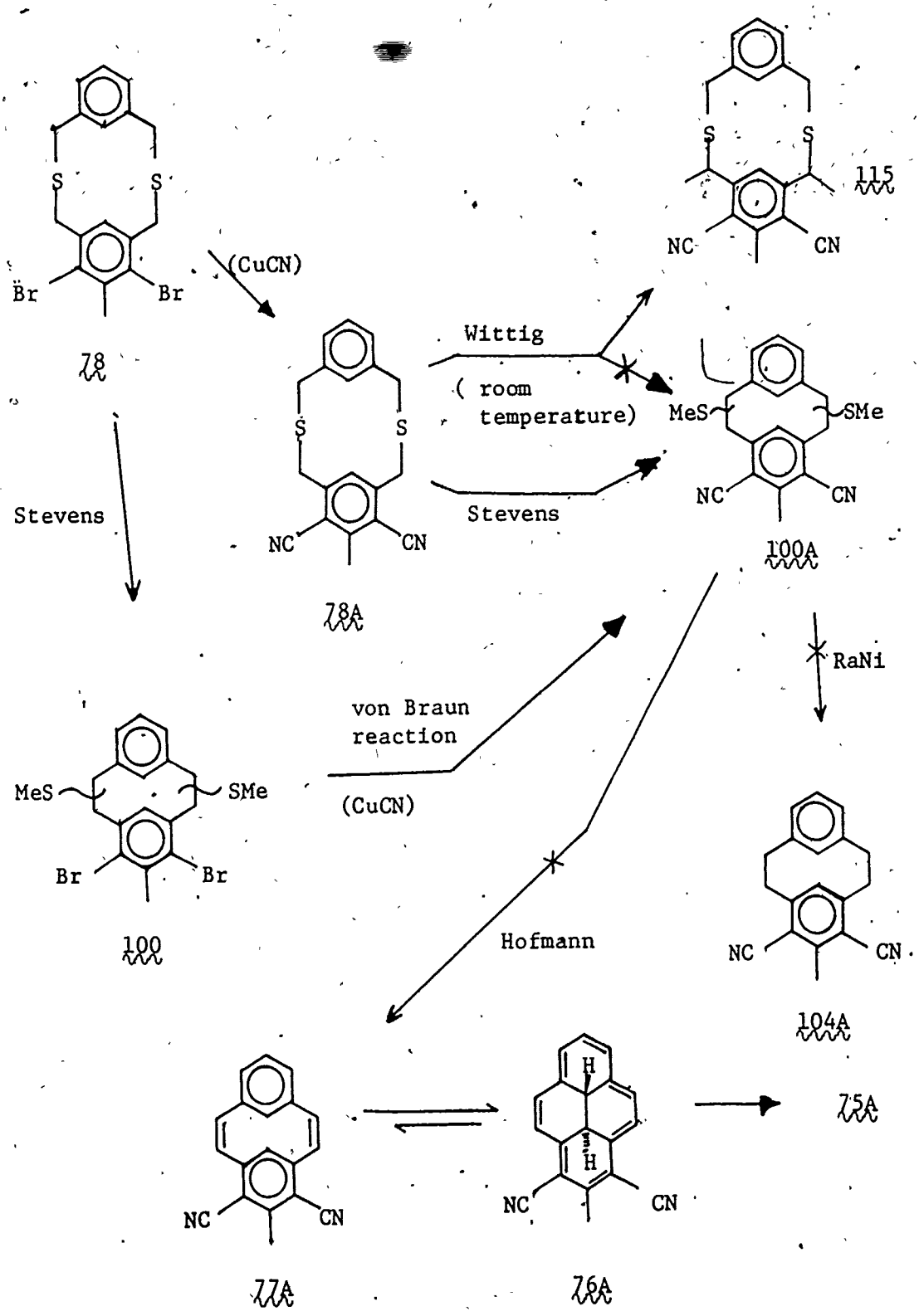


75 75C

Scheme 9

tion of paraformaldehyde and then refluxing for 2 h did not yield any of the dialcohol 75C (see Scheme 9).

A set of reactions similar to those tried earlier were carried out using the dinitrile 100A, which could be prepared from the dithiacyclophane 78 in two ways (see Scheme 10). von Braun reaction[138] of 100 (prepared from 78 by Stevens rearrangement as shown in Scheme 6) in cuprous cyanide in N-methyl-2-pyrrolidinone under reflux conditions gave the dicyano-compound 100A (38% yield), the over-all yield from 78 being 28%. In order to improve the yield, 78 was first converted to the dinitrile 78A which could then be subjected to the

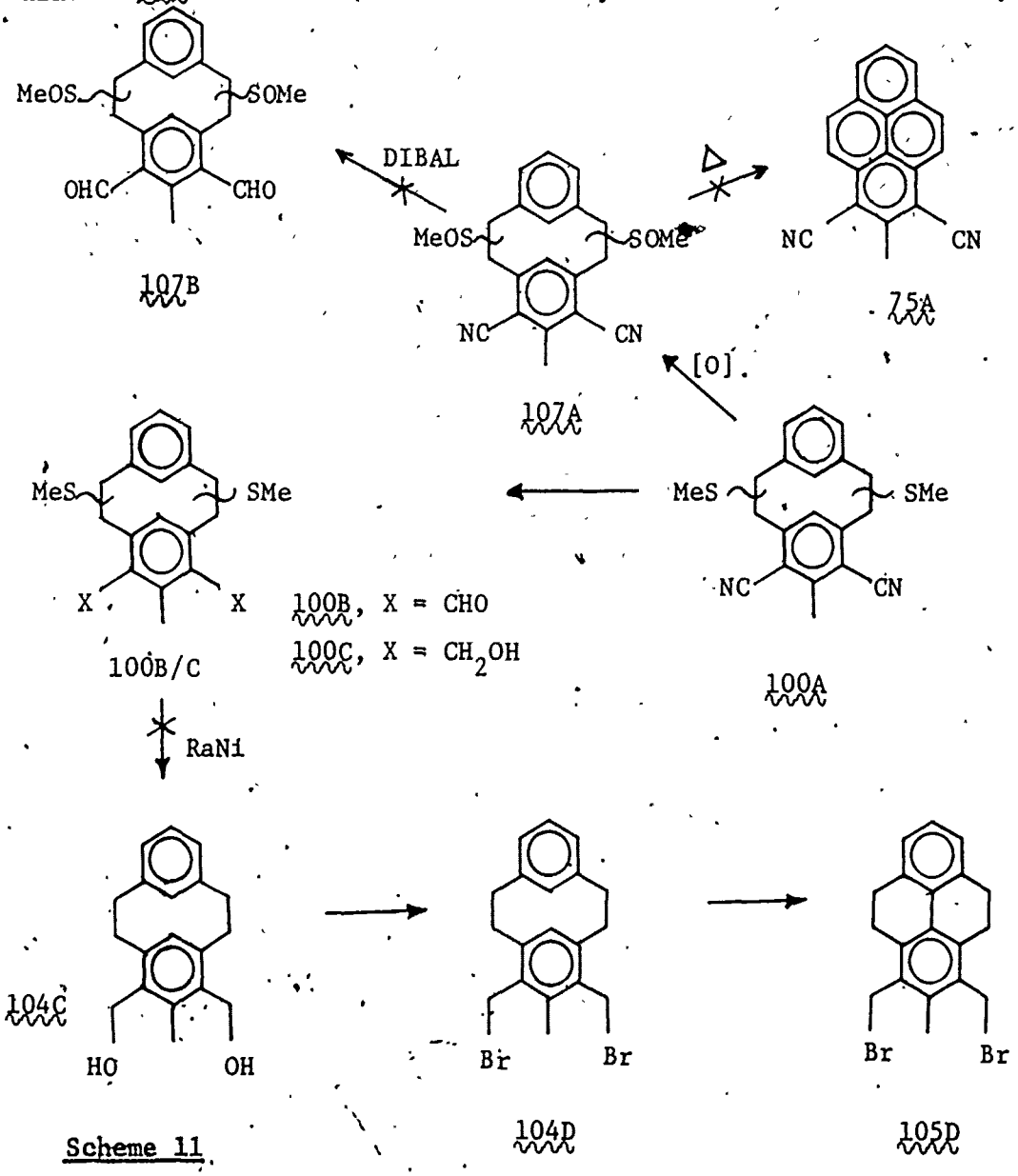

S
S
Br
Br
78
(CuCN)
115
NC
CN
Wittig
(room
temperature)
MeS
SMe
NC
CN
100A
Stevens
78A
Stevens
RaNi
von Braun
reaction
(CuCN)
MeS
SMe
Br
Br
100
Hofmann
NC
CN
104A
H
H
NC
CN
77A
76A
75A

Scheme 10

desired rearrangement. Heating a solution of 78 in N-methyl-2-pyrrolidinone under reflux with an excess of copper(I) cyanide for 24 h gave a 77% yield of the dinitrile 78A, mp 235-237 °C. The presence of molecular ion at m/e 336 in its mass spectrum along with the strong absorption at 2220 cm^{-1} for the -CN stretch in its ir spectrum confirmed its structure. When a solution of 78A in dry tetrahydrofuran was treated with lithium diisopropylamide at 15 °C and the resulting dianion quenched with methyl iodide, the product obtained in 65% yield had a molecular ion at m/e 364 corresponding to 100A. However, its ^{1}Hmr spectrum indicated it to be 115 as shown by a doublet at δ 1.52 (J ≈ 7 Hz). This was probably present as a mixture of isomers, as indicated by the mp range, depending on the pseudo-axial or pseudo-equatorial orientation of the entering methyl group. This was similar to the previous case of 78. Conversion of 78A to the corresponding bis(sulfonium)salt (93% yield) using dimethoxycarbonium fluoroborate and subsequent treatment with potassium t-butoxide in dry tetrahydrofuran gave 100A (25% yield) as a mixture of isomers, the protons of the $-SCH_3$ group appearing as singlets at δ 2.05 and 1.90. The mixture of isomers of 100A, obtained by the von Braun reaction of the bromide 100, was treated with dimethoxycarbonium fluoroborate to give the salt (83%). Hofmann elimination, by treating with potassium t-butoxide in refluxing tetrahydrofuran did not give any identifiable products that would correspond to 77A, 76A or 75A. The mixture of isomers 100A could not be cleanly desulfurized to 104A by using W-7 Raney Nickel.

As the Hofmann route failed, sulfoxide thermolysis was attempted on the dicyano-compound 107A, which was prepared as a mixture of

stereoisomers from 100A in quantitative yield using bromine in aqueous potassium bicarbonate (see Scheme 11). The sulfoxide 107A had the characteristic -CN stretch at 2224 cm^{-1} whereas the absorption at 1050 cm^{-1} corresponds to the sulfoxide (S=O stretch). Thermolysis of a refluxing solution of sulfoxide 107A in N-methyl-2-pyrrolidinone did not lead to the dicyanopyrene 75A. When the dinitrile was reduced with diisobutylaluminum hydride, it gave what appeared to be mostly the sulfide 100A with the -CN functionality untouched as indicated by the

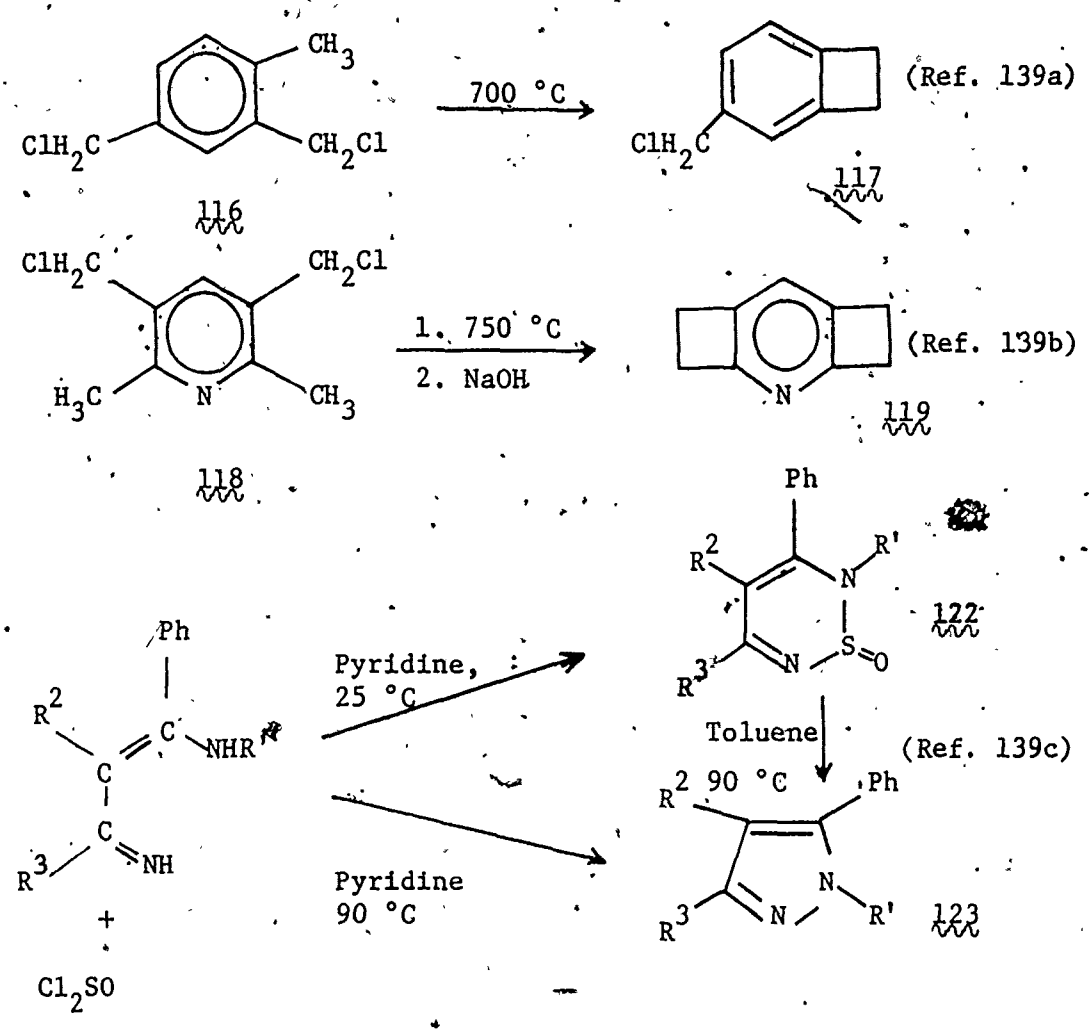


Scheme 11

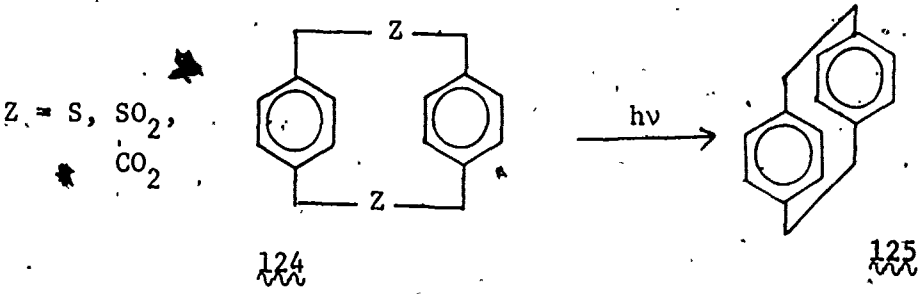
ir spectrum. No evidence for the presence of 107B was obtained. As the reduction of the dinitrile to the dialdehyde failed in the presence of a sulfoxide functionality, diisobutylaluminum hydride was added to a solution of the dinitrile 100A in benzene to give the dialdehyde 100B (97% yield) as a mixture of stereoisomers which had the aldehydic protons at δ 10.72 and 10.66. Sodium borohydride reduction of the dialdehyde 100B in tetrahydrofuran gave 91% yield of the dialcohol 100C. The scheme envisaged hydrogenolysis of the C-S linkage of 100C using Raney Nickel leading to 104C, which could then be converted to the tetrahydropyrene 105D via the metacyclophane 104D. However, Raney nickel treatment of the dialcohol 100C led to the reduction of not only the C-S link, but it also resulted in some reduction of the benzylic alcohol to the corresponding toluene. This was confirmed by refluxing the resulting alcohol with concentrated hydrobromic acid (48%) and the ^{1}Hmr spectrum of the product indicated more than one methyl group. So the approach to bromide 105D from the dialcohol 100C failed.

4.1.4 *Pyrolysis of sulfone to yield metacyclophane* 104.

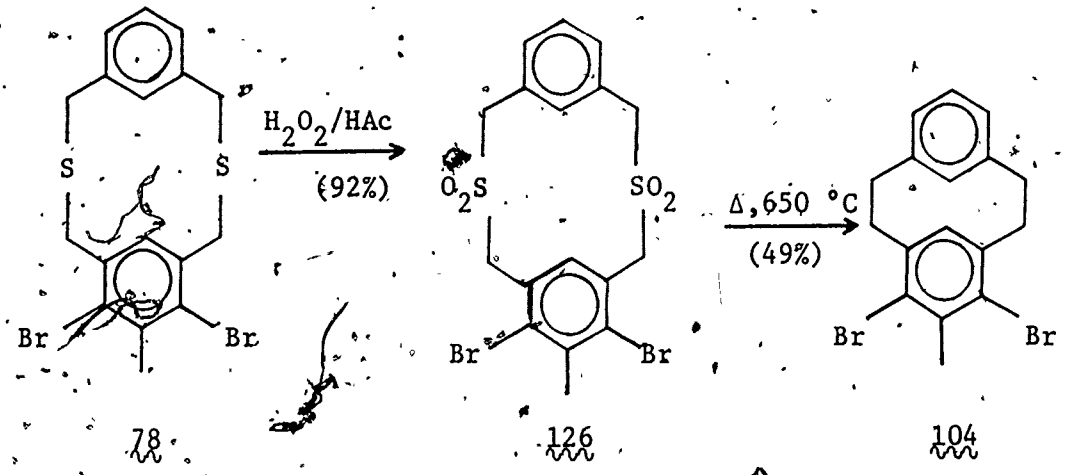
The routes attempted above in which generation of a new C-C bond or C=C bond systems from two C-S-C bonds of a dithiacyclophane by chemical reagents did not prove to be particularly useful. Pyrolysis, however, is a method which is often not explored. It has, however, been used as a technique to generate not only C-C bonds but also N-N bonds in some cases, as shown below :



Such thermolyses or even photolyses have been applied to the synthesis of cyclophanes. For example, the photoextrusion of sulfur,[110,140,141] sulfur dioxide[140,142] or carbon dioxide[143a] from the sulfide, sulfone or ester precursors have been useful and result in high yields.



More generally, however, pyrolysis has been used. This has been recently reviewed.[143b] The sulfone pyrolysis approach results from a facile extrusion of sulfur bonded to benzyl groups forming relatively stable radicals during desulfurization, in contrast to sulfur bonded to alkyl groups. With this in view, dithiacyclophane 78 was oxidized using hydrogen peroxide in acetic acid to the corresponding sulfone 126 in 92 % yield (see Scheme 12). The structure of 126, which was highly insoluble in chloroform, dichloromethane, benzene etc., was confirmed by ^{1}Hmr in CF_3CO_2D as well as by the peak that was seen at m/e 509



78 126 104

Scheme 12

corresponding to MH^+. Photoextrusion of sulfur dioxide from 126 did not give good yield of 104 and it could not be scaled-up easily. However, pyrolysis of 126 under low pressure at 650-700 °C gave a smooth reaction which was complete in about 2 minutes and gave 49% yield of 4,6-dibromo-5-methyl[2,2]metacyclophane 104 as a pale yellow powder, mp 115-117 °C. The internal protons at positions 8 and 16 are well shielded

by the opposite benzene ring as the cyclophane has an *anti*-configuration and the internal protons appear as singlets at δ 4.27 and 4.41 respectively. The protons of the ethano-bridge appear as a complex AA'BB' system and protons of the methyl group appear as a sharp singlet. The compound 104 did not exhibit any temperature-dependant ^{1}Hmr spectrum. Table 12 indicates the chemical shifts of the internal protons of cyclophane 104 along with some other cyclophanes.

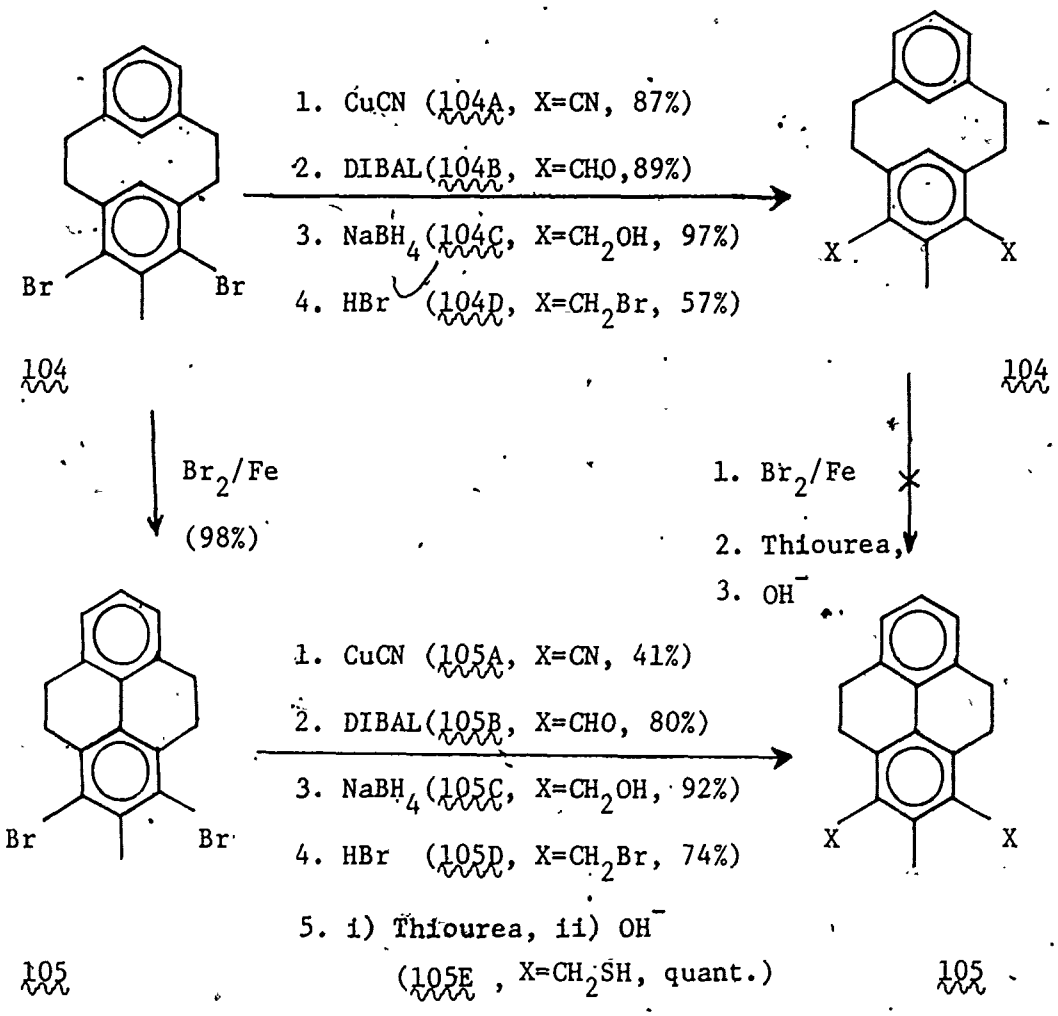
Table 12. ^{1}Hmr data (δ) for the internal protons of some metacyclophanes.

Compound	δ	Ref.
[2,2]metacyclophane		
internal 'H'	4.17	144
8-methyl[2,2]metacyclophane		
internal 'H'	3.72	145
internal 'Me'	0.48	145
4,6-dibromo-5-methyl-[2,2]metacyclophane 104		
H-8	4.27	This work.
H-16	4.41	This work.

Having obtained 4,6-dibromo-5-methyl[2,2]metacyclophane 104, the next objective was its conversion to the bis(bromomethyl)-compound 104D or 105D which, it was hoped, would be more soluble than the bromopyrene 75 or the bromomethylpyrene 74.

4.1.5 *Conversion of metacyclophane 104 to 1,3-bis(bromomethyl)-2-methyl-4,5,9,10-tetrahydropyrene 105D*

The two routes for the conversion of the bromide 104 to 105D are shown in Scheme 13. 4,6-Dibromo-5-methyl[2,2]metacyclophane 104 in carbon tetrachloride was treated with bromine in the presence of iron powder and this gave 98% yield of the tetrahydropyrene 105 with the transannular 10b,10c-bond in place. Conversion of the bromide 105 to the dinitrile 105A was readily accomplished in 41% yield by using cuprous cyanide in N-methyl-2-pyrrolidinone. The dinitrile 105A, mp 224-226 °C, showed in its ir spectrum the -CN stretch at 2230 cm^{-1} and in its mass spectrum the molecular ion at m/e 270 corresponding to the dinitrile. Reduction of the dinitrile 105A to the dialdehyde 105B was achieved in 80% yield by using diisobutylaluminum hydride in hexane. The dialdehyde 105B, mp 147-149 °C, showed the aldehyde proton at δ 10.72 in its ^{1}Hmr spectrum, the aldehydic carbon at 194.2 ppm in the ^{13}Cmr spectrum, the carbonyl stretch at 1682 cm^{-1} in its ir spectrum and the molecular ion at m/e 276, with peaks indicating loss of -CO and -CHO groups, in its mass spectrum. The sodium borohydride reduction of the dialdehyde 105B in tetrahydrofuran led to the required bis(hydroxymethyl)tetrahydropyrene 105C, mp 180-182 °C, in 92% yield. In the ir spectrum of 105C the carbonyl absorption was absent and the -OH stretch of the alcohol appeared at 3280 cm^{-1}. The dialcohol 105C, on refluxing with hydrobromic acid (48%), gave 1,3-bis(bromomethyl)-2-methyl-4,5,9,10-tetrahydropyrene 105D, mp 208-210 °C, in 74% yield. The structure of 105D was clear from the mass spectrum with the

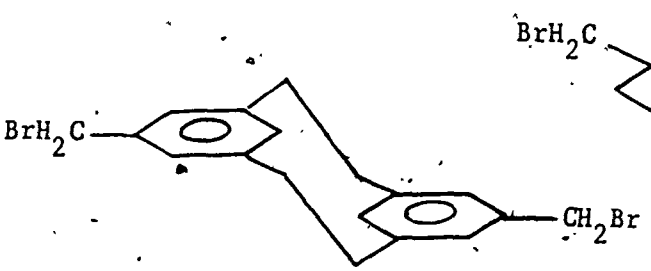


Scheme 13

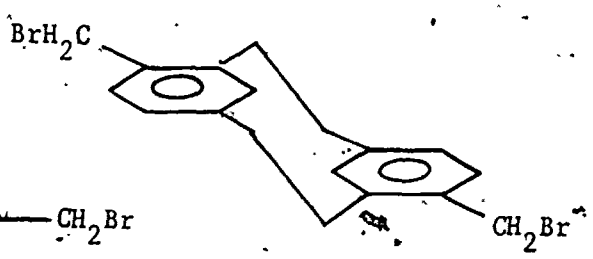
molecular ion at m/e 406 (correct isotope pattern) and the singlet expected for the protons of the $-CH_2Br$ group at δ 4.60 in its ^{1}Hmr spectrum. The overall yield for the conversion of 104 to 105D was 22%.

In order to investigate a method for improved yield, the bromide 104 was converted to the dinitrile 104A in 87% yield by using cuprous cyanide. The dinitrile 104A, mp 201-202 °C, showed the -CN stretch at 2220 cm^{-1} in its ir spectrum and a molecular ion at m/e 272 with a peak indicating the loss of a methyl group. Reduction of dinitrile 104A

with diisobutylaluminum hydride in benzene afforded 89% yield of the dialdehyde 104B, mp 128-130 °C; the structure of which was evident from the aldehydic proton at δ 10.70, the carbonyl stretch at 1690 cm^{-1} and a molecular ion at m/e 278 in its ^{1}Hmr, ir and mass spectra respectively. Further reduction of 104B with sodium borohydride in tetrahydrofuran gave the dialcohol 104C in 97% yield. The dialcohol 104C, mp 214-216 °C, showed a broad -OH absorption at 3400 cm^{-1} in its ir spectrum and a molecular ion at m/e 382 in its mass spectrum. The dialcohol 104C gave, on heating with hydrobromic acid (48%), 57% yield of the bis(bromomethyl) compound 104D, mp 191-192 °C. Its structure was confirmed by a molecular ion at m/e 408 in its mass spectrum and the protons of the $-CH_2Br$ group could be seen at δ 4.65 in its ^{1}Hmr spectrum. Although Misumi[146] has reported the generation of a transannular bond in metacyclophane systems carrying bromomethyl substituents on the aryl ring as in 127 and 128, it was found difficult to obtain pure 105D by treating 104D with bromine in presence of iron powder.

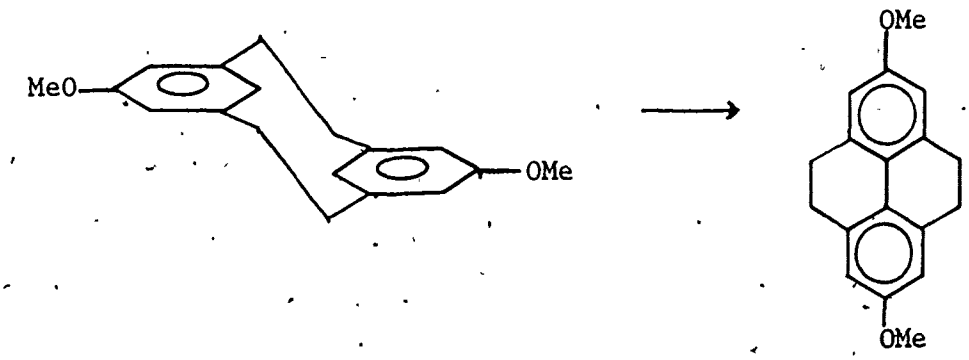


127



128

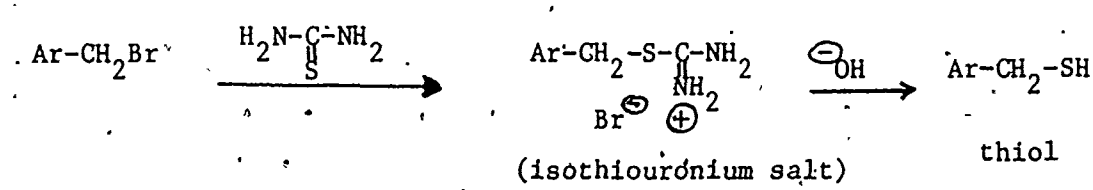
Oxidative coupling reactions have also been carried out using silica-bound ferric chloride[147] as well as by electrochemical oxidations[147]. For example, 5,13-dimethoxy[2,2]metacyclophane 129 can be oxidized



129 130

to 2,7-dimethoxy-4,5,9,10-tetrahydropyrene 130. Attempted oxidation of 104D with ferric chloride did not, however, give pure 105D.

The bromide, 1,3-bis(bromomethyl)-2-methyl-4,5,9,10-tetrahydropyrene 105D, obtained by the alternative route indicated earlier was converted quantitatively to the bis-thiol 105E, through the intermediate bis(isothiouronium)salt using thiourea and then base in the normal way.[85a] The dithiol 105E, mp 146-148 °C, required for synthesizing 48, showed a strong molecular ion at m/e 312 in its mass spectrum

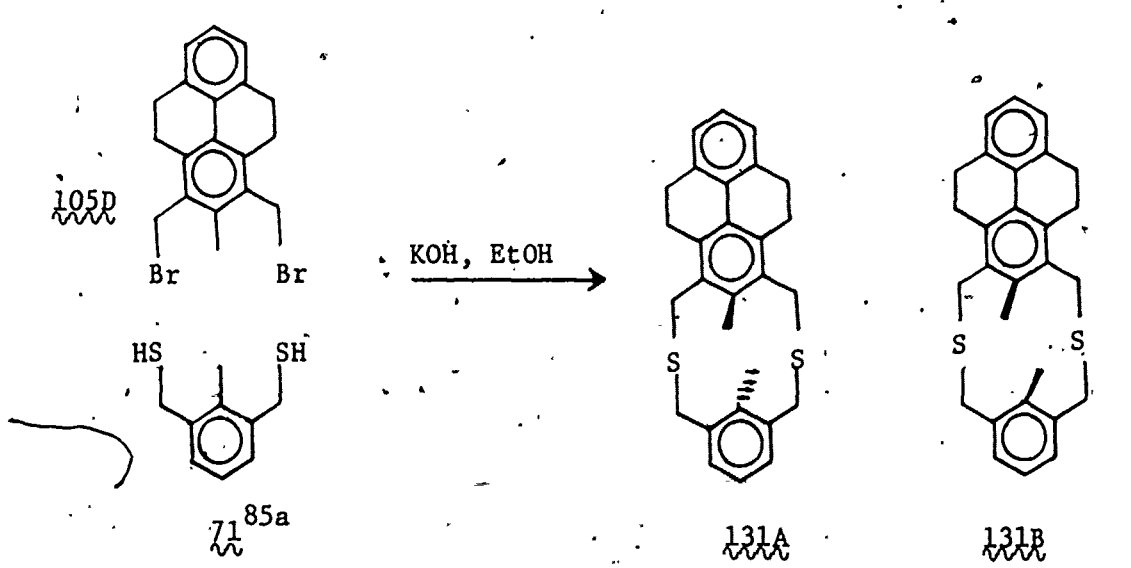


and the structure of the dithiol 105E was eyident from its ^{1}Hmr spectrum. The doublet (coupling constant, J =6.4 Hz) for the $-CH_2-S$ protons at δ 3.85 and the -SH triplet at δ 1.64 were typical of a benzylic thiol. The other two thiols viz., 1,3-bis(thiomethyl)-2-methylnaphthalene 91A and 2,6-bis(thiomethyl)toluene 71 required to ultimately

generate 47 and 46 respectively were prepared from the dibromides 91 and 64 by following the method adopted to convert the dibromide 105D to the bis-thiol 105E. With all the desired thiols and bromides at hand, the couplings to obtain the dithiacyclophanes, en route to the benzannelated systems 46, 47 and 48, were next tried.

4.2 *Synthesis of* trans*-10b,10c-dimethyl-10b,10c-dihydrodibenzo[cd,lm]-perylene* 46 *and* trans*-10b,10c-dimethyl-10b,10c,13,14-tetrahydrodibenzo[cd,lm]perylene* 45

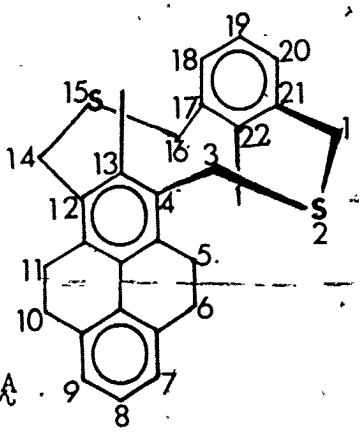
Coupling of the bromide 105D and 2,6-bis(thiomethyl)toluene[85a] 71 under high dilution conditions using potassium hydroxide in ethanol-benzene yielded, after chromatography, 67% yield of the *anti-* isomer 131A and 7.3% yield of the *syn-* isomer 131B (see Scheme 14).



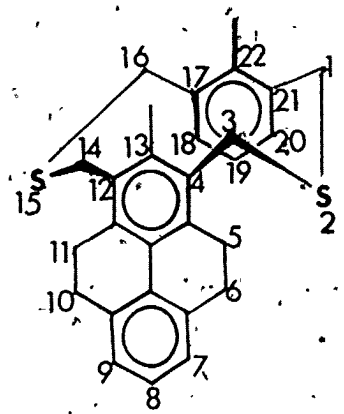
71[85a] 131A (*anti-isomer*) 131B (*syn-isomer*)

Scheme 14

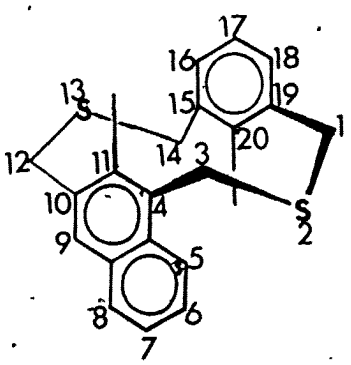
The *anti*-isomer 131A, which was eluted first, crystallized easily from benzene-cyclohexane as white needles and had mp 252-254 °C. The structure of 131A was established on the basis of the molecular ion at m/e 428 in its mass spectrum and by the ^{1}Hmr spectrum which showed the



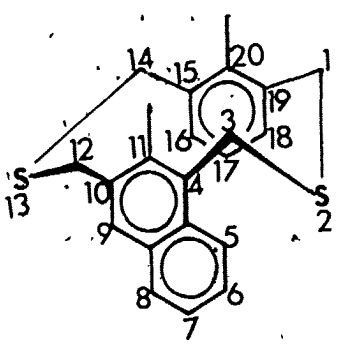
131A



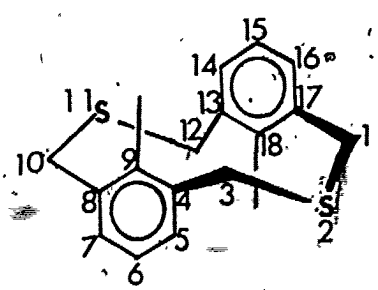
131B



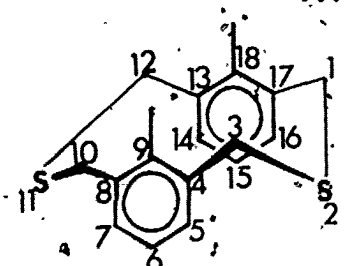
131C



131D



72 85a

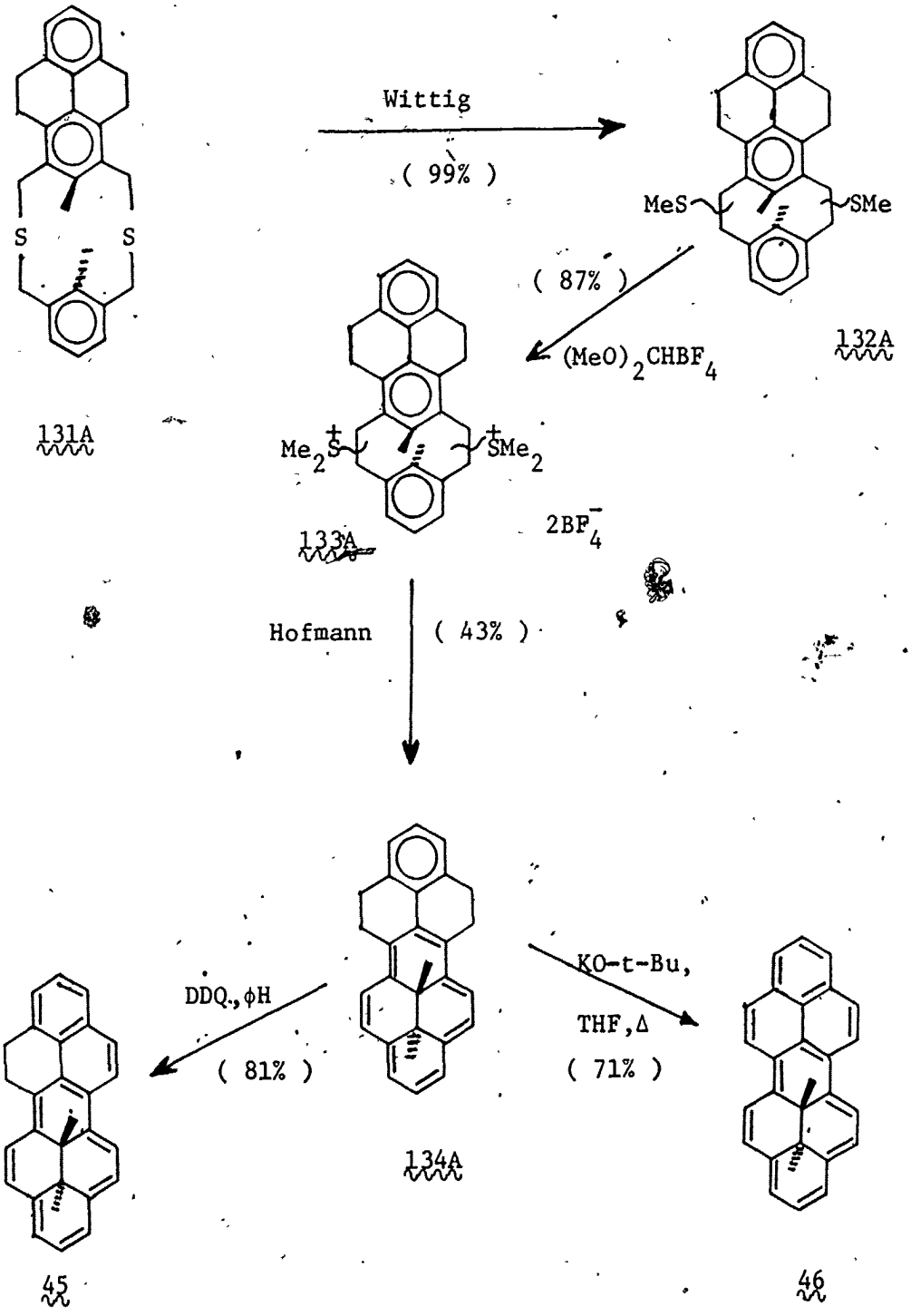


72A 85a

internal 13-CH_3 at δ 1.38 and the 22-CH_3 at δ 1.18 (*cf. anti-* 72,[85a] -CH_3 at δ 1.30 whereas in the case of *anti-* 131C[148] the internal 11-CH_3 is at δ 1.42 and the 20-CH_3 is at δ 0.92). However, the 13-CH_3 (δ 2.48) and the 22-CH_3 (δ 2.44) of the *syn*-isomer 131B appeared like those of the *syn-* 72A (δ 2.54) at the position usual for an aryl methyl group. In the case of *syn-* 131D, the 11-CH_3 appeared at δ 2.62 whereas the 20-CH_3 appeared at δ 2.45 in the ^{1}Hmr. The *syn*-isomer, which was obtained as colorless crystals, had mp of 198-200 °C. The 18-,19- and 20- aryl hydrogens(δ 7.5-7.2) and the 7-,8- and 9- aryl hydrogens of the *anti-* 131A (δ 7.12) appeared at the normal region. In the case of *syn-* 131B, however, the 18-,19- and 20- aryl hydrogens were shielded by the opposite benzene ring and appeared at δ 6.91 (d, 2H, J= 7.2 Hz, H-18 and H-20) and δ 6.4(t, 1H, J= 7.2 Hz, H-19) whereas the aryl hydrogens of the tetrahydropyrene moiety were seen as an 'A_2B' multiplet at δ 7.08. The methylene bridge (CH_2-S-CH_2) protons of the *anti*-isomer 131A appeared as two singlets at δ 3.87 and 3.67, whereas the methylene bridge of the *syn*-isomer 131B appeared as an 'AB' doublet at δ 4.19 and 3.77 (J= 15.3 Hz) and a singlet at δ 4.01. The protons of the -CH_2-CH_2- bridge in both the *anti*-isomer 131A and the *syn*-isomer 131B appeared at about the same region. The shielded *anti*-methyls of 131A can also be noticed in the ^{13}Cmr spectrum at δ 15.7 and 15.0, whereas those for the *syn*-isomer 131B appear at δ 18.5 and 16.8. The trend is similar to those of the *anti*-isomer 132A (δ 15.3 and 14.9) and *syn*-isomer 132B (δ 17.6 and 17.3).

Wittig rearrangement[105] of *anti-* 131A proceeded smoothly with n-BuLi, followed by treatment with methyl iodide to yield quantitatively

132A as a mixture of stereoisomers (see Scheme 15). The protons of the $-SCH_3$ group of 132A appeared as a series of singlets at δ 2.60, 2.12 and 2.08 and the mixture of stereoisomers showed the molecular ion at m/e 456 with peaks corresponding to the loss of methyl and sulfur fragments. The mixture of stereoisomers of 132A were used directly in a Hofmann elimination step by first treating with Borch[149] reagent, i.e. $(MeO)_2CHBF_4$, to yield the greenish-grey sulfonium salts 133A, mp 197-202 °C, in 87% yield. On treatment with potassium t-butoxide in refluxing tetrahydrofuran, the salt 133A underwent Hofmann elimination to give 43% yield (from 133A) of mainly 134A. The shielded internal methyl group appeared at δ - 3.81 and - 3.89 in the ^{1}Hmr spectrum. The presence of the partially oxidized product 45 as well as the completely dehydrogenated product 46 in the resulting mixture, as seen in the ^{1}Hmr of the product, suggests the susceptibility of 134A to oxidation. A recent review by Fu and Harvey[150] deals with the dehydrogenation of polycyclic hydroaromatic compounds. The use of 2,3-dichloro-5,6-dicyanoquinone (DDQ) to aromatize dihydro-systems like 1,4-dihydrobenzocycloalkenes [151] or tetrahydro-systems as in tetrahydropyrene[114] is well known. Attempts to oxidize a refluxing solution of 134A in benzene with DDQ gave *trans*-10b,10c-dimethyl-10b,10c-dihydrodibenzo[*cd,lm*]perylene 46 but the yields were poor and variable (3 - 20 %). However, the fact that Hofmann elimination using potassium t-butoxide gave not only 134A but also the dehydrogenated products 45 and 46 suggested that we could probably carry out the dehydrogenation of 134A using the metal alkoxide as the reagent. The utility of metal alkoxides for dehydrogenation, although little

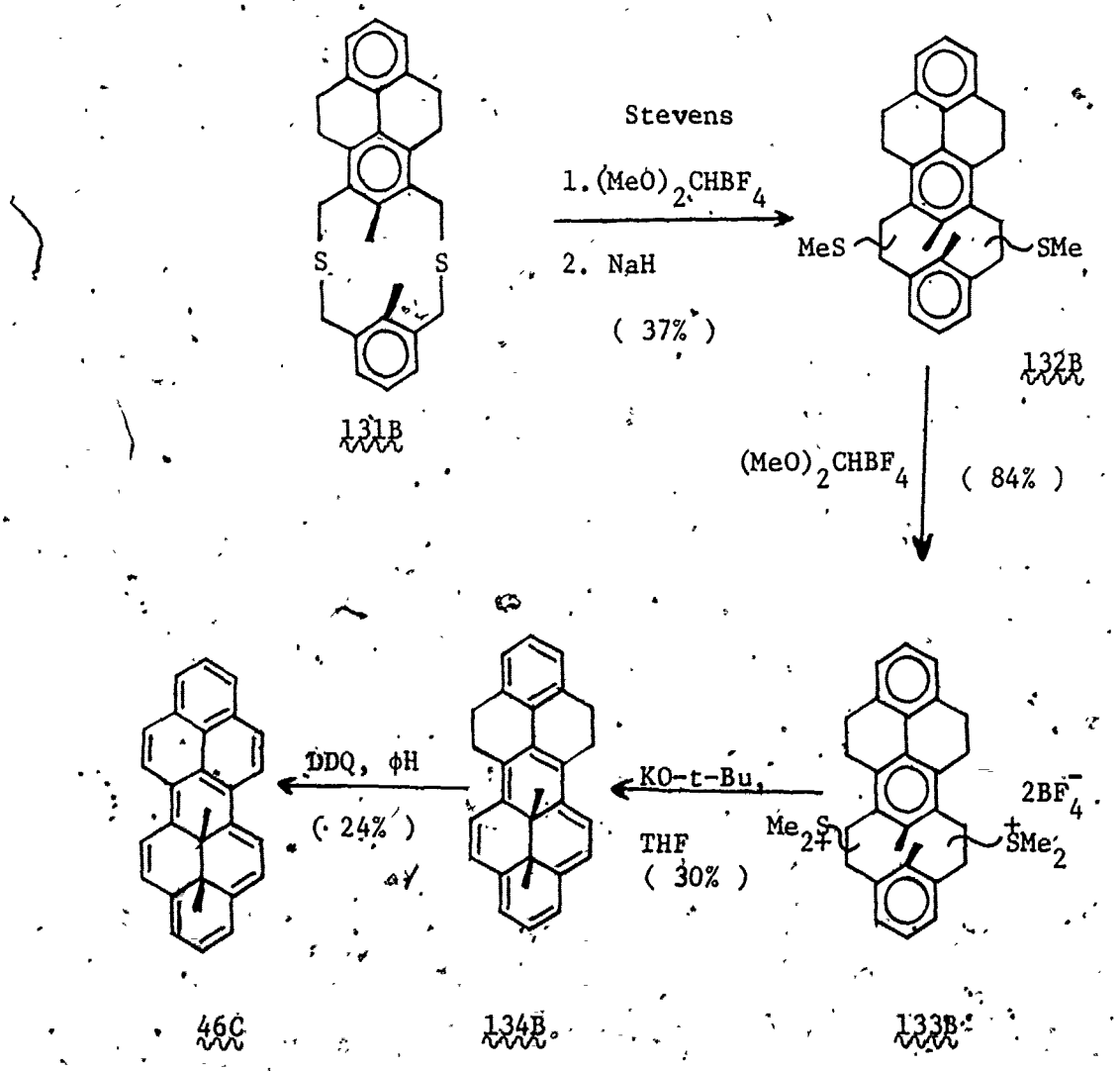

Wittig
(99%)
MeS
SMe
132A
(87%)
(MeO)2CHBF4
S
S
131A
Me2S+
+SMe2
2BF4−
133A
Hofmann
(43%)
DDQ., φH
(81%)
KO-t-Bu,
THF, Δ
(71%)
134A
45
46

Scheme 15

used, is not without precedence. Both Pines[152a] and Barton[152b,c] have used alkoxides in suitable solvents to effect dehydrogenation. With this in mind dehydrogenation of 134A, which already contained some 46 and 45, was carried out by heating a solution of 134A in tetrahydrofuran with potassium t-butoxide when *trans*- 46 was obtained in 71% yield. The perylene 46, mp 198-199 °C, was obtained as orange-red crystals on recrystallization from methanol-benzene and it was characterized by its molecular ion at m/e 356 in its mass spectrum as well as correct CHN analysis. That 46 was actually the product isolated, rather than the cyclophane-diene 46A, was clear from the ^{1}Hmr spectrum of the product which showed the protons of the internal methyl group being highly shielded at δ - 4.19 and - 4.28 and by the presence of the shielded bridging carbons carrying the methyl groups appearing at δ 30.6 and 30.4 in the ^{13}Cmr spectrum. In order to obtain a pure sample of 45, partial dehydrogenation of 134A was necessary. Use of N-bromosuccinimide-base[153] or n-BuLi-Cd(II)[154] to effect such partial dehydrogenation did not prove to be useful. However, the desired hydroaromatic compound 45 was readily obtained as a red-brown product in 81% yield by using 1.1 equivalent of DDQ in benzene and finally separating the desired product by using high pressure liquid chromatography. Its structure was confirmed by the peak seen at m/e 359 (MH^+) in its mass spectrum and the internal methyl protons now appeared as a singlet at δ ~2.78, a downfield shift of ~ 1.4 ppm from those of the completely dehydrogenated product 46.

4.2.1 *Synthesis of cis-10b,10c-dimethyl-10b,10c-dihydrodibenzo[cd,lm]-perylene* 46C

To ensure that the *syn*-isomer did not undergo any conformational interconversion[103] during the rearrangement of the dithiacyclophane, the *syn*-isomer 131B was subjected to a Stevens rearrangement rather than a Wittig rearrangement. Treatment of 131B with dimethoxycarbonium fluoroborate gave the corresponding Stevens salt in 99% yield and subsequent treatment with sodium hydride in tetrahydrofuran gave the



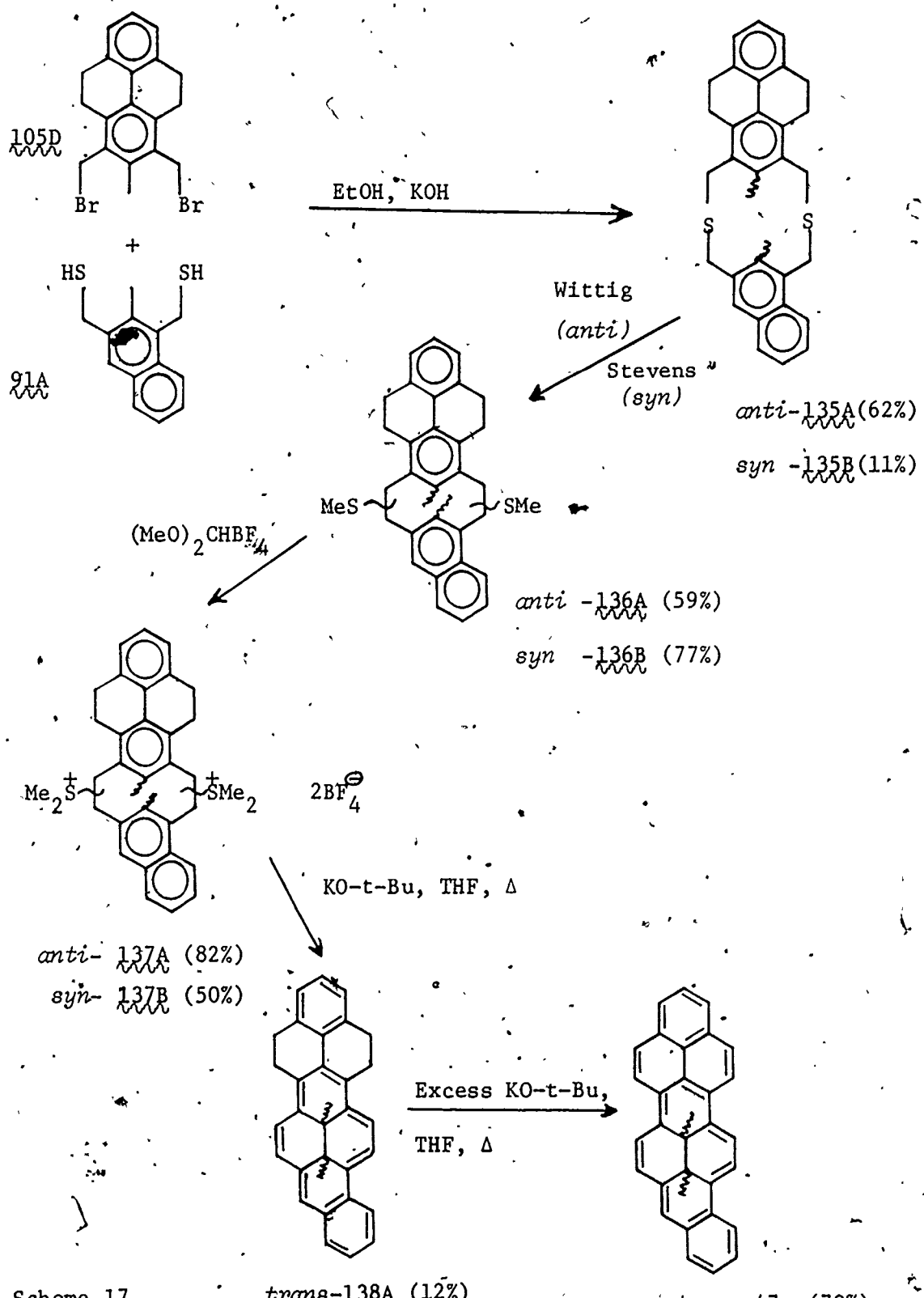
Scheme 16

rearranged product 132B (37% yield) as a mixture of stereoisomers. (see Scheme 16). The signals due to the protons of the $-SCH_3$ group and the internal methyl group overlap and hence cannot be assigned definitively. However, the molecular ion at m/e 456 is evidence that the rearranged anion had been alkylated successfully. As in the earlier case, 132B was remethylated using dimethoxycarbonium fluoroborate in 84% yield and Hofmann elimination using potassium t-butoxide in tetrahydrofuran gave 30% yield of 134B. The ^{1}Hmr of 134B showed the shielded internal methyl groups at δ - 1.82 and - 1.89 and the presence of partially oxidized product was indicated by the singlets seen at δ - 0.99 and - 1.44. Dehydrogenation of 134B was carried out by refluxing a solution of 134B in benzene with 2,3-dichloro-5,6-dicyanoquinone to give *cis*- 46C as a pale yellow green solid in 24% yield. The protons of the internal methyls of 46C appear at δ -1.85 and -2.14, unlike the internal methyls of 46A which are much more shielded.

4.2.2 *Synthesis of trans-12c,12d-dimethyl-12c,12d-dihydrobenzo-[rst]naphtho[8,1,2-cde]pentaphene* 47

The bis-thiol 91A was obtained from 2,3-dimethylnaphthalene[155] in 7 steps in an overall yield of about 7%. Coupling of the bromide 105D with the bis-thiol 91A proceeded smoothly to give, after column chromatography, 62% yield of the *anti*-dithiacyclophane 135A and 11% yield of the *syn*-dithiacyclophane 135B (see Scheme 17).

The *anti*-isomer 135A, mp 226-227 °C, showed clearly a peak at m/e 479 corresponding to MH^+. Its structure was established by its


105D
Br
Br
+
HS
SH
91A
EtOH, KOH
S
S
Wittig
(anti)
Stevens
(syn)
anti-135A(62%)
syn -135B(11%)
MeS
SMe
anti -136A (59%)
syn -136B (77%)
(MeO)2CHBF4
Me2S
SMe2
2BF4
KO-t-Bu, THF, Δ
anti- 137A (82%)
syn- 137B (50%)
Excess KO-t-Bu,
THF, Δ
trans-138A (12%)
cis-138B (23%)
trans-47 (70%)
cis-47B (30%)

Scheme 17

^{1}Hmr spectrum which showed the internal methyl (11-CH_3) at δ 1.50 and 24-CH_3 at δ 0.72 (*cf. anti-* 131C : 11-CH_3 at δ1.42 and 20-CH_3 at δ 0.92). In contrast, the 11-CH_3 (δ 2.63) and the 24-CH_3 (δ 2.49) of the *syn*-isomer 135B like those of the *syn-* 131D (11-CH_3 at δ 2.62 and 20-CH_3 at δ 2.45) were normal for an aryl methyl. The *syn*-isomer 135B was recrystallized pure from benzene-cyclohexane, mp 204-206 °C, and only H-9, which appeared as a doublet at δ 8.0 in the ^{1}Hmr, seemed to be deshielded because of the thiacyclophane bridge, similar to the 1,8- interaction in naphthalene. In the *anti*-isomer 135A, again the H-9 proton at δ 8.29 appeared to be deshielded. The protons of the $-CH_2-S-CH_2$ bridges appeared separate from the $-CH_2-CH_2$ bridges in the case of the *syn*-isomer but overlapped in the case of the *anti*-isomer. The shielded methyls of the *anti*-isomer 135A can also be observed in the carbon spectrum at δ 16.3 and 15.4, whereas those for the *syn*-isomer 135B are seen at δ 18.8 and 18.1.

Wittig rearrangement[105] of *anti*-135A occurred with n-BuLi and the addition of methyl iodide gave the rearranged product 136A in about 60% yield, as a mixture of stereoisomers. ^{1}Hmr of 136A showed the protons of the $-SCH_3$ group as a series of singlets in the region δ 2.30 - 2.14 and the shielded internal methyl groups appear at δ 1.62 - 0.97, again as a series of singlets. Treatment with Borch[149] reagent i.e., dimethoxycarbonium fluoroborate, gave the sulfonium salts 137A in 82% yield and subsequent Hofmann elimination with potassium t-butoxide in tetrahydrofuran gave 12% yield of the hydroaromatic compound 138A. The internal methyl protons appear at δ - 1.41 in the case of 138A, confirming that it does not exist as the open cyclophane-diene valence tautomer.

A smaller singlet at δ - 1.35, probably due to the dehydrogenated product, could also be seen in the ^{1}Hmr of 138A. As seen in the earlier case of *trans*-isomer 46, oxidation of 138A with potassium t-butoxide in refluxing tetrahydrofuran gave *trans*- 47 in 70% yield, mp 219 - 221 °C. The shielded internal methyl protons appeared at δ - 1.35 and - 1.41 in the ^{1}Hmr spectrum and the peak at m/e 407 (MH^+) was added confirmation of the structure of *trans*- 47.

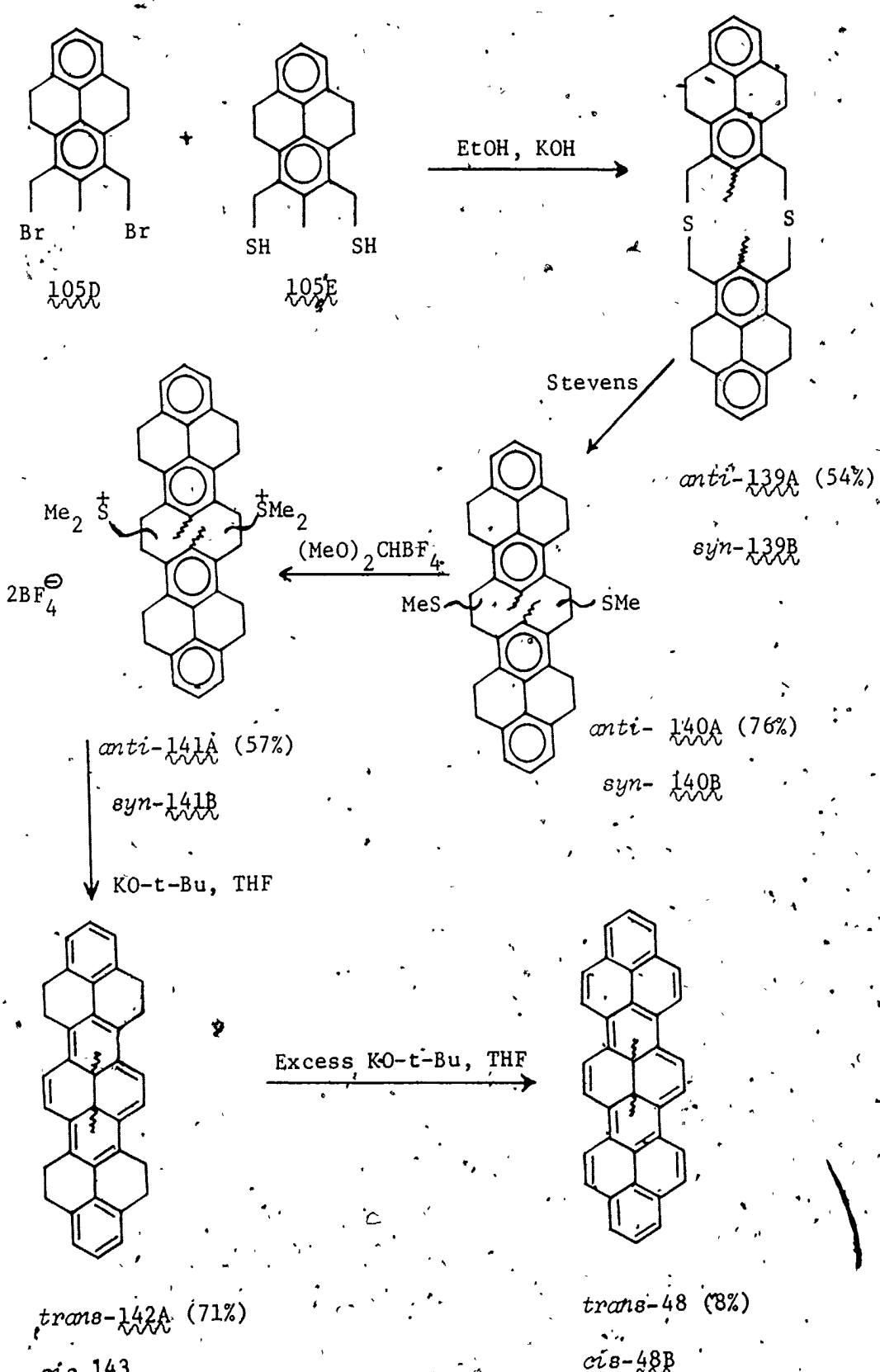
4.2.3 *Synthesis of cis-12c,12d-dimethyl-12c,12d-dihydrobenzo[rst]-naphtho[8,1,2-cde]pentaphene* 47B.

As shown in Scheme 17, the *syn*-dithiacyclophane 135B was first methylated using Borch reagent and the rearrangement of the sulfonium salts successfully accomplished by using sodium hydride in dry tetrahydrofuran. This gave 136B as a mixture of stereoisomers in an overall yield of 77% from 135B. This mixture was used directly in the Hofmann elimination step, by firstly reacting with Borch reagent[149] to get the sulfonium salt 137B (50% yield) and then treatment with potassium t-butoxide in dry tetrahydrofuran at room temperature to give 23% yield of 138B as a red product. The protons of the shielded internal methyl group appeared at δ 0.05 and - 0.08. ^{1}Hmr also indicated that some dehydrogenation had taken place, the peaks due to the partially dehydrogenated system appearing at δ 0.49 and 0.45 (CH_3 groups at positions 12c and 12d). Dehydrogenation of 138B with potassium t-butoxide in dry tetrahydrofuran gave, on refluxing for 0.5 h under nitrogen, 30% yield of the *cis*-isomer 47B. The shielded internal methyl protons of *cis*-isomer 47B appeared at δ -0.10 and -0.14.

4.2.4 *Synthesis of trans-14c,14d-dimethyl-14c,14d-dihydrobenzo[rst]-dinaphtho[8,1,2-cde:2',1',8'-klm]pentaphene* 48.

To get the thiacyclophanes 139A and 139B, coupling of the bromide 105D and the bis-thiol 105E was carried out in alcoholic potassium hydroxide under high dilution conditions, whereby the *anti*-isomer 139A was obtained pure in 54% yield after chromatography (see Scheme 18). However, it was not possible to get a pure sample of the *syn*-isomer 139B free of the *anti*-isomer (as seen by ^{1}Hmr)

A sample of pure *anti*-isomer 139A recrystallized from benzene-cyclohexane had mp 289-291 °C. In its ^{1}Hmr spectrum, the protons H-7, H-8, H-9, H-20, H-21 and H-22 appeared as an 'A$_2$B' multiplet at δ 7.12 and the internal methyl protons appeared shielded at δ 1.32 (*cf.* δ 1.30 for -CH$_3$ of *anti*-72) and the compound had a peak at m/e 557 corresponding to (MH^+). The protons of the internal methyls of the *syn*-isomer 139B appeared at δ 2.14 (by subtracting the spectrum of the *anti*-isomer). In the ^{13}Cmr spectrum, the internal methyl carbons appeared at δ 16.0. This was then converted to *anti*-140A as a mixture of stereoisomers by Stevens rearrangement in about 76% yield and ^{1}Hmr of the product showed the singlets due to -SMe groups at δ 2.82 and 2.21. As in previous cases, 140A was remethylated to 141A in 57% yield using Borch reagent and Hofmann elimination with potassium t-butoxide in dry tetrahydrofuran gave *trans*-142A. The ^{1}Hmr of 142A showed the shielded internal methyl protons at δ - 4.10 (*cf.* those for 15,16-dimethyldihydropyrene appear at δ - 4.25). The peaks seen at δ -3.20 corresponded to the internal methyl protons of the dehydrogenated product *trans*- 48. Attempts to dehydrogenate 142A using potassium


Br
Br
105D
SH
SH
105E
EtOH, KOH
S
S
anti-139A (54%)
syn-139B
Stevens
Me2 S
SMe2
2BF4⊖
(MeO)2CHBF4
MeS
SMe
anti- 140A (76%)
syn- 140B
anti-141A (57%)
syn-141B
KO-t-Bu, THF
Excess KO-t-Bu, THF
trans-142A (71%)
cis-143
trans-48 (8%)
cis-48B

Scheme 18

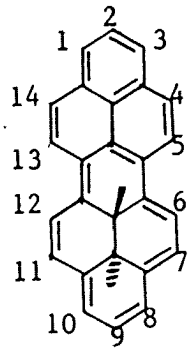
t-butoxide resulted in the disappearance of the signal at δ -3.20. leaving behind the one at δ - 4.11 that actually corresponds to the unoxidized 142A. Hence a pure sample of 48 could not be isolated.

As the *syn*-139B could not be obtained pure, the sequence leading to the formation of 48B could not be followed up.

4.2.5 *Nitration of benzannelated perylene 46*

The nitration of 46 was undertaken to examine whether benzannelated perylene 46 would exhibit the substitution reaction typically associated with benzene. Such electrophilic substitutions have been carried out on [18]annulene[156] 5, 1,6-methano[10]annulene[63b] 16 and *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene[156d] 43. Under very mild conditions, cupric nitrate in acetic anhydride at 0 °C, nitration of 46 followed by separation on a Varian High Pressure Liquid Chromatograph unit gave three nitro compounds, of which two could be identified (see Scheme 19).

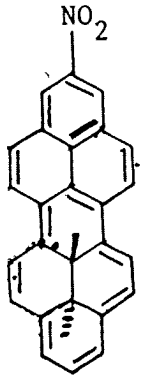
The compound that came off first from the column was obtained as dark-reddish black crystals 147, mp 222-224 °C; the nitro compound 147 also indicated a peak at m/e 402 (MH^+) and hence this was clearly a mononitro derivative. The second compound to be eluted 145, mp 228 - 230 °C, had a slight greenish tinge and this also exhibited a peak at m/e 402 (MH^+). Thus both the derivatives obtained were actually mononitro compounds. In the case of 15,16-dimethyldihydropyrene 25, nitration occurs at position C-2 whereas in the case of pyrene itself it occurs at the C-1 position. The dibenzannelated perylene 46 is characterized by both a dimethyldihydropyrene nucleus as well as a



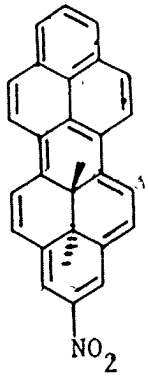
46

$Cu(NO_3)_2$,

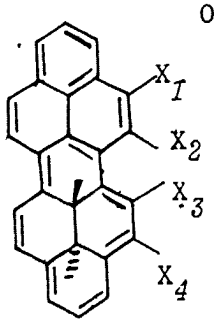
acetic anhydride, 0 °C



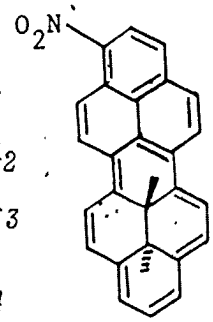
144



146



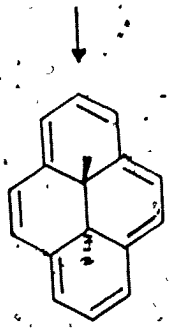
145



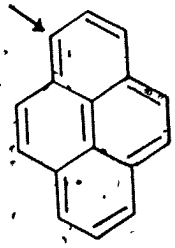
147

[X_1 or X_2 or X_3 or X_4 = $-NO_2$]

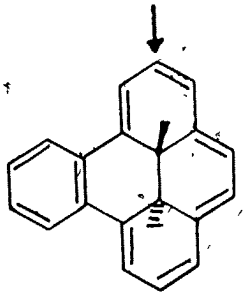
Scheme 19



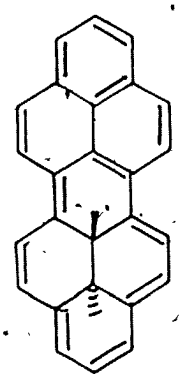
25



63



43



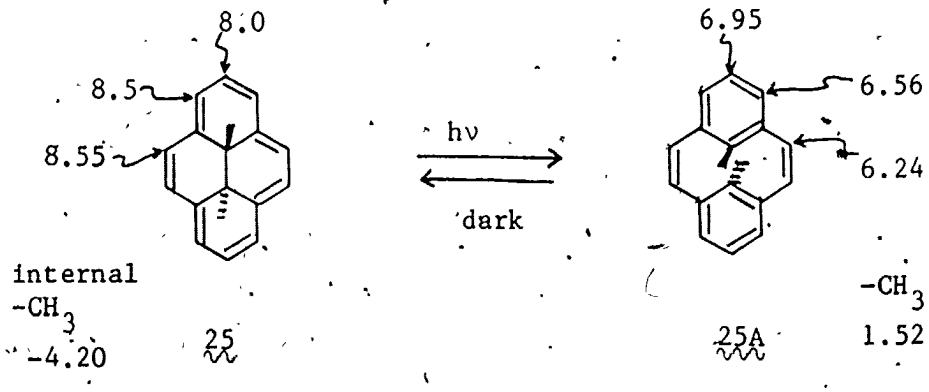
46

pyrene nucleus. So one might expect the incoming nitro group to attack the position C-1 or C-9 in such a case. The ^{1}Hmr of both 147 and 145 indicated the protons of the internal methyl groups at δ - 3.99, - 4.03 and -3.92, - 4.00 respectively, whereas the internal methyl protons of 46 appeared at δ - 4.19 and - 4.28. This can be compared to the internal methyl protons of the 2-nitro-43 at δ - 1.85 (δ for 43 is - 1.85) and - 4.03 for 2-nitro-25 (δ for 25 is - 4.25). Thus the entry of a nitro group does not seem to affect the chemical shift of the protons of the internal methyl group as seen by the ^{1}Hmr spectrum of the compounds under consideration. The low field ^{1}Hmr spectrum of 147 (see Fig. 12) has a triplet at δ 8.14 (1H) and a sharp singlet at 9.93 (2H). The rest appeared as doublets, in fact 9 doublets (one of the doublets corresponds to 2H), and thus accounts for 13 hydrogens. However, ^{1}Hmr of 145 (see Fig. 13) showed a sharp singlet at δ 10.54 (1H) and two triplets at δ 8.58 (1H) and 8.14 (1H) along with nine doublets (corresponding to 10 hydrogens). The parent compound itself has the triplets at δ 8.28 (H-2) and 8.05 (H-9). So 147 which has only one triplet is assigned the structure indicated wherein the nitro group is at C-1, the triplet due to H-9 appearing to be nearly unaffected (from the parent 46) due to the nitro-substituent. However, 145 shows two triplets and this indicates that the nitro group has not entered positions C-1, C-2, C-8 or C-9 as it would lead to the disappearance of one of the triplets seen in the ^{1}Hmr of 46. The ^{1}Hmr suggests that in case of 145 the positions C-4, C-5, C-6 or C-7 to be the most likely site of attack. Although

one cannot unequivocally state as to which is the actual site of attack, the presence of the highly deshielded singlet at δ 10.54 (1H) leads one to believe that the nitro group is either at C-5 or at C-6, with a greater likelihood of it being at C-5.

4.2.6 *Photochemistry of* 46

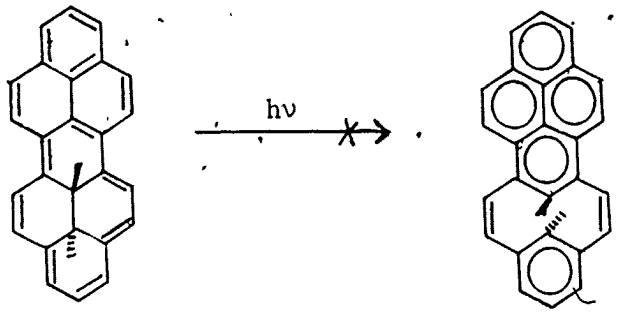
The UV spectra of 45, 46, 46C, 47, 47B and nitro-compounds 145 and 147 were determined in cyclohexane and the λ_{max} along with the extinction coefficients are given in Table 13. All of them absorb strongly in the visible region of the spectrum. As seen earlier, 15,16-dimethyldihydropyrene 25 can be converted[100] by visible light to its valence tautomer, the metacyclophane-diene 25A, which does not



absorb above 300 nm. This could be followed by ^{1}Hmr as the ^{1}Hmr resonance of 25A does not overlap with that of 25. With this in view, a solution of 46 in cyclohexane was irradiated using a Mardi Gras Movie light (General Electric, model MG, 650 Watts) lamp. The UV spectrum of the sample before and after irradiation showed no change. Therefore, it appears that 46 is more favored than 46A, the energy required to

Table 13. UV, $\lambda_{max}^{cyclohexane}$ (ε) of some benzannelated systems and some nitroderivatives.

Compound	$\lambda_{max(m\mu)}$ (ε)
trans- 45	232 (12,615), 260 (5,796), 301 (5,796), 376 (31,879), 409 (10,910), 484 (3,068), and 514 (2,386)
trans- 46	254 (19,580), 272 (99,700), 306 (10,680), 396 (53,408), 416 (202,920), 446 (29,104), 465 (23,410) and 495 (26,344)
cis- 46C	263 (5,461), 276 (4,854), 310 (2,832), 322 (3,155), 368 (sh, 3,317), 386 (9,142), 407 (30,534), 432 (8,090), 437 (9,102), 468 (4,975) and 494 (3,326)
trans- 47	226 (26,643), 264 (13,956), 296 (11,419), 410 (69,147), 427 (96,806), 505 (5,075), 535 (6,724) and 575 (5,075)
cis- 47B	252 (12,992), 262 (12,992), 283 (9,338), 295 (10,150), 335 (6,699), 352 (10,556), 403 (35,728), 466 (7,308), 473 (7,511), 487 (6009) and 520 (5,481)
trans- 147	254 (10,776), 298 (6,265), 373 (7,769), 442 (48,019), 514 (9,524) and 557 (9,674)
trans- 145	254 (6,874), 315 (5,156), 428 (30,361), 440 (32,939), 470 (12,316), 508 (7,734), 571 (3,720) and 774 (1145)



46 46A

disrupt the benzene rings in 46A being more than offset by the relief of strain energy that is present in the cyclophane-diene 46A.

4.2.7 *Discussion*

The shielding effect of the benzene ring on the methyl group that is positioned above its π-electron cloud is seen clearly in the ^{1}Hmr spectra of the thiacyclophanes. The protons of the $-CH_3$ group in the *anti*-isomer appear in the region δ 1.55- 0.76 whereas those for the *syn*-isomer appear around δ ∿ 2.5, the normal region for the methyl group of toluene (see Table 14). This is further confirmed from the ^{13}Cmr spectra where for the *anti*-isomer the internal methyl carbons appear around 15- 16 ppm whereas for the *syn*-isomer they are seen around 18 ppm. This trend is also seen when one compares the chemical shifts for the $-CH_2-S-CH_2$ bridge of the *anti*- and *syn*- dithiacyclophanes (see Table 15).

Table 14. ^{1}Hmr (δ) values for some dithiacyclophanes

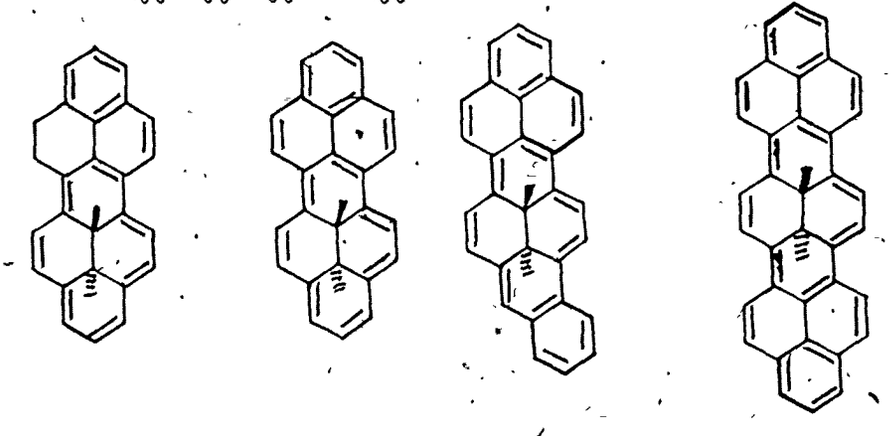
Compound	Internal $-CH_3$	$-CH_2-CH_2-$	$-CH_2-S-CH_2$
anti- 72	1.30		3.68
syn- 72A	2.51		'AB' quartet, 4.00 (A) and 3.80 (B)
anti- 131A	1.38, 1.18	3.4 - 2.6	3.78, 3.67
syn- 131B	2.48, 2.44	3.2 - 2.6	4.01, 'AB' quartet, 4.19 (A) and 3.77 (B)
anti- 135A	1.55, 0.76	4.4 - 2.7	4.4 - 2.7
syn- 135B	2.65, 2.51	3.15 - 2.03	4.8 - 3.53
anti- 139A	1.34	3.4 - 3.25 3.05 - 2.80	3.85 (d) and 3.80 (d)

Table 15. ^{13}C chemical shifts (ppm) of some dithiacyclophanes

Compound	Internal $-CH_3$	$-CH_2-CH_2-$	$-CH_2-S-CH_2-$
anti- 72	15.1		31.9
syn- 72A	17.7		37.3
anti- 131A	15.7, 15.0	28.0, 25.8	32.4, 28.4
syn- 131B	18.5, 16.8	27.9, 25.5	31.1, 24.9
anti- 135A	16.3, 15.4	28.0, 26.4, 26.0	32.4, 28.6
syn- 135B	18.8, 18.0	35.9, 31.6, 31.0, 28.0, 25.9, 25.2	
anti- 139A	16.0	28.7	26.4

The difference in diatropicity of the annelated systems synthesized is shown in Fig. 6. The chemical shift of the internal methyl protons of 46 is very close to that of the internal methyl protons of 15,16-dimethyldihydropyrene 25 (δ - 4.25). Addition of one ring as in 47 reduces not only the shielding of the internal methyl protons but also those of the internal methyl carbons and the bridge carbons which carry the methyl groups. When we go to a much more annelated system like 48, the shielding effect becomes pronounced once more as seen in the ^{1}Hmr spectrum.

Fig. 6 Calculated and determined chemical shifts (δ) for *trans*- 45, 46, 47 and 48.



45 46 47 48

δ_{CH_3}

	45	46	47	48
Calculated	- 2.75	- 3.97	- 1.73	- 2.99
Found	- 2.78	- 4.19 - 4.28	- 1.35 - 1.41	- 3.20

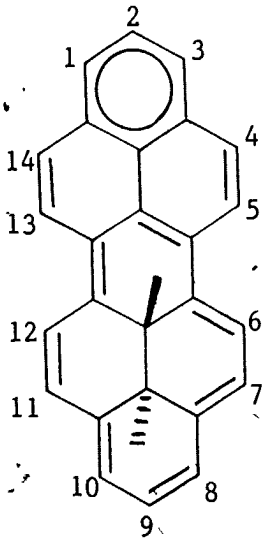
Table 16. Chemical shift (δ) of the internal $-\underline{C}H_3$ and the internal bridge carrying the methyl groups from the ^{13}Cmr of several dimethyldihydropyrenes.

Compound	Internal methyl	Internal bridge
15,16-dimethyldihydropyrene 25	14.0	30.0
monobenz-40	17.0, 17.7	35.5, 36.0
monobenz-43	16.8	35.2
dibenz-41	19.2	39.5
dibenz-42	15.9	32.8
trans -45	16.0, 16.3	29.9, 30.1
trans- 46	14.3	30.4, 30.6
trans- 47	17.8, 17.6	36.9, 37.2

From the trend detected in Table 16, it would be quite reasonable to suggest that the internal carbons carrying the methyl substituents and the $-\underline{C}H_3$ groups would be both shielded in case of *trans*-48; which could have been confirmed if sufficient quantities of the compound were available subsequent to dehydrogenation of its precursor 142A.

The diatropicity of 46 can be rationalized[67,78] on the basis of the Kekulé structures involved. The annelated system 46 could be conceived as 46 or its Kekulé equivalent 46D among other Kekulé contributors. Whereas 46D is a [22] annulene with the 14b,14c-bond being just a 'minor' perturbation of the annulene system, 46 could be construed either as a [14]annulene system of the familiar dimethyldihydropyrene type with the

C_{4-5} and C_{13-14} linkage being formal double bonds or the delocalization extending over to the benzene ring may result in a [22]annulene with the C_{4-5} (or alternatively C_{13-14}) link being a formal double bond.



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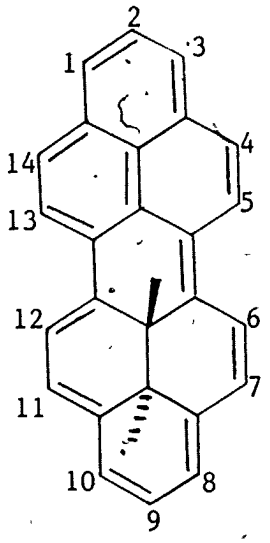
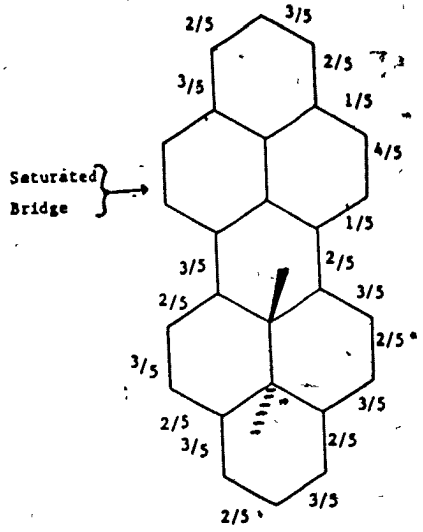


46D

Consideration of all the Kekulé structures (uncharged and non-radicaloid species) and giving equal weighting to all the contributors leads us to designate the bond orders for the molecular perimeter as shown in Fig. 7.



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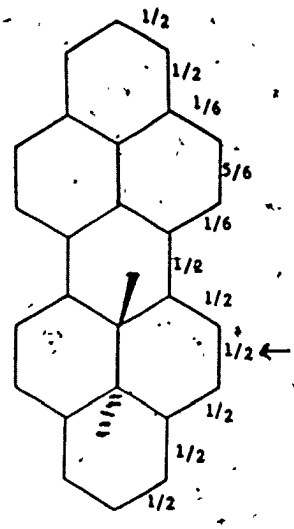

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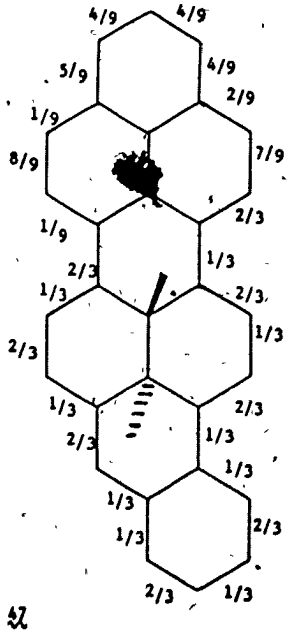

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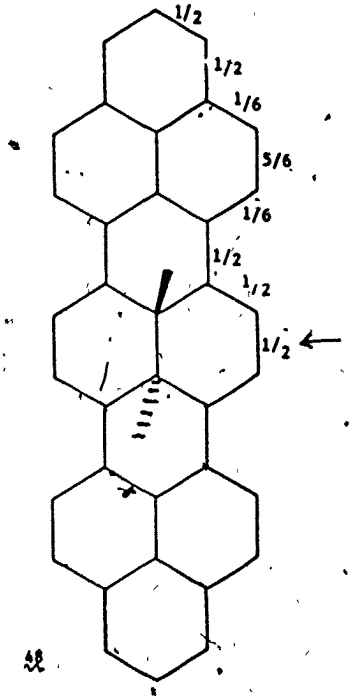

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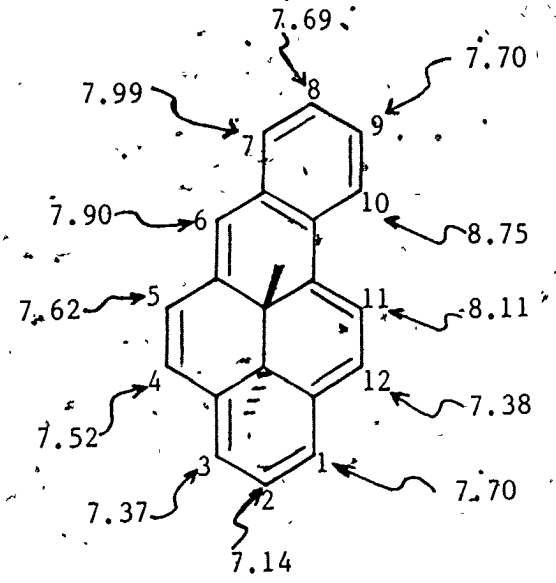
Fig. 7 Kekulé bond orders for 45, 46, 47 and 48.

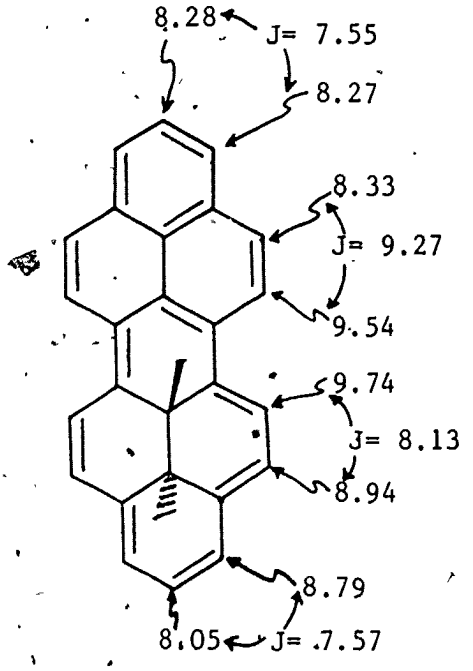
In a similar way the Kekulé bond orders for 45, 47 and 48 are also determined and are shown along with the values obtained for 46. In 46 and 48 the bonds arrowed both have bond orders of 0.5, similar to that in benzene and they should exhibit diatropicity, as is the case. So, 46 behaves more like a [14]annulene system with the π-electrons of the benzannelating ring not being delocalized over the 14π-electron periphery. To get a localized bond i.e a formal double bond, only at C_{4-5} but not at C_{14-15} would be at the expense of effective delocalization in both the 6π- and the 14π-electron systems of the benzene ring and the dimethyldihydropyrene system. This would result in a significant reduction of the diamagnetic ring current. However, the extent of shielding retained by 46 (*cf.* 25) is a reflection of the independant delocalization prevalent in the 6π and the 14π -electron systems, with the C_{4-5} and the C_{13-14} linkages being highly localized bonds.

From Fig. 6, we find that the predicted chemical shifts (calculated chemical shifts) agree reasonably well with the chemical shifts experimentally determined and provide considerable support for the original hypotheses. We next attempted to see whether we could relate calculated bond orders to the experimentally determined ^{1}Hmr coupling constants. The 250 MHz ^{1}Hmr spectra of 46 (see fig. 9 and 10) and of the corresponding *cis*-isomer 46C (see fig. 11) can be used to determine the coupling constants in each case (see fig. 8 for values).

The assignment for the *trans*-isomer 46 was worked out as follows: Comparing the ^{1}Hmr of 46 with the values obtained for the hydrocarbon 40, the bay protons of 46, H-6, H-12 and H-5, H-13 appear as doublets at



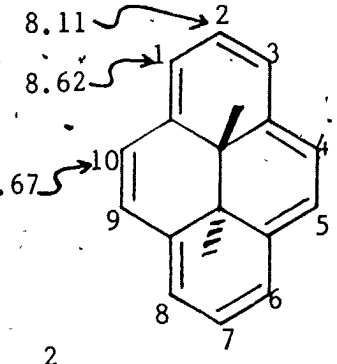
trans-40 (Int. $-CH_3$ at -1.60)

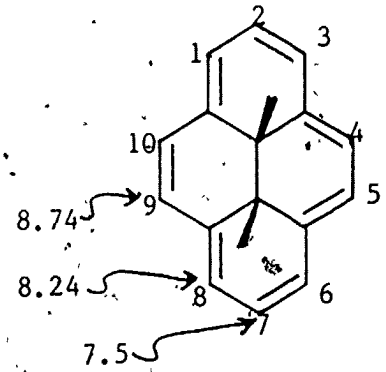


trans-46 (Int. $-CH_3$ at -4.14, -4.24)

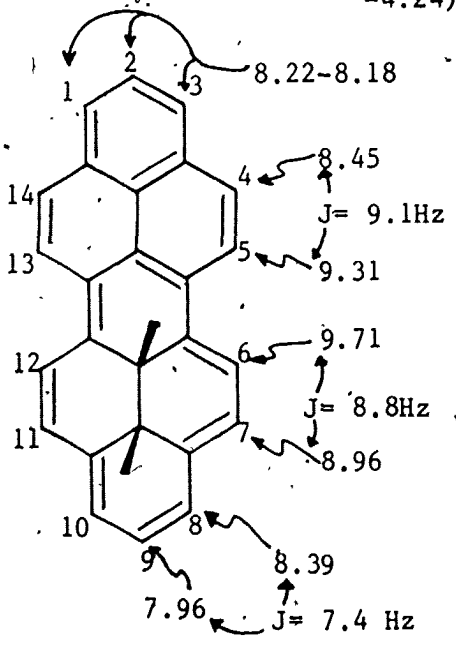
trans-25

(Int. -Me at -4.25)





cis-27 (Int. $-CH_3$ at - 2.06)



cis- 46C (Int.-CH_3 at -1.85, -1.24)

Fig. 8 Chemical shift assignment of *trans*-46 and *cis*-46C

δ 9.74 (J = 8.1 Hz) and 9.54 (J = 9.3 Hz) respectively, the H-6 and H-12 being more deshielded because of the 'phenanthrene type' steric compression in addition to the diamagnetic ring current of the [14]-annulene system. The doublet at δ 8.94 is readily assigned to H-7 and H-11 because of the coupling constant (J = 8.1 Hz). The protons H-8 and H-10 appear as a doublet at δ 8.79 (J = 7.6 Hz) and comparing of the coupling constants identifies the triplet due to H-9 as being the most shielded of all the aromatic protons of 46 and H-9 appears at δ 8.05. The doublet at δ 8.33 (J = 9.3 Hz) is ascribed to H-4 and H-14 as they are coupled to H-5 and H-13 respectively. This leaves us with the protons H-1, H-2 and H-3, i.e., the protons of the 'benzene' ring, as an 'AB_2' system, the proton H-2 being seen at δ 8.28 whereas H-1 and H-3 appear at δ 8.27. The protons of the internal methyl groups appear as a singlets at δ - 4.14 and - 4.24 in the ^{1}Hmr spectrum of the compound *trans*- 46. In a similar fashion, the assignment for the protons of the *cis*-isomer 46C was done. While the influence of geometry on the magnitude of ring current and hence the extent of shielding as determined by the chemical shifts is evident when one looks at the chemical shifts of the internal methyl protons of *cis*- 46C at δ - 1.85 and - 2.14 (*cf. trans* -46 at δ - 4.14 and -4.24), the effect on the protons lying on the molecular periphery is not so pronounced. This is not unlike the results obtained in the case of *trans*-15,16-dimethyldihydropyrene and *cis*-15,16-dimethyl-dihydropyrene where again one can see the chemical shift of the internal methyl protons of the *cis*-isomer moving downfield by about 2.2 ppm compared to the *trans*-isomer but the outer protons seem less affected.

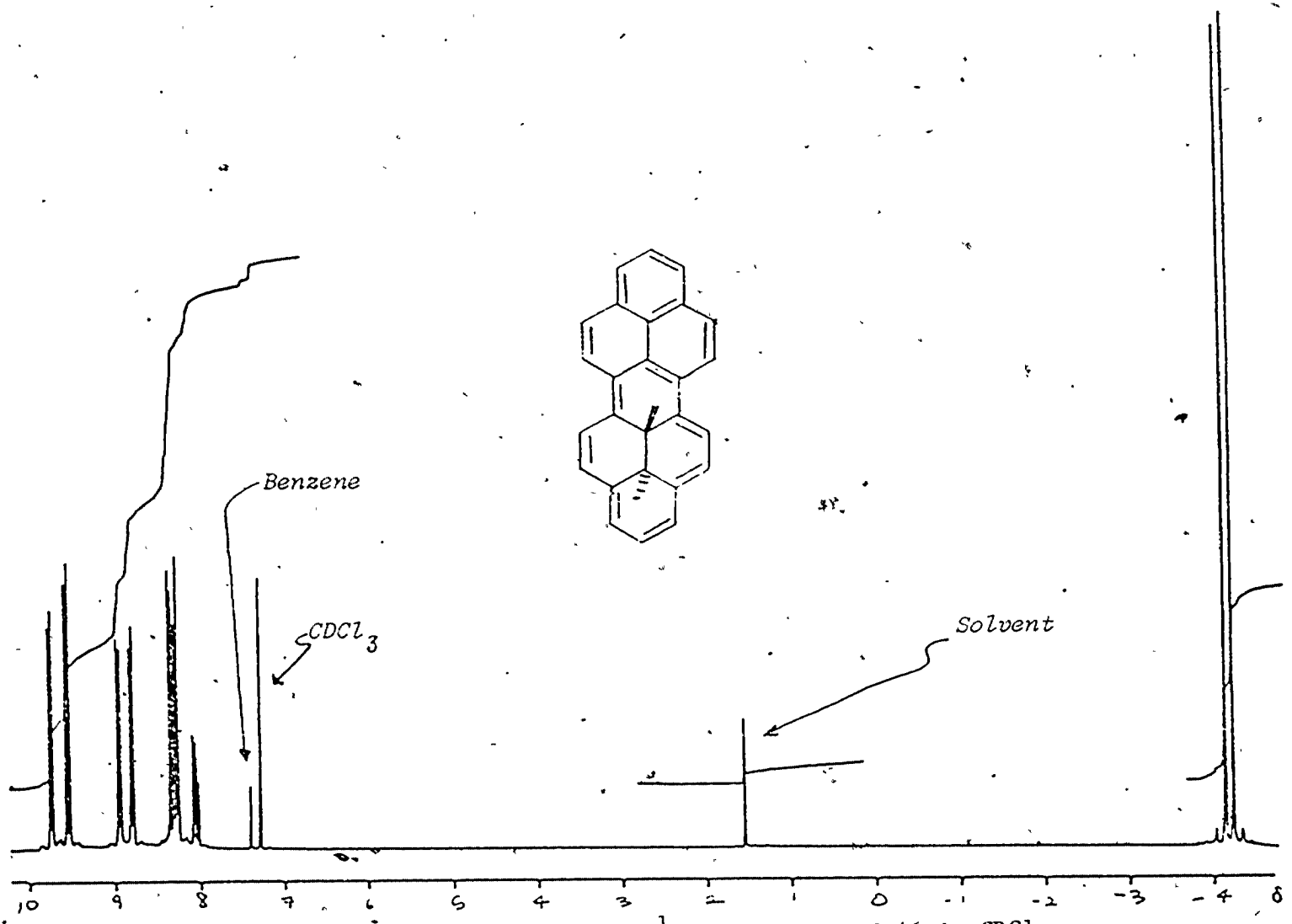


Fig. 9: The 250 MHz (Bruker WM250) ^{1}Hmr spectrum of 46 in $CDCl_3$.

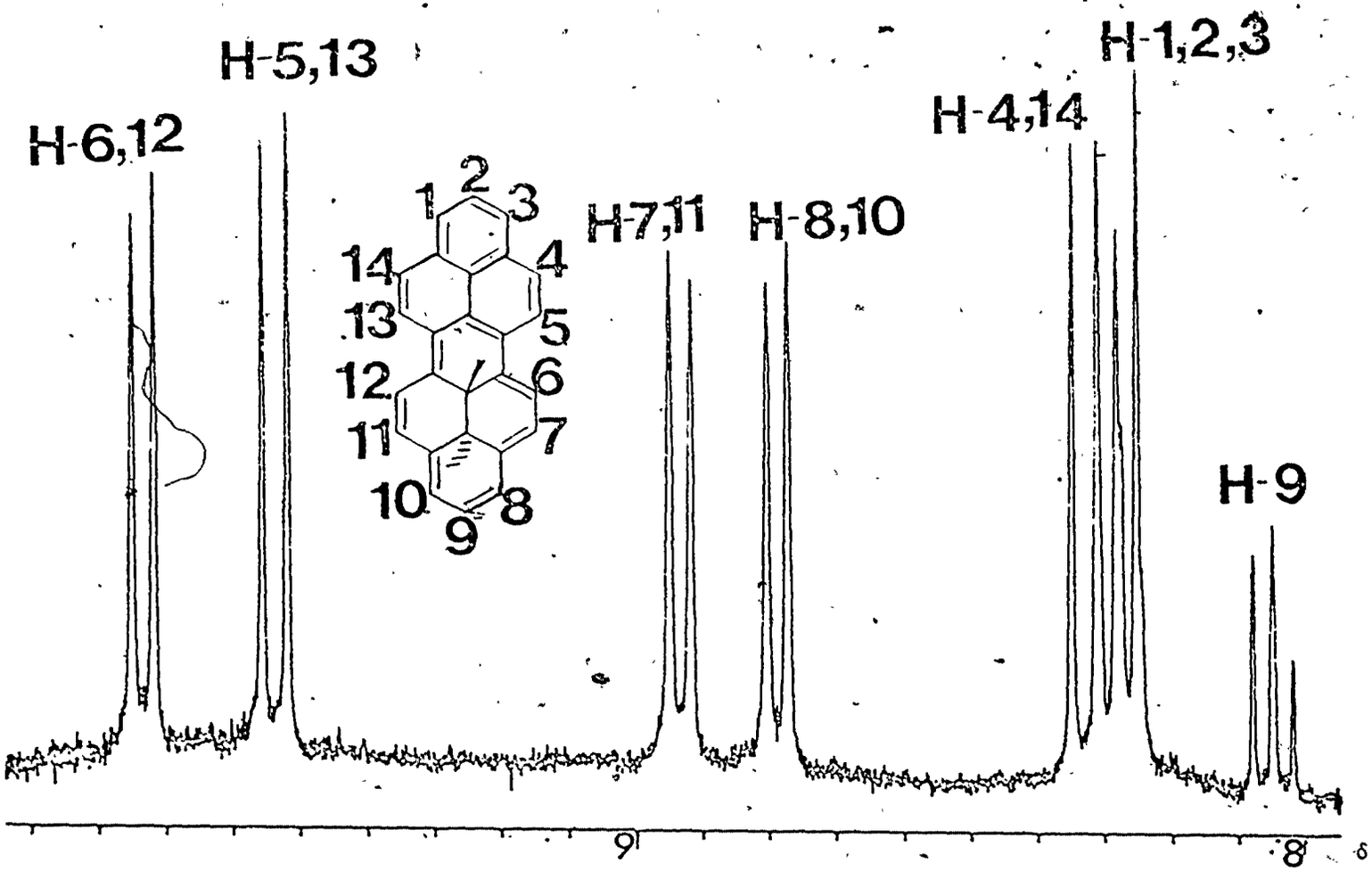


Fig. 10: The 250 MHz (Bruker WM250) ^{1}Hmr spectrum of 46 (aryl protons only) in $CDCl_3$.

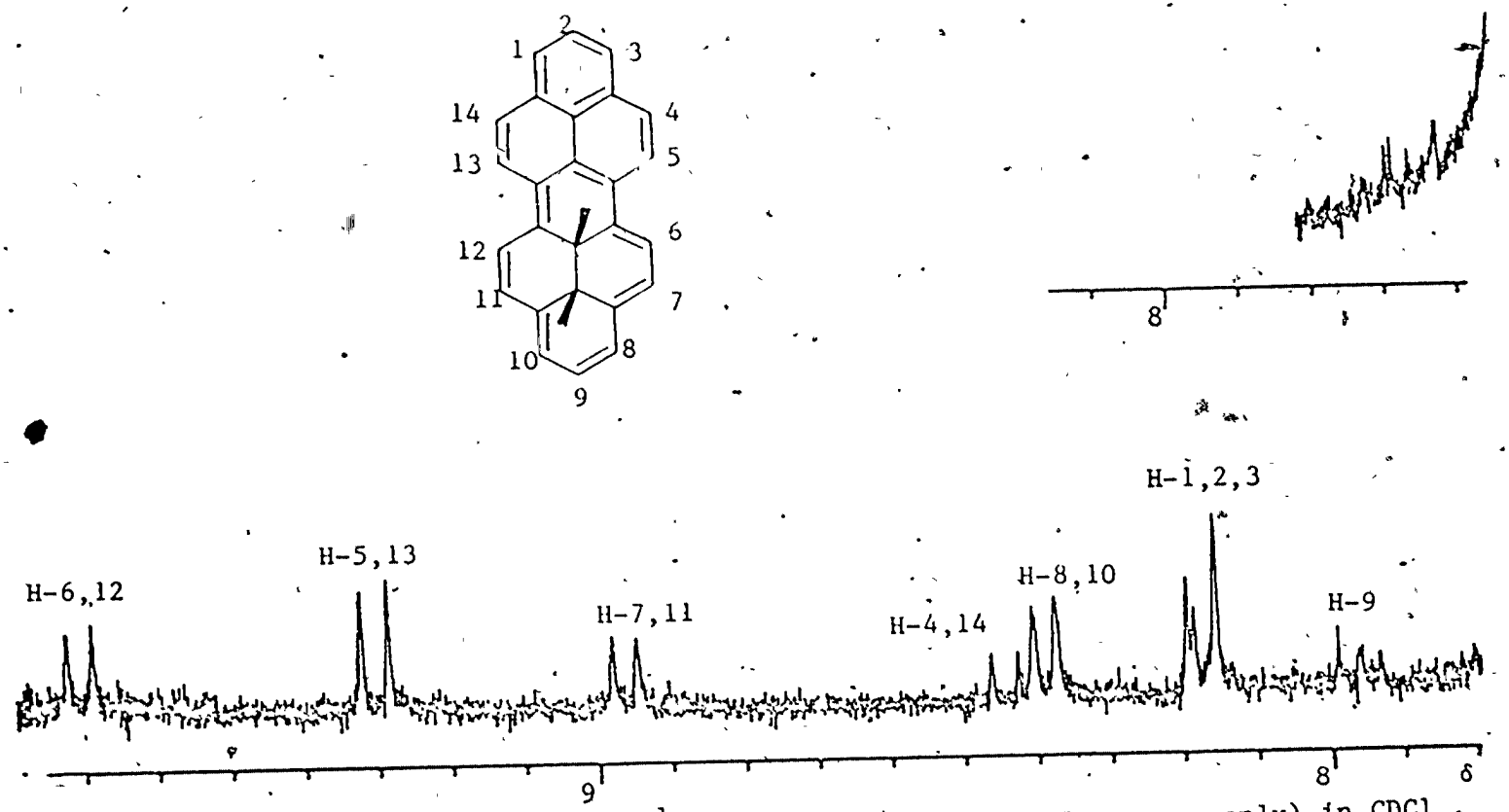


Fig. 11: The 250 MHz (Bruker WM250) ^{1}Hmr spectrum of 46C (aryl protons only) in $CDCl_3$.

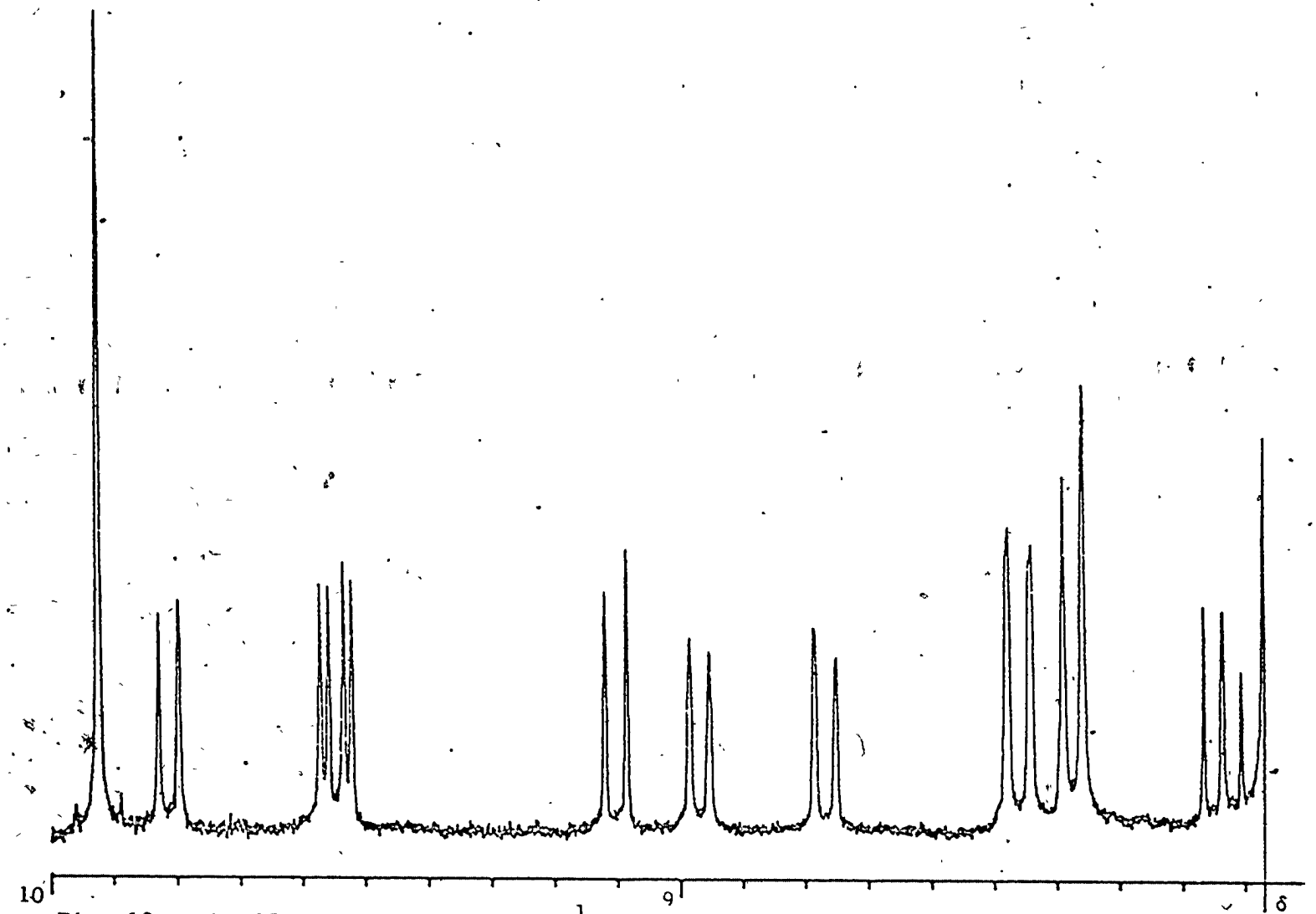


Fig. 12: The 250 MHz (Bruker WM250) ^{1}Hmr spectrum of 147 (aryl protons only) in $CDCl_3$.

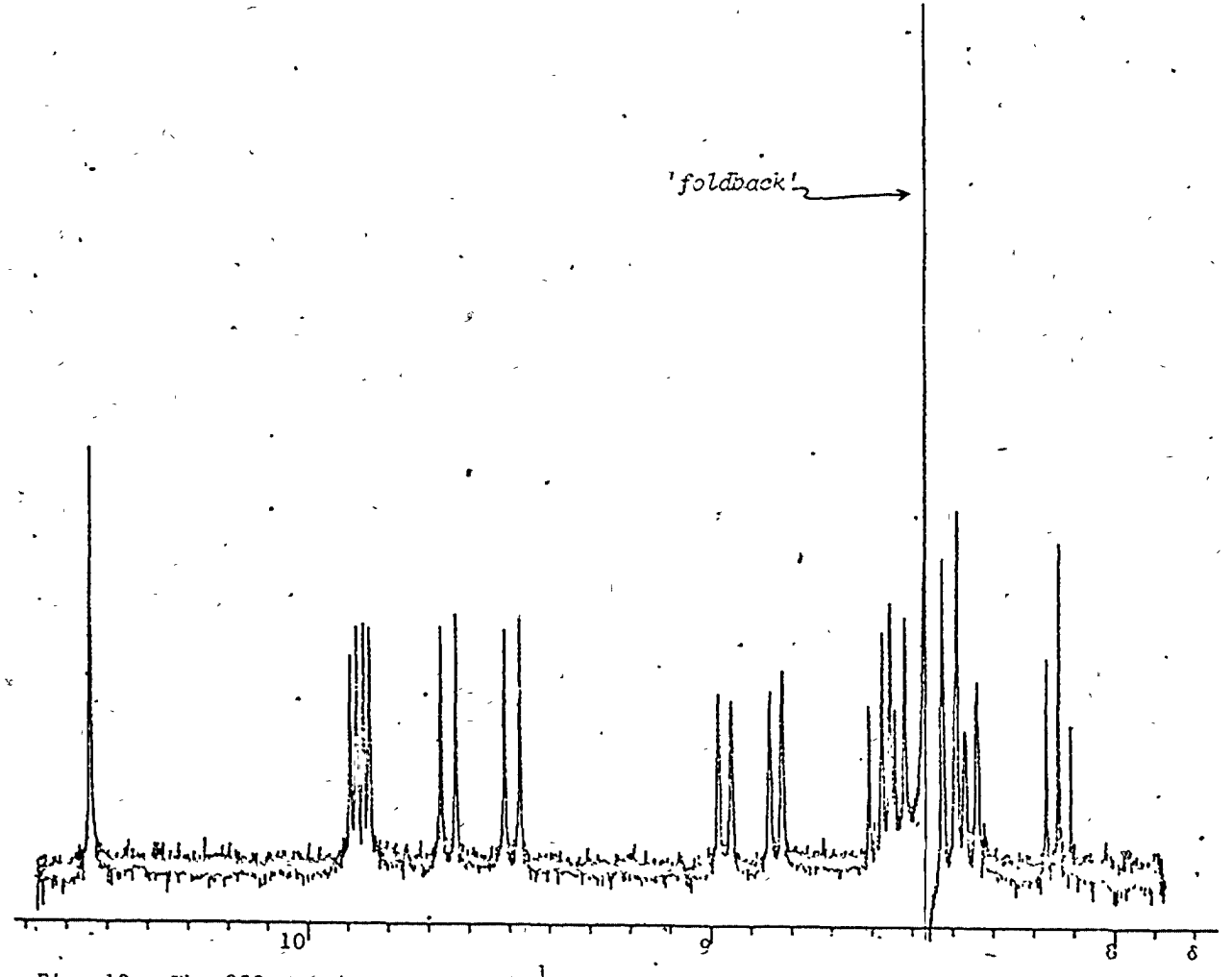


Fig. 13: The 250 MHz (Bruker WM250) ^{1}Hmr spectrum of 145 (aryl protons only) in $CDCl_3$.

As already mentioned in 'Chapter Two', Günther[84] *et al.* have, used the benzene nucleus of benzannulenes as a probe to investigate the π-electronic structure of the annulene nucleus itself. The *alternance parameter 'Q'* is the quotient of the bond order (SCF) i.e., $Q = P_{23}/P_{34}$. For (4n+2) delocalized systems Q > 1.10 and for (4n) delocalized systems Q < 1.04. The bond order, P, is related to the vicinal H-H coupling constants by the equation[84a] (2) mentioned earlier.

$$P_{\mu,\nu}\ (SCF) = 0.104\ {}^{3}J_{\mu,\nu} - 0.120 \qquad \ldots (2)$$

So, if the coupling constants are known, we could calculate 'Q' value.

Table 17. Calculated[93] bond orders ($P_{\mu,\nu}$), alternance parameters (Q) and coupling constants ${}^{3}J_{\mu,\nu}$ for 46

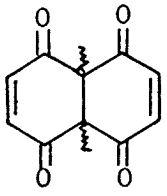
μ,ν	$P_{\mu,\nu}$	Q	${}^{3}J_{\mu,\nu}$(calc., Hz)	${}^{3}J_{\mu,\nu}$ (calc., corrected for steric effect, Hz)	${}^{3}J_{\mu,\nu}$(exp., Hz, ±.07Hz)
9,8	.648	1.025	7.38	7.46[a]	7.57
8,7a	.632	1.022	–	–	–
7a,7	.646	1.027	–	–	–
7,6	.629		7.20	7.58[b]	8.13
2,3	.670	1.111	7.60	7.68[a]	7.55
3,3a	.603	1.272	–	–	–
3a,4	.474	1.673	–	–	–
4,5	.793		8.78	9.16[b]	9.27

a = correction 0.08 Hz, b = correction 0.38 Hz

Alternatively, one could calculate the coupling constants and see how well they match with experimentally determined values. Table 17 represents the calculated bond orders ($P_{\mu,\nu}$), alternance parameter (Q) and the coupling constants $^{3}J_{\mu,\nu}$ for the *trans*-isomer 46. In order to account for the steric compression of the protons 5-6 and 7-8, coupling constants corrections[157] of *ca.* +0.30 Hz (phenanthrene type) and *ca.* +0.08 Hz (naphthalene type) should be added to the calculated values from equation (2) to get the estimated corrected calculated values of the coupling constants for the system under consideration. For correcting the calculated $J_{H(4-5 \text{ or } 6-7)}$, we need to take into account the fact that the 5- and 6- protons are of the phenanthrene type whereas the 4- and 7- protons are of the naphthalene type. Hence we add both the correction factors i.e., 0.30 + 0.08 Hz, to get a total correction factor of 0.38 Hz. The estimated corrected calculated coupling constants and the experimentally determined values seem to be in good agreement and the value of 1.673 ('Q' value) for the 4-5 protons suggests a greater localization or double bond character for the C_{4-5} linkage.

We have seen that it is possible to derive an empirical relationship between the standard bond order deviation (π-SCF bond order values taken into consideration) from the Hückel bond order of 0.642 and the chemical shift of the internal methyl protons, relative to some chosen standard as the model compound. The equation derived earlier (see eqn. 3) indicated a close agreement between the chemical shifts, calculated and those actually observed in the case of a series of benzannelated *trans*-15,16-dimethyldihydropyrenes. The observed chemical

shifts for the *cis*-compounds 46C and 47B are at variance with the calculated chemical shifts for the *trans*-series of compounds. There are not sufficient examples of annelated *cis*-15,16-dimethyldihydropyrenes available, which could be used to derive an empirical relationship between the calculated chemical shifts of the protons of the internal methyl group and those actually observed experimentally. Besides, one is hampered by the absence of the known chemical shift for a standard like 59A where the methyl groups are oriented *cis* to



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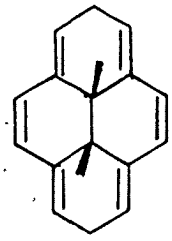


cis-15,16-Dimethyl-2,7,15,16-tetrahydropyrene 59A

each other. In the *trans*-series, where the model *trans*-59 and the protons of the methyl groups appear at δ 0.93, the choice has been justified on the grounds of virtually unchanged geometry of the molecule in the absence of an aromatic ring current, compared to the geometry of the internal framework of 15,16-dimethyldihydropyrene 26 and its annelated derivatives. In the absence of available data about 59A or a substitute like 148 (both the *cis*- and the *trans*- isomers), the chemical shifts for the protons of the methyl group of *trans*-59 were taken for comparison. The effect of steric compression on the chemical shifts of the methyl protons of 59A is assumed to be negligible. As

the standard π-bond order (SCF) deviations for the molecular periphery of 45, 46, 47 and 48 are already known, it would be relatively simple to calculate the chemical shifts of the internal methyl protons of the annelated *cis*- isomers. However, as *cis*-dimethyldihydropyrene is the only known *cis*-compound for which the chemical shift values of the internal methyl protons are available, it becomes necessary to derive an empirical relation using the experimentally determined chemical shifts of the internal methyl protons of *cis*-45B, 46C and 47B.

Table 18. Average standard π-SCF bond order deviation ($x10^3$) Δr and the calculated Δδ for *cis*- 27, 45B, 46C & 47B

Compound	Δr	δ		Δδ	Δδ
		Found	Average	Found	Calc.,
cis- 27	5.143	- 2.06	- 2.06	3.03	3.17
cis- 45B	65.692	- 0.99 - 1.04	- 1.01	1.98	1.92
cis- 46C	21.667	- 1.85 - 2.14	- 2.00	2.97	2.83
cis- 47B	103.091	- 0.10 - 0.14	- 0.12	1.09	1.15

Table 18 indicates the average standard π-SCF bond order deviations Δr (as indicated in 'Chapter Two') along with the observed chemical shifts δ for the internal methyl protons and Δδ where

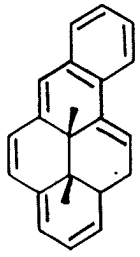
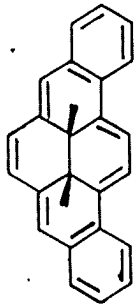
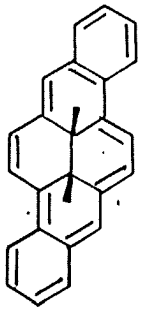
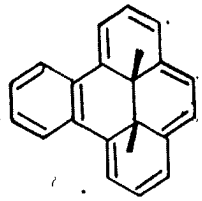
$$\Delta\delta = \delta_{CH_3}(59) - \delta_{CH_3}(\text{annulene})$$
$$= 0.97 - \delta_{CH_3}(\text{annulene})$$

and $\Delta\delta$ represents the shielding of the internal methyl protons of the annulene from those of the unconjugated model 59. This deviation Δr was plotted against $\Delta\delta$(found). A least squares fit gave the equation

$$\Delta\delta = 3.2757 - 0.02062\ \Delta r \quad \ldots\ (5)$$

with a correlation coefficient of $\rho = 0.9908$. The chemical shifts for a series of benzannelated 15,16-dimethyldihydropyrenes can now be calculated using the equation (5) and the results for some of them are shown below in Table 19.

Table 19. Predicted $\Delta\delta$ for some benzannelated *cis*-dimethyldihydropyrenes

	Δr	$\Delta\delta_{calc.}$	$\delta_{calc.}$
40A 	98.385	1.25	- 0.28
41A 	167.417	- 0.18	1.15
42A 	48.667	2.27	- 1.30
43A 	100.231	1.21	- 0.24

4.2.8 *Conclusion*

We have shown the feasibility of synthesizing highly annelated dimethyldihydropyrene systems. It was also seen that benzannulene 46 is diatropic and stable enough to undergo an electrophilic aromatic substitution reaction. We have successfully synthesized the first examples of annelated *cis*-dimethyldihydropyrenes and shown them to be diatropic.

A simple linear relationship between the degree of bond localization in a series of benzannulenes and the strength of the ring current as measured by the chemical shifts has been established and its validity confirmed for a series of *trans*-compounds that were made. The results obtained from the *cis*-series have been used to derive an analogous relationship between the degree of bond localization and the strength of the ring current as measured by the chemical shifts of the internal methyl protons for a series of *cis*-systems and confirmation of the validity of this relationship in the *cis*-series awaits the actual synthesis of these compounds.

EXPERIMENTAL

All melting points were determined on a Kofler hot stage and are uncorrected. The ^{1}Hmr spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin-Elmer R12A (60 MHz), R12B (60 MHz) or R32 (90 MHz) spectrometer and are reported in ppm downfield from tetramethylsilane as internal standard. The variable-temperature ^{1}Hmr studies were carried out on a R32 (90 MHz) spectrometer, using $CDCl_3$, CD_2Cl_2, or $CDCl_3$:CD_2Cl_2 (1:1) as solvent for variable temperature (-100 to + 60 °C) studies. ^{13}Cmr spectra were determined in $CDCl_3$ on a Nicolet TT-14 Fourier Transform spectrometer operating at 15.1 MHz or on a Bruker WM-250 operating at 62.9 MHz. U.v spectra were recorded on a Cary-17 spectrophotometer or a Beckmann DU-8 spectrophotometer. The ir spectra were recorded on a Pye-Unicam SP 1000 or on a Perkin-Elmer 283 infrared spectrometer [medium (m) and strong (s) bands are given; weak (w) bands are given only to indicate specific functional groups]. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E or Finnigan 3300 mass spectrometer at 70 eV using electron impact (EI) or chemical ionization (CI) [M^+ = molecular ion in mass spectra]. Where mass spectra of bromides are given, the correct isotope patterns were always found, but only the most intense peak of each multiplet is recorded. Microanalyses were performed by this department or Canadian Microanalytical Service Ltd. (Vancouver, B.C.). All evaporations were carried out under reduced pressure on a rotary evaporator at *ca.* 40 °C. All organic layers were washed with water (unless otherwise stated) and dried over anhydrous sodium sulfate or magnesium sulfate. A Varian Model 5000 liquid chromatograph was employed for semi-preparative work. All

column chromatography was done by preadsorption of the material on silica gel (unless otherwise stated) and then chromatographed over a column of silica gel (Davison Chemical, 60 - 200 mesh size).

1. *2,4-Dibromo-1,3,5-trimethylbenzene* 84.

Bromine (680 g, 218 mL, 4.25 mol) was added dropwise over 4 h to a mechanically stirred mixture of mesitylene 83 (250 g, 290 mL, 2.08 mol), iron powder (7.5 g) and iodine crystals (15 mg) in chloroform (300 mL) in a flask equipped with a drying tube. At the end of addition, the reaction mixture was stirred for an additional hour. The contents of the flask were filtered over Celite which was then washed with chloroform (300 mL). The filtrate was successively washed with water, aqueous sodium bisulfite, aqueous sodium thiosulfate, aqueous sodium bicarbonate and finally water. The organic layer was dried and concentrated to yield a reddish-green product. This was subjected to fractional distillation under reduced pressure (0.2 torr Hg) to give 84 (506 g, 87%) as a colorless solid. A sample was recrystallized from ethanol to give colorless crystals, mp 62-64 °C [lit.[115] mp 64 °C]; ^{1}Hmr, δ, (90 MHz); 6.98 (s, 1H, Ar-H), 2.60 (s, 3H, Ar-CH$_3$(a)) and 2.31 (s, 6H, Ar-CH$_3$(b)); ir (KBr), 2960 (w), 2920 (w), 1450 (m), 1435 (m), 1394 (w), 1376 (m), 1215 (w), 1045 (m), 1030 (m), 960 (s), 850 (m), 692 (w), 629 (s) and 518 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 278 (M^+, $C_9H_{10}Br_2$, 100, correct isotope pattern), 199 (52), 197 (55), 118 (19), 117 (25) and 115 (25); ^{13}Cmr (15.1 MHz), δ, 137.1 (C-3), 136.7 (C-1 and C-5), 129.6 (C-6), 124.7 (C-2 and C-4), 24.9 (CH$_3$(a)) and 23.8 (CH$_3$(b)).

2. *Attempted synthesis of 4,6-Dibromo-5-methylisophthalic acid* 85.

A. Using nitric acid:

A mixture of 2,4-dibromomesitylene 84 (3 g, 10.8 mmol), conc. nitric acid (7.76 g) and water (11 mL) was heated under reflux for 60 h. It was cooled, made alkaline using sodium bicarbonate solution to separate the acidic component from the non-acidic compounds. ^{1}Hmr of the products did not indicate the presence of 85.

B. 'Purple benzene' oxidation:

Potassium permanganate (9.6 g, 61 mmol) and water (100 mL) were stirred vigorously for 15 min and then cooled in a water bath while benzene (60 mL), tetrabutylammonium iodide (1.22 g, 4.68 mmol) and 2,4-dibromomesitylene 84 (2 g, 7.19 mmol) were added. The mixture was stirred for 12 h at ambient temperature and worked-up by the addition of sodium bisulfite, acidification and drying of the organic layer followed by the removal of benzene under reduced pressure. ^{1}Hmr and thin layer chromatography (tlc) of the product showed it to be mainly unreacted starting material.

3. *2,4,6-Trimethylisophthalonitrile* 84A.

Cuprous cyanide (26.1 g) was added to a well stirred solution of 84 (30 g, 0.11 mol) in N-methyl-2-pyrrolidinone (60 mL). This was heated under reflux under nitrogen. Further portions of cuprous cyanide (6.5 g and 6.5 g) were added at the end of 8 h and 16 h and then the mixture was heated for an additional 8 h. The mixture was cooled to 100 °C and poured into a mixture of conc. NH_4OH-water (1:1, 300 mL). This was filtered, washed well with water and dried. The solids were

extracted using dichloromethane (5 x 200 mL) in a blender. The organic layers were combined, washed, dried and concentrated. This was next filtered through a short column of silica gel using dichloromethane as the eluant and gave 2,4,6-trimethylisophthalonitrile 84A (15.2 g, 83%) as pale yellow needles. Recrystallization from ethanol gave pure 84A, mp 144-146 °C [lit.[123] mp 142 °C]; ^{1}Hmr, δ, (90 MHz), 7.12 (s, 1H, Ar-H), 2.69 (s, 3H, Ar-CH_3(a)) and 2.52 (s, 6H, Ar-CH_3(b)); ir (KBr), 2962 (w), 2228 (s, -CN stretch), 1600 (s), 1462 (w), 1458 (w), 1440 (w), 1384 (s), 1305 (w), 1028 (m), 881 (s), 547 (m) and 475 (m) cm^{-1}; ms peaks at m/e (relative intensity) 170 (M^+, $C_{11}H_{10}N_2$, 100), 169 (22) and 155 (91).

4. *Attempted synthesis of 4,6-Bis(bromomethyl)-2-methylisophthalonitrile* 82A.

N-Bromosuccinimide (3.56 g, 20 mmol) was added in four portions 0.5 h apart to a solution of 2,4,6-trimethylisophthalonitrile 84A (1.7 g, 10 mmol) in refluxing carbon tetrachloride (45 mL), followed after each addition by a few mg of benzoyl peroxide. After a total reflux of 3 h, the reaction mixture was cooled and succinimide removed by filtration. The filtrate was washed once with water, dried and concentrated. ^{1}Hmr and tlc of the product indicated it to be a mixture of compounds from which the desired compound 82A could not be isolated in satisfactory yields by recrystallization and/or chromatography.

5. *4,6-Dibromo-5-methylisophthalaldehyde* 94.

A. Attempted oxidation using Ce^{IV}.

A solution of ceric ammonium nitrate (4.38 g, 8 mmol) in acetic acid (50%, 20 mL) was added dropwise at constant temperature with stirring to a refluxing solution of 84 (0.56 g, 2 mmol) in acetic acid

(50%, 10 mL) at such a rate that the reaction mixture became pale yellow. At the end of the reaction, it was nearly colorless. This was heated under reflux overnight, cooled to room temperature, diluted with water (100 mL) and extracted using ether (3 x 50 mL). The organic extracts were combined, washed, dried and concentrated. ^{1}Hmr and tlc indicated that a major proportion of the mixture was unreacted starting material along with some aldehyde.

B. Oxidation with chromic acid:

A mixture of 2,4-dibromo-1,3,5-trimethylbenzene 84 (100 g, 0.360 mol), glacial acetic acid (1200 g, 1144 mL) and acetic anhydride (1224 g, 1132 mL) was stirred at room temperature for 0.5 h. This was then cooled to 0 °C and conc. sulfuric acid (170 mL) was added dropwise over 1 h with stirring, maintaining the temperature below 5 °C. When the mixture had cooled to 0 °C, chromium trioxide (200 g, 2 mol) was added in portions such that the temperature did not rise above 15 °C and mechanical stirring was continued for an additional 15 min after the addition was complete. The contents of the flask were poured into three 4 L beakers two-thirds filled with chipped ice and cold water. It was stirred well and left to stand for 4 h. The solids were separated by suction filtration and washed with cold water until the washings were colorless. The product was suspended in 1 L of 2% aqueous sodium bicarbonate and stirred vigorously for 0.5 h. It was then filtered, washed well with water and allowed to air-dry. This gave about 110 g of a yellow powder.

A mixture of the yellow powder (108 g), ethanol (400 mL), water

(350 mL) and conc. sulfuric acid (30 mL) was heated under reflux, with stirring for 45 min. This was filtered hot and washed well with water till neutral. The product was air-dried and extracted with dichloromethane (6 x200 mL). The organic layer was washed with water, dried and concentrated to give a yellowish product. This was filtered through a silica gel column in dichloromethane and then recrystallized from carbon tetrachloride to give 94 (24.2 g, 22%) as pale yellow needles, mp 172-174 °C; ^{1}Hmr, δ, (90 MHz), 10.43 (s, 2H, Ar-C<u>H</u>O), 8.23 (s, 1H, Ar-<u>H</u>) and 2.74 (s, 3H, Ar-C<u>H</u>$_3$); ir (KBr), 3060 (w), 2880 (w), 1686 (-CO stretch, s), 1565 (s), 1380 (w), 1363 (w), 1275 (m), 1170 (m), 1053 (m), 1015 (w), 998 (m), 990 (m), 942 (w), 902 (w), 720 (w) and 705 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 306 (M^+, $C_9H_6O_2Br_2$, 25), 305 (35), 277 (5), 249 (3), 196 (10), 170 (15), 145 (8), 118 (9), 90 (23) and 89 (100); ^{13}Cmr (15.1 MHz), δ, 190.8 (1-C<u>H</u>O and 3-C<u>H</u>O), 141.0 (C-5), 134.5 (C-1 and C-3), 133.6 (C-4 and C-6), 128.3 (C-2) and 23.4 (5-C<u>H</u>$_3$).

Anal. Calcd. for $C_9H_6O_2Br_2$: C 35.33, H 1.98

Found : C 35.51, H 1.99

6. *2,6-Dibromo-3,5-bis(hydroxymethyl)toluene* 87.

A solution of dialdehyde 94 (62 g, 0.203 mol) in tetrahydrofuran (1900 mL) was added dropwise to a slurry of sodium borohydride (6.3 g, 0.167 mol) in tetrahydrofuran (50 mL) at room temperature. After 20 h, the mixture was cooled in an ice-salt bath and decomposed by the dropwise addition of conc. hydrochloric acid - water (1:1) until the resulting solution was slightly acidic. The aqueous layer was saturated with sodium chloride and extracted with ether (8 x 200 mL). The organic

layers were combined, washed once with water, dried and concentrated to give a pale yellow, sticky product. Benzene (1200 mL) was added to this product in order to remove water using a Dean-Stark trap (reflux was continued for about 2 h). Hot filtration followed by washing the residue with benzene (100 mL) gave the dialcohol 87 (63 g, quant.) as a free-flowing white powder. It was recrystallized from methanol-benzene to give colorless crystals of 87, mp 192-194 °C. No ^{1}Hmr could be obtained because of its near insolubility in most organic solvents; ir (KBr), 3330 (broad, -OH stretch, s), 1575 (w), 1440 (w), 1392 (m), 1378 (w), 1070 (s), 1038 (w), 1022 (w), 1005 (w), 982 (w), 962 (w), 919 (m) and 885 (m) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 310 (M^+, $C_9H_{10}O_2Br_2$, 28), 293 (18), 278 (12), 262 (16), 251 (4), 231 (23) and 91 (100).

Anal. Calcd. for $C_9H_{10}O_2Br_2$: C 34.87, H 3.25

Found : C 34.78, H 3.22

7. *2,6-Dibromo-3,5-bis(bromomethyl)toluene* 82.

The diol 87 (80 g, 0.258 mol) was added to a well stirred mixture of conc. sulfuric acid (7 mL) and hydrobromic acid (48%, 300 mL, 2.598 mol) and the mixture was heated under reflux for 22 h. This was cooled to room temperature and cold water (250 mL) was added and then it was extracted well with benzene (6 x 250 mL). The organic layers were combined, washed well with water, 10% aqueous sodium bicarbonate solution, water till neutral, dried and concentrated to yield the bromide 82 (97.4 g, 87%). A sample was then recrystallized from cyclohexane to give nearly colorless crystals of 82, mp 120-122 °C; ^{1}Hmr, δ,

(90 MHz), 7.42 (s, 1H, Ar-H), 4.56 (s, 4H, $-CH_2Br$) and 2.64 (s, 3H, Ar-CH_3); ir (KBr), 1575 (w), 1440 (m), 1410 (w), 1385 (w), 1305 (w), 1270 (w), 1215 (s), 1040 (m), 978 (s), 890 (w), 882 (w), 850 (w), 725 (m), 680 (w) and 628 (m) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 436 (M^+, $C_9H_8Br_4$, 2, correct isotope pattern), 357 (25), 355 (27), 276 (18), 197 (9), 195 (10), 116 (61) and 115 (100); ^{13}Cmr (15.1 MHz), δ, 140.1 (C-1), 137.0 (C-3 and C-5), 130.3 (C-4), 127.4 (C-2 and C-6), 33.6 (3-CH_2 and 5-CH_2) and 25.2 (1-CH_3).

Anal. Calcd. for $C_9H_8Br_4$: C 24.80, H 1.85

Found : C 25.12, H 1.81

8. *5,7-Dibromo-6-methyl-2,11-dithia*[3,3]*metacyclophane* 78.

A solution of the bromide 82 (21.8 g, 0.050 mol) and m-xylylene dithiol[85a] 81 (8.5 g, 0.050 mol) in deoxygenated benzene (900 mL) was added dropwise at room temperature over 60-70 h to a well stirred deoxygenated solution of potassium hydroxide [prepared by dissolving KOH (85%, 8.0 g, 0.121 mol) in water (80 mL) and adding ethanol (1900 mL)]. When the addition was complete, the solution was stirred for an additional 2 h. The solvent was removed under reduced pressure and water (400 mL) was added to the residue. It was acidified and extracted with dichloromethane (4 x 250 mL). The organic layers were combined, washed well with water, aqueous sodium bicarbonate and water till neutral. It was dried and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant. Recrystallization from cyclohexane gave 78 (16.65 g, 75%), mp172-173 °C; ^{1}Hmr, δ, (90 MHz), 7.28 (broad s, 1H, H-18), 7.0-6.9 (A_2B multiplet, 3H, Ar-H), 6.62 (s,

1H, H-9), 3.76 and 3.73 (s, each 4H, $-CH_2S$) and 2.45 (s, 3H, Ar-$\underline{CH}_3$); ir (KBr), 1420 (m), 1222(m), 1083 (w), 1048 (m), 1038 (m), 975 (m), 945 (w), 895 (m), 875 (w), 808 (w), 800 (s), 750 (w), 732 (w), 720(s), 708 (m), 698 (s) and 660 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 444 (M^+, $C_{17}H_{16}S_2Br_2$, 100), 365 (63) and 277 (29); ^{13}Cmr (15.1 MHz), δ, 137.2 (C-4, C-6 and C-8), 135.3 (C-13 and C-17), 131.9 and 131.1 (C-9 and C-18), 128.3 (C-15), 127.3 (C-14 and C-16), 124.8 (C-5 and C-7), 38.6 and 38.2 (C-1, C-12 and C-3, C-10) and 24.6 (6-$\underline{CH}_3$).

Anal. Calcd. for $C_{17}H_{16}S_2Br_2$: C 45.96, H 3.63

Found : C 46.36, H 3.57

9. *Wittig rearrangement of dithiacyclophane* 78 *to* 100.

A solution of lithium diisopropylamide [prepared from n-BuLi (6.76 mmol) in hexane (4 mL) and diisopropylamine (0.95 mL, 6.76 mmol)] in dry THF (20 mL) was added dropwise over 10 min to a solution of the dithiacyclophane 78 (1 g, 2.25 mmol) under N_2 in dry THF (20 mL) at 20-21 °C. The initially colorless solution turned dark brown. After stirring for 10 min, methyl iodide (1.92 g, 13.55 mmol) was added gradually using a syringe and stirred for 10 min. Water, dil. HCl and dichloromethane (30 mL) were then added. The layers were separated and the aqueous layer was extracted with dichloromethane (4 x 100 mL). The organic extracts were combined, washed with water, dried and concentrated. It was chromatographed over silica gel and eluted with dichlorbomethane-pentane (3:7) to yield 100 (0.6 g, 56%) as a yellow product, mp of the mixture of stereoisomers 80-109 °C: ^{1}Hmr indicated it to be a mixture of isomers, δ, (60 MHz), 7.6-6.4 (m, aromatic H's), 5.4-4.3 (m, internal H's and -$\underline{CH}$S), 4.0-2.0 (m, $-CH_2$), 2.68 (s, Ar-$\underline{CH}_3$),

and 1.88, 1.85 (s, $-SCH_3$).

Note: When the reaction was done using 20 g of the dithiacyclophane 78 it was found advisable to add lithium diisopropylamide to the solution of the dithiacyclophane heated under reflux over a period of 45 min, continue reflux for 0.5 h, cool it to room temperature and quench the dianion with methyl iodide. Usual work-up followed by chromatography gave the Wittig rearrangement product 100 (16.47 g, 77%) as a mixture of stereoisomers as indicated by ^{1}Hmr; ms peaks (EI) at m/e (relative intensity) 472 (24), 425 (10) and 377 (100).

10. *Stevens rearrangement of dithiacyclophane* 78 *to* 100.

A. Bis(sulfonium)salt 101 of dithiacyclophane 78.

A solution of the dithiacyclophane 78 (1 g, 2.25 mmol) in dichloromethane (30 mL) was added to a stirred suspension of $(MeO)_2CHBF_4$[149] (1.02 g, 80% as oil, 5.04 mmol) in dichloromethane (10 mL) at -30 °C under N_2. After the addition, the mixture was allowed to warm to room temperature and stirred for 4 h. Ethyl acetate (30 mL) was added and stirring continued for 0.5 h. This was filtered, washed with ethyl acetate (30 mL) and dried under vacuum to give the salt 101 (1.26 g, 86%) as a white powder, mp 190-191 °C.

B. Stevens rearrangement of the sulfonium salt 101 to give 100.

The bis(sulfonium)salt 101 (1.26 g, 1.94 mmol) was added to a suspension of anhydrous potassium t-butoxide (0.6 g, 5.35 mmol) in dry THF (30 mL) under N_2 and stirred for 0.5 h. This was acidified using dil. HCl and extracted using dichloromethane (4 x 50 mL). The organic layers were combined, washed, dried and concentrated to yield a yellow

product. This was chromatographed over silica gel using dichloromethane-pentane (3:7) as the eluant to give 100 (0.79 g, 86%) as a mixture of stereoisomers; ^{1}Hmr, δ, (60 MHz), 7.8-6.3 (m, aromatic H's), 5.4-4.3 (m, internal H's and -CHS), 4.3-1.8 (m, $-CH_2$), 2.72 (s, Ar-CH_3), 2.2 and 1.9 (s, SCH_3); ms peaks (EI) at m/e (relative intensity) 472 (M^+, $C_{19}H_{20}S_2Br_2$, 38), 457 (50) and 377 (100).

11. *Oxidation of 100 to the sulfone 106.*

Hydrogen peroxide (30%, 2 mL) was added to a warm solution of the sulfide 100 (0.405 g, 0.86 mmol) in acetic acid (7 mL) and benzene (14 mL). The reaction mixture was refluxed for 5 h, cooled and the layers separated. The aqueous layer was extracted well with dichloromethane. The organic layers were combined, washed with water, dried and concentrated to give the sulfone 106 (0.45 g, 97%) as a yellow powder, a mixture of stereoisomers with mp 120-141 °C; ^{1}Hmr, δ, (60 MHz), 8.0-6.3 (m, aromatic H's), 5.4-2.0 (m, $-CH_2-CH-SO_2$ and internal H's), 3.1, 2.68 and 2.60(s, SO_2-CH_3 and Ar-CH_3).

12. *Sulfoxides 107 of the stereoisomers of 100.*

A solution of bromine (1.34mmol) in dichloromethane was added slowly using a syringe to a solution of 10% aqueous potassium bicarbonate (10 mL) and a mixture of isomers of 100 (0.32 g, 0.67 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 0.5 h. Dichloromethane (100 mL) was added and the organic layer separated, washed with 10% sodium bicarbonate solution, water, dried and concentrated. The residue was filtered through a short column of silica gel using dichloromethane followed by methanol to yield the sulfoxide 107

(0.26 g, 77%) as a buff colored product, mp 89-98 °C; ^{1}Hmr, δ, (60 MHz), only the singlets at 2.94 (Ar-C$\underline{H}_3$) and 2.77, 2.74 (-SOC$\underline{H}_3$) were clearly visible; ms peaks (CI) at m/e (relative intensity) 505 (MH^+, $C_{19}H_{20}O_2S_2Br_2$, 39), 425 (16), 377 (100) and 297 (52).

13. *Synthesis of 1,3-dibromo-2-methylpyrene* 75 *by thermalysis of* 107.

A solution of a mixture of the stereoisomers of 107 (0.62 g, 1.23 mmol) in N-methyl-2-pyrrolidinone (20 mL) was heated at reflux under N_2 for 20 h. The mixture was cooled to room temperature, poured into dil. HCl and then extracted with dichloromethane (3 x 100 mL). The organic layer was washed, dried and concentrated. Chromatography of the residue over silica gel using dichloromethane-pentane (3:7) gave 75 (0.30 g, 65%) as a yellow product. Recrystallization from benzene gave pale yellow crystals of 75, mp 238-240 °C; ^{1}Hmr, δ, (60 MHz), (CD_2Cl_2), 8.51 (d, 2H, J = 9.3 Hz, H-4 and H-10), 8.18 (d, 2H, J = 9.3 Hz, H-5 and H-9), 8.36- 7.97 (m, 3H, H-6, H-7 and H-8) and 3.13 (s, 3H, Ar-C$\underline{H}_3$); ir (KBr), 3040 (w), 1600 (w), 1582 (w), 1575 (w), 1456 (w), 1450 (w), 1415 (m), 1372 (m), 1334 (m), 1129 (m), 1080 (s), 1024 (m), 975 (m), 833 (s), 815 (s), 790 (w), 779 (w), 747 (w) and 695 (s) cm^{-1}; ms peaks (CI) at m/e (relative intensity) 375 (MH^+, $C_{17}H_{10}Br_2$, 100), 296 (65) and 294 (65).

Anal. Calcd. for $C_{17}H_{10}Br_2$: C 54.58, H 2.70

Found : C 54.63, H 2.41

14. *Benzyne-induced Stevens rearrangement of* 78 *to* 108.

A filtered and deoxygenated solution of anthranilic acid (1.54 g, 11.25 mmol) in 1,2-dichloroethane (100 mL) was added dropwise under N_2

over 10 h to a hot solution of 78 (2 g, 4.5 mmol) and iso-amyl nitrite (4.74 g, 40.5 mmol) in $ClCH_2CH_2Cl$ (100 mL). After a 15 min reflux, the reaction mixture was concentrated under reduced pressure and the residue transferred to a silica gel column using dichloromethane-pentane (1:1). Elution with dichloromethane-pentane (1:1) gave 108 (1.96 g, 73%) as a pale yellow semi-solid material; ^{1}Hmr, δ, (90 MHz), 7.7-6.9 (m, Ar-H), 6.1-5.0 (m, -CHS and internal H's), 4.7-2.0 (m, $-CH_2$) and 2.62 (s, $Ar-CH_3$); ms peaks (CI) at m/e (relative intensity) 597 (MH^+, $C_{29}H_{24}S_2Br_2$, 8) and 393 (100).

15. *Oxidation of Benzyne-induced Stevens rearrangement product* 108 *to its sulfone* 109.

Hydrogen peroxide (30%, 60 mL) was added to a warm solution of 108 in acetic acid (30 mL) and benzene (60 mL). The reaction mixture was refluxed for 5 h. The product was transferred to a separatory funnel and the layers separated. The aqueous layer was neutralized using sodium bicarbonate solution and extracted using benzene (3 x 100 mL). The organic extracts were combined, washed, dried and then concentrated. This was then filtered through a silica gel column using benzene-dichloromethane (1:1) as the eluant to yield the sulfone 109 (1.84 g, 90%) as a yellow solid. Recrystallization from benzene gave almost colorless crystals, mp 308-311 °C; ir (KBr), 1325 ($-SO_2$ stretch; s), 1292 (m), 1160 ($-SO_2$, s), 1145 (m), 1092 (m), 728 (s) and 695 (w) cm^{-1}; ms peaks (CI) at m/e (relative intensity) 661 (MH^+, $C_{29}H_{24}O_4S_2Br_2$, 30), 519 (18) and 379 (100).

16. *Sulfoxides 110 of the stereoisomers of 108.*

A solution of bromine (6.43 mmol) in dichloromethane was added slowly using a dropping funnel to a 10% aqueous solution of potassium bicarbonate (55 mL) and the mixture of stereoisomers of 108 (1.68 g, 2.81 mmol) in dichloromethane (60 mL) and the mixture was stirred at room temperature for 0.5 h. Dichloromethane (200 mL) was added and the organic layer separated, washed with 10% sodium bicarbonate solution and water, dried and concentrated. The residue was filtered through a column of silica gel using dichloromethane and then then methanol to yield the sulfoxide 110 (1.25 g, 71%); mp 243-246 °C. In the ^{1}Hmr spectrum only the aryl protons at δ 7.8 - 6.9 and the aryl-CH_3 at δ ∿2.6 were clearly visible; ms peaks at m/e (relative intensity) 629 (MH^+, $C_{29}H_{24}O_2S_2Br_2$, 22), 613 (64), 467 (25), 403 (24) and 377 (100).

17. *Attempted preparation of 1,3-bis(hydroxymethyl)-2-methylpyrene 75c.*

n-BuLi (108 mg, 1.69 mmol) in hexane (1 mL) was added with stirring to 75 (147 mg, 0.39 mmol) in dry THF (40 mL) under N_2 at room temperature. After a further 0.5 h, powdered paraformaldehyde (404 mg, 13.48 mmol , previously dried in a vacuum desiccator over P_2O_5) was added and the mixture was stirred for 0.5 h. It was then refluxed for 2 h before being cooled, acidified with aqueous hydrochloric acid and extracted with dichloromethane (3 x 100 mL). This was dried and concentrated to give a dark, reddish-brown semi-solid (121 mg) which could not be identified.

18. *Formation of dinitrile 100A via von Braun reaction.*

Cuprous cyanide (3.3 g, 36.8 mmol) was gradually added to a stirred solution of the bromide 100 (13.1 g, 27.8 mmol) in N-methyl-2-pyrrolidinone (150 mL) and the mixture was heated under reflux. Further additions of cuprous cyanide (2 g, 2 g and 2.6 g) were made at the end of 3, 6 and 8 h and the reaction mixture was refluxed for a total of 24 h. The mixture was cooled to 100 °C and poured into water-NH_4OH (1:1, 800 mL). After stirring for 2 h, the solids were collected by filtration and air-dried. The solids were extracted using dichloromethane (3 x 200 mL) in a blender and the organic layers were combined, washed, dried and concentrated. The residue was chromatographed over silica gel using dichloromethane as an eluant and gave 100A (3.88 g, 38%) as yellow crystals; ^{1}Hmr, δ, (60 MHz), 7.8 - 7.0 (m, aromatic H's), 5.1 - 4.3 (m, -CHS and internal H's), 4.1 - 2.0 (m, $-CH_2-$), 2.87 (s, Ar-CH_3), 2.12 and 1.97 (s, -SCH_3); ms peaks (CI) at m/e (relative intensity) 365 (MH^+, $C_{21}H_{20}N_2S_2$, 100) and 270 (56).

19. *5,7-Dicyano-6-methyl-2,11-dithia*[3,3]*metacyclophane 78A.*

Cuprous cyanide (4 g, 44.7 mmol) was gradually added to a stirred solution of the bromide 78 (2 g, 4.5 mmol) in N-methyl-2-pyrrolidinone (50 mL) and the mixture was heated under reflux. A second portion of cuprous cyanide (3.3 g, 36.8 mmol) was added at the end of 7 h and the mixture was heated for an additional 17 h. The mixture was cooled to about 100 °C and poured into water-NH_4OH (1:1, 400 mL). After the mixture had been stirred with cooling for 1 h, the solids were collected by filtration and air-dried. It was extracted using dichloromethane (5 x 100 mL) in a blender and the organic layers were combined, washed,

dried and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and gave 78A (1.17 g, 77%) as a pale yellow product. Recrystallization from benzene gave nearly colorless crystals, mp 235-237 °C; ^{1}Hmr, δ, (60 MHz), 7.41, 7.34 (bs, 1H each, H-9 and H-18), 6.88 (s, 3H, H-14, H-15 and H-16), 3.96 and 3.86 (s, each 4H, -C$\underline{H}_2$-S-C$\underline{H}_2$-) and 2.53 (s, 3H, Ar-C$\underline{H}_3$); ir (KBr), 2220 (-CN stretch, s), 1592 (m), 1442 (m), 1422 (w), 1400 (w), 1222 (m), 905 (s), 792 (s), 724 (s) and 698 (s) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 336 (M^+, $C_{19}H_{16}N_2S_2$, 100), 321 (5) and 304 (15).

20. *Attempted Wittig rearrangement of dithacyclophane 78A to 100A.*

(Methylation of 78A to 115)

A solution of lithium diisopropylamide [prepared from n-BuLi (17.75 mmol) in hexane (8.1 mL) and diisopropylamine (2.48 mL, 17.75 mmol)] in dry THF (50 mL) was added dropwise over 10 min to a solution of the dithiacyclophane 78A (2.39 g, 7.1 mmol) under N_2 in dry THF (80 mL). After a further 5 minutes of stirring, methyl iodide (3.01 g, 21.2 mmol) was added gradually. Water, aqueous HCl and dichloromethane were then added and the organic layer was washed, dried and concentrated. It was filtered through a short column of silica gel to yield 115 (1.68 g, 65%) as a 4:1 mixture of two isomers, mp 165-193 °C; ^{1}Hmr, δ , (60 MHz), 7.7-6.5 (m, 5H, Ar-H), 4.5 - 4.0 (m, 2H, -CHS), 3.8 (s, 4H, Ar-C$\underline{H}_2$-S), 2.46, 2.43 (s, 3H total, Ar-C$\underline{H}_3$), 1.60 and 1.51 (d, 3H total, J = 7 Hz each, C$\underline{H}_3$-CH-S); ms peaks (EI) at m/e (relative intensity) 364 (M^+, $C_{21}H_{20}N_2S_2$, 24) and 349 (100).

21. *Stevens rearrangement of dithiacyclophane* 78A *to* 100A.

A. Bis(sulfonium) salt 101A of dithiacyclophane 78A.

A solution of the dithiacyclophane 78A (1.09 g, 3.24 mmol) in dichloromethane (25 mL) was added to a stirred suspension of $(MeO)_2CHBF_4$ (1.57 g, 80% as oil, 7.76 mmol) in dichloromethane (15 mL) at -30 °C under N_2. After the addition, the mixture was allowed to warm to room temperature and stirred for an additional 4 h. Ethyl acetate (20 mL) was added and the mixture stirred for an additional hour. It was filtered, washed with ethyl acetate (15 mL) and dried under vacuum to yield the sulfonium salt 101A (1.63 g, 93%) as a nearly colorless powder.

B. Rearrangement of the sulfonium salt 101A to 100A.

The bis(sulfonium)salt 101A (1.63 g, 3.03 mmol) was added to a suspension of potassium t-butoxide (1.02 g, 9.09 mmol) in dry THF under N_2 and stirred for 0.5 h at room temperature. This was acidified using aqueous HCl and extracted using dichloromethane (4 x 75 mL). The organic layers were combined, washed, dried and concentrated. This was chromatographed over silica gel using dichloromethane-pentane (8:2) as the eluant to give 100A (274 mg, 25%) as a pale yellow product; ^{1}Hmr, δ, (60 MHz), 8.4 - 8.1 and 7.6 - 6.9 (aromatic H's), 4.0 - 2.0 ($-CH_2-CH$ and internal H's), 3.0, 2.75 (Ar-CH_3), 2.05 and 1.09 (S-CH_3).

22. *Attempted Hofmann elimination to give* 75A.

A solution of the mixed isomers of 100A from the von Braun reaction of 100 (330 mg, 0.91 mmol) in dichloromethane (20 mL) was added to $(MeO)_2CHBF_4$ (0.44 g, 80% as oil, 2.17 mmol) in dichloromethane (5 mL) stirred at -30 °C under N_2. The deep-red mixture was then stirred for 4 h without further cooling. Ethyl acetate (25 mL) was then added and

stirring continued for 0.5 h. The cream-yellow product was collected by filtration and dried under suction to give the bis(sulfonium)salts 102A (0.424 g, 83%). These salts were suspended in dry THF (25 mL) under N_2 and anhydrous potassium t-butoxide (0.33 g, 2.98 mmol) was added to the solution. This was heated to reflux with stirring under N_2 for 4 h. It was cooled, acidified with aqueous HCl and extracted using dichloromethane (4 x 100 mL). The organic layers were combined, washed, dried and concentrated. ^{1}Hmr of the product did not indicate the presence of any 75A.

23. *Sulfoxides 107A of the stereoisomers of 100A.*

A solution of bromine (1.51 mmol) in dichloromethane was added slowly using a syringe to a 10% aqueous solution of potassium bicarbonate (15 mL) and the mixture of stereoisomers of 100A (275 mg, 0.76 mmol) in dichloromethane (15 mL) and the mixture was stirred at room temperature for 0.5 h. Dichloromethane (50 mL) was added and the organic layer separated, washed with 10% sodium bicarbonate solution and water, dried and concentrated. The residue was filtered through a column of silica gel using dichloromethane and then methanol as eluant to yield the sulfoxide 107A as a mixture of stereoisomers (297 mg, 99%), mp 96-118 °C; ^{1}Hmr, δ, (60 MHz), 7.7 - 7.0 (m, Ar-H), 5.5 - 2.5 (m, -CH, $-CH_2$ and internal H's), 2.85, 2.80 (singlets, $-SOCH_3$), 2.56 and 2.52 (singlets, Ar-CH_3); ir (KBr), 2224 (-CN stretch, m), 1050 (S=O stretch, m) and 775 (w) cm^{-1}.

24. *Attempted thermolysis of* 107A *to* 75A.

A solution of a mixture of the stereoisomers of 107A (276 mg, 0.7 mmol) in N-methyl-2-pyrrolidinone (25 mL) was heated to reflux under N_2 for 24 h. After cooling to room temperature, the mixture was poured into dil.HCl (100 mL) and extracted with benzene (5 x 75 mL). The organic layers were combined, washed, dried and concentrated. Chromatography over silica gel and elution with dichloromethane-pentane (1:1) did not give any 75A.

25. *Attempted reduction of dinitrile* 107A *to dialdehyde* 107B.

A solution of diisobutylaluminum hydride (3.2 g, 22.5 mmol) in hexane (13 mL), was added dropwise with stirring under N_2 to a solution of 107A (3.72 g, 9.39 mmol) in dry benzene (250 mL) at room temperature. After the addition was complete, the solution was stirred for an additional 4 h before being decomposed by the careful addition, with ice-bath cooling when necessary, of methanol (12 mL), methanol-water (1:1, 20 mL) and finally water-conc. HCl (1:1, 20 mL). The aqueous layer was extracted using benzene (5 x 100 mL) and the organic layers were combined, washed with water, dried and concentrated to 1.66 g of a yellow product. ^{1}Hmr, δ, (90 MHz), 7.4 - 7.2 (m, aromatic H's), 4.40, 4.28 (s, internal H's) and 5.2 - 1.9 ($-\underline{CH}_2-$, $-\underline{CH}-$, $S-\underline{CH}_3$ and $Ar-\underline{CH}_3$); ir (KBr), 2220 (-CN stretch, m) cm^{-1}. [Note : ^{1}Hmr did not indicate any aldehydic proton and no absorption due to -C=O stretch could be seen in the ir.]

26. *Reduction of dinitrile* 100A *to dialdehyde* 100B.

A solution of diisobutylaluminum hydride (0.75 g, 5.28 mmol) in hexane (3 mL) was added with stirring under N_2 to a solution of the

dinitrile 100A (0.8 g, 2.2 mmol) in dry benzene (60 mL) at room temperature. After the addition was complete, the solution was allowed to stir at room temperature for 6 h and then it was decomposed by the careful addition, with ice-bath cooling when necessary, of methanol (10 mL), methanol-water (1:1, 20 mL), conc.HCl-water (1:1, 20 mL) and benzene (100 mL). The organic layer was separated, washed, dried and concentrated to give 100B (0.79 g, 97%) as a mixture of stereoisomers; ^{1}Hmr, δ, (60 MHz), 10.72, 10.66 (s, 2H total, Ar-C<u>H</u>O), 7.7 - 7.0 (m, Ar-<u>H</u>), 5.2 - 4.0 (m, -C<u>H</u>-S and internal H's), 3.9 - 2.0 (m, -C<u>H</u>$_2$-), 2.85, 2.78 (singlets, total 3H, Ar-C<u>H</u>$_3$), 2.22 and 1.96 (singlets, -SC<u>H</u>$_3$).

27. *Sodium borohydride reduction of* 100B *to the dialcohol* 100C.

A solution of the dialdehyde 100B (0.79 g, 2.14 mmol) in THF (30 mL) was added dropwise to a slurry of sodium borohydride (0.125 g, 3.3 mmol) in THF 95 mL) with stirring at room temperature. After the mixture had been stirred at room temperature for 3 h, it was cooled to 0 °C and decomposed by the gradual addition of water-conc.HCl (1:1, 30 mL). The aqueous layer was saturated with sodium chloride solution, dried and concentrated to give the dialcohol 100C (0.73 g, 91%); ^{1}Hmr, δ, (60 MHz), 7.8 - 7.0 (m, Ar-<u>H</u>), 4.83 (bs, -C<u>H</u>$_2$-O), 4.6 - 2.0 (-C<u>H</u>,-CH$_3$, -C<u>H</u>$_2$ and internal H's), 2.15 and 1.94 (s,-SC<u>H</u>$_3$).

28. *Oxidation of dithiacyclophane* 78 *to bis(sulfone)* 126.

Hydrogen peroxide (30%,50 mL) was added to a solution of the dithiacyclophane 78 (5 g, 11.26 mmol) in acetic acid (150 mL, dissolved hot and then cooled). This was then heated to reflux and stirred for 18 h. The mixture was cooled, filtered, washed with water, aqueous

sodium bicarbonate and finally water till neutral. The product was dried at 80 °C under vacuum for 6 h to yield the bis(sulfone) 126 (5.28 g, 92%) as a free-flowing shiny white powder, mp 325-327 °C (dec.); ^{1}Hmr, δ, (90 MHz, CF_3COOD), 7.38, 7.24 (s, ∿5H, Ar-H), 4.95, 4.70 (s, ∿4H each, $-CH_2$) and 2.59 (s, ∿3H, $-CH_3$); ir (KBr), 1405 (s), 1315 ($-SO_2$, s), 1295 ($-SO_2$, s), 1230 (w), 1155 ($-SO_2$, s), 1130 (w), 1105 (s), 1035 (m), 975 (m), 910 (m), 884 (w), 848 (m), 815 (w), 694 (s), 535 (w), 495 (m) and 468 (m) cm^{-1}; ms peaks (CI) at m/e (relative intensity) 509 (MH^+, $C_{17}H_{16}O_4S_2Br_2$, 100), 481 (35), 427 (28), 380 (40), 352 (68) and 300 (34).

Anal. Calcd. for $C_{17}H_{16}O_4S_2Br_2$: C 40.17, H 3.17

Found : C 40.14, H 3.06

29. *4,6-Dibromo-5-methyl[2,2]metacyclophane 104 by pyrolysis of bis(sulfone) 126.*

The bis(sulfone) 126 (1 g, 1.97 mmol) in a porcelain boat (9 x 1.5 x 1 cm) was placed in a Pyrex tube sealed at one end (31 cm long and 2.5 cm in diameter). The open end was connected to a cold finger which was attached to a high vacuum system. The entire system was evacuated to 0.05 torr Hg pressure. The tube was slid smoothly into a furnace (15 cm in length and preheated to 650 °C) in such a way that the porcelain boat could be maintained in the hot zone. As soon as the reaction started the colorless product condensed on the ice-water cooled cold finger. The reaction was complete in about 2 min. The entire tube and the cold finger was washed well with dichloromethane and the solvent stripped off. The residue was extracted with hot pentane and the

pentane extract, chromatographed over silica gel column to give the metacyclophane 104 (0.366 g, 49%) as a pale yellow powder. A sample was recrystallized from benzene-ethanol as nearly colorless crystals, mp 115-117 °C; ^{1}Hmr, δ, (90 MHz), 7.4 - 7.0 (m, 3H, Ar-H), 4.41 (bs, 1H, H-16), 4.27 (s, 1H, H-8), 3.8 - 1.7 (m, 8H, $-CH_2-CH_2$) and 2.68 (s, 3H, Ar-CH_3); ^{1}Hmr, δ, (250 MHz), 7.30 -7.20, 7.05 -7.02 (m, 3H, Ar-H), 4.37 (bs, 1H, H-16), 4.24 (s, 1H, H-8), 3.64 - 3.56, 3.05 - 2.97, 2.27 - 2.16, 1.93 - 1.83 (m, total 8H, $-CH_2-CH_2$) and 2.60 (s, 3H, Ar-CH_3); ir (KBr), 1482 (m), 1440 (m), 1430 (w), 1400 (w), 1380 (w), 1333 (w), 1178 (s), 1165 (m), 1078 (w), 1038 (w), 972 (m), 952 (w), 947 (m), 869 (s), 854 (m), 833 (w), 790 (s), 727 (s), 716 (s), 708 (m), 620 (m) and 602 (s) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 380 (M^+, $C_{17}H_{16}Br_2$, 5), 352 (7), 300 (4), 286 (2), 220 (100), 205 (33), 192 (24), 177 (5) and 165 (9); ^{13}Cmr (15.1 MHz), δ, 138.5 (C-5), 137.3, 137.1 (C-3, C-7 and C-11, C-15), 136.1 (C-8 and C-16), 129.4 (C-13, J = 158.5 Hz), 125.7 (C-12 and C-14), 123.8 (C-4 and C-6), 41.8, 38.1 (C-1, C-10, C-2 and C-9, J_{CH_2} = 128.5 and J'_{CH_2} = 130.4) and 25.3 (5-CH_3, J = 128.6 Hz).

Anal. Calcd. for $C_{17}H_{16}Br_2$: C 53.71, H 4.24

Found : C 53.81, H 4.29

30. *1,3-Dibromo-2-methyl-4,5,9,10-tetrahydropyrene* 105.

A solution of bromine (5.43 g, 33.9 mmol) in dry carbon tetrachloride (125 mL) was added to magnetically-stirred mixture of 104 (10 g, 26.31 mmol) and iron powder (0.5 g) in carbon tetrachloride (500 mL) under N_2. The mixture was stirred for 80 h in the dark. It was then filtered and the solids washed with carbon tetrachloride (100 mL). The filtrate was washed with water, aqueous sodium bisulfite, water ,sodium

bicarbonate solution and finally with water. It was dried and concentrated to give an orange-red product. Column chromatography over silica gel using pentane as an eluant gave 1,3-dibromo-2-methyl-4,5,9,10-tetrahydropyrene 105 (9.74 g, 98%) as a pale yellow powder. A sample was recrystallized from cyclohexane as pale yellow crystals, mp 128-130 °C; ^{1}Hmr, δ, (90 MHz), 7.3 - 7.0 (A_2B multiplet, 3H, Ar-H), 3.2 - 2.7 (m, 8H, $-CH_2-CH_2$) and 2.68 (s, 3H, Ar-CH_3); ms peaks (EI) at m/e (relative intensity) 378 (M^+, $C_{17}H_{14}Br_2$, correct 1:2:1 isotope pattern, 31), 298 (8), 218 (100) and 203 (65).

31. *1,3-Dicyano-2-methyl-4,5,9,10-tetrahydropyrene* 105A.

Cuprous cyanide (3 g) was added to a solution of the dibromide 105 (10.35 g, 27.38 mmol) in N-methyl-2-pyrrolidinone (130 mL) and was refluxed under N_2. Further portions of cuprous cyanide (4 g, 4 g and 6.2 g) were added after 4 h, 12 h and 25 h and the reaction mixture was stirred for an additional 3 h. The product was cooled to 100 °C and poured into water-NH_4OH (1:1, 600 mL). After the solution had been stirred for 24 h, the solids were collected by filtration and air-dried. The solids were extracted using dichloromethane (4 x 300 mL) in a blender and the organic layers were combined, washed, dried and concentrated. The residue was chromatographed over silica gel using dichloromethane-pentane (1:1) and gave 105A (3.02 g, 41%) as a pale yellow product. Recrystallization from benzene-ethanol gave 105A as colorless crystals, mp 224-226 °C; ^{1}Hmr, δ, (250 MHz), 7.3 - 7.0 (m, 3H, Ar-H), 3.17, 2.94 (AA'BB' multiplet, 8H, $-CH_2-CH_2$) and 2.78 (s, 3H, Ar-CH_3); ir (KBr), 2230 (-CN stretch, m), 1437 (s), 1413 (w), 1248 (w), 1205 (w), 860 (w), 798 (s), 772 (s) and 741 (w) cm^{-1}; ms peaks (EI) at m/e (relative

intensity) 270 (M^+, $C_{19}H_{14}N_2$, 100) and 255 (23); ^{13}Cmr (62.9 MHz), δ, 144.0 (C-2), 143.2, 134.9, 131.0 (3a, 10a, 5a, 8a, 10b and 10c), 129.3 (C-7), 126.6 (C-6 and C-8), 115.7 (-CN), 112.5 (C-1 and C-3), 27.5 and 27.2 (C-4, C-10, C-5 and C-9) and 20.2 ($-CH_3$).

Anal. Calcd. for $C_{19}H_{14}N_2$: C 84.41, H 5.22, N 10.37

Found : C 84.22, H 5.12, N 10.33

32. *1,3-Diformyl-2-methyl-4,5,9,10-tetrahydropyrene* 105B.

A solution of diisobutylaluminum hydride (11.25 g, 79.2 mmol) in hexane (75 mL) was added dropwise with stirring under a N_2 atmosphere to a solution of 105A (8.47 g, 31.37 mmol) in benzene (250 mL) at room temperature. After the addition was complete, the solution was allowed to stir for an additional 24 h before being decomposed by the careful successive addition, with ice-bath cooling when necessary, of methanol (100 mL), water-conc.HCl (1:1, 200 mL) and benzene (500 mL). The organic layer was separated, washed, dried and concentrated to give 1,3-diformyl-2-methyl-4,5,9,10-tetrahydropyrene 105B (6.93 g, 80%). A sample recrystallized from carbon tetrachloride gave colorless crystals of 105B, mp 147-149 °C; ^{1}Hmr, δ, (90 MHz), 10.72 (s, 2H, Ar-CHO), 7.2 - 7.1 (A_2B multiplet, 3H, Ar-H), 3.4 - 2.8 (m, 8H, $-CH_2-CH_2$) and 2.73 (s, 3H, $Ar-CH_3$); ^{1}Hmr, δ, (250 MHz), 10.69 (s, 2H, Ar-CHO), 7.20 (A_2B multiplet, 1H, J = 7 Hz, H-7), 7.10 (d, 2H, J = 7 Hz, H-6 and H-8), 3.23 - 3.13, 2.93 - 2.78 (m, 8H, $-CH_2-CH_2$) and 2.74 (s, 3H, $Ar-CH_3$); ir (KBr), 3010 (w), 2940 (w), 2895 (w), 2840 (w), 1682 (s), 1548 (m), 1430 (m), 1420 (m), 1298 (m), 1240 (w), 1199 (w), 1065 (w), 875 (w), 858 (w), 825 (w) and 770 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 276 (M^+,

$C_{19}H_{16}O_2$, 75), 247 (43), 229 (25), 219 (100), 215 (45), 205 (36) and 202 (92); ^{13}Cmr (62.9 MHz), δ, 194.2 (-CHO), 141.2 (C-2), 139.5, 135.3, 132.9, 130.9, 126.1 (C-1, C-3, C-3a, C-10a, C-5a, C-8a, C-10b and C-10c), 128.1 (C-7), 125.8 (C-6 and C-8), 27.5, 25.0 (C-4, C-10, C-5 and C-9) and 15.5 ($-CH_3$).

Anal. Calcd. for $C_{19}H_{16}O_2$: C 82.58, H 5.84

Found : C 81.79, H 5.90

33. *1,3-Bis(hydroxymethyl)-2-methyl-4,5,9,10-tetrahydropyrene* 105C.

A solution of the dialdehyde 105B (6.86 g, 24.86 mmol) in THF (200 mL) was added dropwise to a slurry of sodium borohydride (1.88 g, 49.68 mmol) in THF (50 mL) with stirring at room temperature. After the mixture had been stirred at room temperature for 24 h, it was cooled to 0 °C and decomposed by the gradual addition of water-conc.HCl (1:1, 100 mL). The aqueous layer was saturated with sodium chloride and extracted with ether (7 x 200 mL). The organic layers were combined, dried and evaporated to give 1,3-bis(hydroxymethyl)-2-methyl-4,5,9,10-tetrahydropyrene 105C (6.39 g, 92%). Recrystallization from carbon tetrachloride gave 105C as colorless crystals, mp 180-182 °C; ^{1}Hmr, δ, (90 MHz), 7.09 (s, 3H, Ar-H), 4.80 (s, 4H, $-CH_2-O$), 3.1 - 2.7 (m, 8H, $-CH_2-CH_2$), 2.54 (s, 3H, Ar-CH_3) and 1.52 (s, 2H, -OH, exchanged with D_2O); ir (KBr), 3280 (-OH stretch, s), 2920 (s), 1465 (m), 1430 (m), 1025 (s), 990 (s), 765 (s), 752 (w) and 714 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 280 (M^+, $C_{19}H_{20}O_2$, 60), 231 (100), 221 (52) and 202 (32).

Anal. Calcd. for $C_{19}H_{20}O_2$: C 81.39, H 7.19

Found : C 80.86, H 7.39

34. *1,3-Bis(bromomethyl)-2-methyl-4,5,9,10-tetrahydropyrene* 105D.

The dialcohol 105C (6.34 g, 22.64 mmol) was added to a mixture of hydrobromic acid (48%, 300 mL, 2.6 mol) and conc.H_2SO_4 (2 mL) and the mixture was heated under reflux with stirring for 7 h. The reaction mixture was cooled to room temperature, ice-cold water (200 mL) added and then it was extracted with dichloromethane (6 x 200 mL). The organic layers were combined, washed with water, aqueous sodium bicarbonate solution, water till neutral, dried and concentrated to yield the bromide 105D as a yellow product. This gave, on chromatography over silica gel using dichloromethane-pentane (3:7) as the eluant, the desired 1,3-bis-(bromomethyl)-2-methyl-4,5,9,10-tetrahydropyrene 105D (6.79 g, 73.8%). A sample recrystallized from cyclohexane gave nearly colorless crystals, mp 208-210 °C; ^{1}Hmr, δ, (90 MHz), 7.09 (m, 3H, Ar-H), 4.60 (s, 4H, $-CH_2Br$), 2.89 (bs, 8H, $-CH_2-CH_2$) and 2.48 (s, 3H, Ar-CH_3); ir (KBr), 1458 (m), 1203 (s), 799 (w), 763 (s), 663 (w), 560 (m) and 550 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 406 (M^+, $C_{19}H_{18}Br_2$, 42), 327 (100), 325 (100), 245 (36) 231 (34), 216 (52) and 202 (41); ^{13}Cmr (15.1 MHz), δ, 135.9, 135.0, 131.6, 130.1, 129.9 (all quaternary Ar-C); 127.3 (C-7), 125.7 (C-6 and C-8), 29.3, 27.8 (C-4, C-10 and C-5, C-9); 24.7 ($-CH_2Br$) and 15.1 (CH_3-C_2).

Anal. Calcd. for $C_{19}H_{18}Br_2$: C 56.18, H 4.47

Found : C 56.48, H 4.55

35. *4,6-Dicyano-5-methyl[2,2]metacyclophane* 104A.

Cuprous cyanide (5.2 g, 58 mmol) was added gradually to a stirred solution of the bromide 104 (22.8 g, 60 mmol) in N-methyl-2-pyrrolidinone

(100 mL) and the mixture was heated under reflux. Further 5 g additions of cuprous cyanide were done at the end of 4 h, 8 h and 20 h and the mixture was refluxed for an additional 6 h. The product was cooled to 100 °C and poured into a mixture of water-NH_4OH (1:1, 600 mL). After the solution had been stirred for 24 h, the solids were collected by filtration and air-dried. The solids were collected by filtration and air-dried. The solids were extracted using dichloromethane (4 x 200 mL) in a blender and the organic layers were combined, washed, dried and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and gave 104A (14.24 g, 87%) as a pale yellow product. Recrystallization from benzene-ethanol gave 104A as colorless crystals, mp 201-202 °C; ^{1}Hmr, δ, (90 MHz), 7.5 - 7.0 (m, 3H, Ar-H), 4.30 (bs, 1H, H-16), 4.25 (s, 1H, H-8), 3.7 - 3.0 , 2.4 - 1.9 (m, 4H each, $-CH_2-CH_2$) and 2.79 (s, 3H, Ar-CH_3); ^{1}Hmr, δ, (250 MHz), 7.38 (t; 1H, J = 7.5 Hz, H-13), 7.14 (dd, 2H, H-12 and H-14), 4.33 (bs, 1H, H-16), 4.28 (s, 1H, H-8), 3.70 - 3.56, 3.37 - 3.23, 2.34 - 2.06 (m, 8H total, $-CH_2-CH_2$) and 2.83 (s, 3H, Ar-CH_3); ir (KBr), 2220 (-CN stretch, s), 1582 (m), 1480 (s), 1455 (w), 1435 (w), 1410 (w), 1231 (s), 1180 (s), 1170 (s), 1080 (m), 1000 (w), 952 (m), 872 (s), 798 (s), 760 (w), 720 (s) and 710 (w) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 272 (M^+, $C_{19}H_{16}N_2$, 100), 257 (49) and 244 (93); ^{13}Cmr (62.9 MHz), δ, 146.8, 146.3, 137.8 (C-3, C-5, C-7, C-11 and C-15), 135.7, 135.6 (C-8 and C-16), 130.2 (C-13), 126.1 (C-12 and C-14), 115.6 (-CN), 111.3 (C-4 and C-6), 40.3, 39.5 (C-1, C-10, C-2 and C-9) and 20.1 (CH_3-C_5).

Anal. Calcd. for $C_{19}H_{16}N_2$: C 83.79, H 5.92, N 10.29

Found : C 83.59, H 5.90, N 10.22

36. *4,6-Diformyl-5-methyl[2,2]metacyclophane* 104B.

A solution of diisobutylaluminum hydride (19 g, 134 mmol) in hexane (127 mL) was added dropwise with stirring under N_2 to a solution of the dinitrile 104A (14 g, 51.5 mmol) in dry benzene (250 mL) at room temperature. After the addition was complete, the solution was allowed to stir for 5 h before being decomposed by the careful addition, with ice-water bath cooling when necessary, of methanol (40 mL), methanol-water (1:1, 60 mL), water-conc.HCl (140 mL: 80 mL) and benzene (400 mL). The organic layer was separated, washed, dried and concentrated to give 4,6-diformyl-5-methyl[2,2]metacyclophane 104B (12.77 g, 89%). A sample was recrystallized from carbon tetrachloride and gave pale yellow crystals of 104B, mp 128-130 °C; ^{1}Hmr, δ, (90 MHz), 10.70 (s, 2H, Ar-C<u>H</u>O), 7.5 - 7.0 (m, 3H, H-6, H-7 and H-8), 4.32 (s, 2H, H-8 and H-16), 4.1 -3.9, 3.3 - 3.1, 2.4 - 1.6 (m, 8H total, -C<u>H</u>$_2$-C<u>H</u>$_2$) and 2.80 (s, 3H, Ar-C<u>H</u>$_3$); ^{1}Hmr, δ, (250 MHz), 10.71 (s, 2H, Ar-C<u>H</u>O), 7.34 (t, 1H, J = 7.5 Hz, H-13), 7.10 (dd, 2H, H-12 and H-14), 4.35 (bs, 1H, H-16), 4.34 (s, 1H, H-8), 4.09 - 3.96, 3.29 - 3.16, 2.29 - 2.11, 1.92 - 1.77 (m, total 8H, -C<u>H</u>$_2$-C<u>H</u>$_2$) and 2.84 (s, 3H, Ar-C<u>H</u>$_3$); ir (KBr), 1690 (-C=O stretch, s), 1182 (m) and 720 (m) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 278 (M^+, $C_{19}H_{18}O_2$, 100), 249 (20) and 221 (32); ^{13}Cmr (62.9 MHz), δ, 193.0 (-<u>C</u>HO), 144.9, 142.7, 138.7, 138.2, 135.3, 132.1 (C-3, C-4, C-5, C-6, C-7, C-8, C-11, C-15 and C-16), 129.7 (C-13), 125.7 (C-12 and C-14), 40.2, 38.0 (C-1, C-10, and C-9, C-2) and 15.5 (Ar-<u>C</u>H$_3$).

Anal. Calcd. for $C_{19}H_{18}O_2$: C 81.98, H 6.52

Found : C 79.73, H 6.31

37. *4,6-Bis(hydroxymethyl)-5-methyl[2,2]metacyclophane* 104C.

A solution of the dialdehyde 104B (12.63 g, 45.4 mmol) in THF (250 mL) was added dropwise to a stirred slurry of sodium borohydride (3.44 g, 90.86 mmol) in THF (50 mL) at room temperature. After stirring for 4 h, the mixture was cooled to 0 °C and decomposed by the gradual addition of water-conc.HCl (1:1, 100 mL). The aqueous layer was saturated with sodium chloride and extracted with ether (7 x 200 mL). The organic layers were combined, dried and concentrated to give 4,6-bis-(hydroxymethyl)-5-methyl[2,2]metacyclophane 104C (12.48 g, 97%). Recrystallization from carbon tetrachloride gave 104C as colorless crystals, mp 214-216 °C; ^{1}Hmr, δ, (90 MHz), 7.4 - 6.9 (m, ~3H, Ar-H), 4.81 (s, ~4H, -CH$_2$-O), 4.34, 4.23 (s, ~1H each, internal H's, H-8 and H-16) 3.7 - 2.8, 2.5 - 1.5 (m, ~4H each, -CH$_2$-CH$_2$) and 2.55 (s, 3H, Ar-CH$_3$); ir (KBr), 3400 (-OH stretch, s), 1178 (w), 1070 (w), 1000 (m), 988 (s), 950 (w), 788 (w) and 715 (m) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 282 (M^+, $C_{19}H_{22}O_2$, 52) 234 (24), 222 (19) and 221 (100).

Anal: Calcd. for $C_{19}H_{22}O_2$: C 80.81, H 7.86

Found : C 78.33, H 7.86

38. *4,6-Bis(bromomethyl)-5-methyl[2,2]metacyclophane* 104D.

The dialcohol 104C (12.3 g, 43.62 mmol) was added to a mixture of hydrobromic acid (48%, 300 mL, 2.6 mol) and conc.H_2SO_4 and the mixture was heated under reflux with stirring for 9 h. The reaction mixture was cooled to room temperature, ice-cold water (200 mL) added and it was extracted with dichloromethane (7 x 200 mL). The organic layers

were combined, washed with water, aqueous sodium bicarbonate solution, water till neutral, dried and concentrated to yield the bromide 104D as a yellow product. This, on chromatography over silica gel using dichloromethane-pentane (3:7), gave 4,6-bis(bromomethyl)-5-methyl[2,2]-metacyclophane 104D (10.17 g, 57%). A sample recrystallized from cyclohexane gave nearly colorless crystals, mp 191-192 °C; ^{1}Hmr. δ, (90 MHz), 7.4 - 7.0 (m, 3H, Ar-H), 4.65 (s, 4H, -CH_2Br), 4.43 (bs, 1H, H-16), 4.12 (s, 1H, H-8), 3.6 - 3.0, 2.4 - 1.7 (m, 4H each, -CH_2-CH_2) and 2.47 (s, 3H, Ar-CH_3); ir (KBr), 3048 (m), 3010 (m), 2950 (s), 2924 (w), 2850 (w), 1580 (m), 1557 (w), 1482 (m), 1472 (w), 1442 (m), 1430 (s), 1372 (w), 1330 (m), 1268 (w), 1248 (s), 1238 (w), 1209 (s), 1200 (s), 1175 (s), 1162 (w), 1078 (m), 1000 (w), 955 (s), 873 (s), 788 (s), 781 (s), 760 (m), 715 (s), 706 (s), 682 (m), 615 (s), 578 (s), 543 (s), 490 (m) and 465 (w); ms peaks (EI) at m/e (relative intensity) 408 (M^+, $C_{19}H_{20}Br_2$, 53), 329 (100), 327 (98) and 249 (34); ^{13}Cmr (62.9 MHz), δ, 138.6, 138.4, 137.5, 136.5, 136.2, 132.0 (C-3, C-4, C-5, C-6, C-7, C-8, C-11, C-15 and C-16), 129.3 (C-13), 125.6 (C-12 and C-14), 39.3, 38.0 (C-1, C-10, and C-2, C-9), 29.0 (-CH_2Br) and 14.9 (CH_3-C_5).

Anal. Calcd. for $C_{19}H_{20}Br_2$: C 55.90, H 4.94

Found : C 56.45, H 5.20

39. *1,3-Bis(mercaptomethyl)-2-methyl-4,5,9,10-tetrahydropyrene* 105E.

A stirred solution of the bromide 105D (2.1 g, 5.2 mmol) and thiourea (0.98 g, 12.9 mmol) in 95% ethanol (40 mL) was heated under reflux for 3 h. After cooling, about half of the solvent was removed under reduced pressure using a rotary evaporator. Then, after further

cooling in an ice-box, the precipitate of the bis-isothiouronium salt was collected and dried under vacuum to give the salt (2.88 g, quant.) as a white powder.

The salt was then heated under reflux with a deoxygenated solution of potassium hydroxide (15 g, 85%, 0.23 mol) [deoxygenated by bubbling N_2 for 0.5 h] in water (50 mL) under N_2 for 7 h. After ice-bath cooling, conc. H_2SO_4-water (1:1, 60 mL) was added dropwise. The thiol was then extracted using ether (4 x 150 mL). The organic layers were combined, washed with water, saturated sodium bicarbonate solution, water till neutral, dried and concentrated to give the bis-thiol 105E as a yellow product. This was chromatographed over silica gel using initially pentane as the eluant and then dichloromethane-pentane (1:1) to give the bis-thiol 105E (1.6 g, quant.) as a cream colored product. A sample was recrystallized from benzene-hexane mixture to give the thiol 105E, mp 146-148 °C; ^{1}Hmr, δ, (90 MHz), 7.08 (A_2B multiplet, 3H, Ar-H), 3.79 (d, 4H, J = 6.9 Hz, $-CH_2S-$), 2.86 (bs, 8H, $-CH_2-CH_2$), 2.45 (s, 3H, Ar-CH_3) and 1.59 (t, 2H, J = 6.9 Hz, -SH); ^{1}Hmr, δ, (250 MHz), 7.11 (A_2B multiplet, 3H, Ar-H), 3.85 (d, 4H, J = 6.4 Hz, $-CH_2-S$), 2.94, 2.90 (AA'BB' multiplet, 8H, $-CH_2-CH_2$), 2.51 (s, 3H, Ar-CH_3) and 1.64 (t, 2H, J = 6.4 Hz, -SH); ir (KBr), 2970 (w), 2930 (m), 2885 (m), 2830 (w), 2555 (-SH stretch, w), 1465 (w), 1450 (m), 1440 (s), 1245 (m), 1240 (m), 1202 (w), 798 (w), 765 (-C-S stretch, s) and 680 (m) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 312 (M^+, $C_{19}H_{20}S_2$, 100), 271 (29), 247 (26), 246 (34), 245 (98), 232 (20), 231 (62), 230 (34), 216 (31), 215 (29) and 202 (23); ^{13}Cmr (62.9 MHz), δ, 135.4, 135.0, 133.1 (C-1, C-3, C-3a, C-10a, C-5a and C-8a), 133.5, 131.0, 129.9 (C-2, C-10b and C-10c),

127.2 (C-7), 125.8 (C-6 and C-8), 28.5, 25.1 (C-4, C-10, and C-5, C-9), 23.4 ($-\underline{C}H_2-S$) and 15.7 ($\underline{C}H_3-C_2$).

Anal. Calcd. for $C_{19}H_{20}S_2$: C 73.03, H 6.45

Found : C 73.30, H 6.38

40. *Anti- and Syn- dithiacyclophane* 131A *and* 131B.

A solution of the bromide 105D (3 g, 7.39 mmol) and 2,6-bis-(mercaptomethyl) toluene 71[85a] (1.36 g, 7.39 mmol) in deoxygenated benzene (800 mL) was added dropwise with stirring at room temperature over 75 h to a deoxygenated solution of potassium hydroxide [prepared by dissolving potassium hydroxide (85%, 5.1 g, 72.11 mmol) in water (84 mL) and adding ethanol (1916 mL)]. The solvent was then removed under reduced pressure. The residue was aicdified with water-conc.H_2SO_4 (50 mL : 15 mL) mixture and extracted with dichloromethane(6 x 150 mL). The organic layers were combined , washed with water, aqueous sodium bicarbonate and water till neutral. It was dried and concentrated to give a pale yellow product whose ^{1}Hmr spectrum showed it to be a mixture of *anti-* and *syn-* dithiacyclophanes. This was then chromatographed over silica gel using dichloromethane-pentane (3:7) as the eluant.

Eluted first was the *anti*-isomer 131A (2.113 g, 67%) which on recrystallization from benzene-cyclohexane gave white needles, mp 252-254 °C; ^{1}Hmr, δ, (90 MHz), 7.5 - 7.2 (m, 3H, H-18, H-19 and H-20), 7.12 (s, 3H, H-7, H-8 and H-9), 3.78, 3.67 (s, each 4H, $-\underline{C}H_2-S-\underline{C}H_2$), 3.4 - 2.6 (m, 8H, $-\underline{C}H_2-\underline{C}H_2$), 1.38 and 1.18 (s, each 3H, $Ar-\underline{C}H_3$); ir (KBr), 3000(w), 2930 (m), 2884 (m), 2830 (m), 1465 (s), 1455 (s), 1435 (s), 1209 (m), 1203 (m), 785 (s), 768 (s), 730 (s) and 715 (m); ms peaks (EI) at m/e (relative intensity) 428 (M^+, $C_{28}H_{28}S_2$, 1), 360 (1), 345 (2),

330 (1), 277 (8), 260 (1), 258 (1), 245 (46), 244 (100), 229 (68), 216 (47) and 202 (32); ^{13}Cmr (15.1 MHz), δ, 139.6, 137.8, 135.9, 135.2, 135.1, 130.8, 130.2, 129.7, 128.2, 126.6, 125.5 (all quaternary Ar-C and C-7, C-8, C-9, C-18, C-19 and C-20), 32.4, 28.4 (1, 3, 14 and 16 -$\underline{C}H_2$-S), 28.0, 25.8 (5, 6, 10 and 11 -$\underline{C}H_2$), 15.7 and 15.0 (Ar-$\underline{C}H_3$).

Anal. Calcd. for $C_{28}H_{28}S_2$: C 78.46, H 6.58

Found : C 78.08, H 6.63

Eluted next was the *syn*-isomer 131B (231 mg, 7.3%) which was obtained as colorless crystals, mp 198-200 °C; ^{1}Hmr, δ, (90 MHz), 7.08 (A_2B multiplet, 3H, H-7, H-8 and H-9), 6.91 (d, 2H, J = 7.2 Hz, H-18 and H-20), 6.4 (t, 1H, J = 7.2 Hz, H-19), an AB quartet with the A-doublet at 4.19 (2H, J = 15 Hz, -$\underline{C}H_2$-S) and B-doublet at 3.77 (2H, J = 15 Hz, -$\underline{C}H_2$-S), 4.01 (s, 4H, -$\underline{C}H_2$-S), 3.2 - 2.6 (m, 8H, -$\underline{C}H_2$-$\underline{C}H_2$), 2.48 and 2.44 (s, each 3H, Ar-$\underline{C}H_3$); ms peaks (EI) at m/e (relative intensity) 428 (M^+, $C_{28}H_{28}S_2$, 6), 360 (4), 345 (5), 330 (2), 277 (18), 245 (52), 244 (100), 243 (45), 231 (34), 230 (28), 229 (55), 216 (38), 215 (37) and 202 (26); ^{13}Cmr (15.1 MHz), δ, 136.3, 135.3, 135.0, 134.0, 132.8, 130.9, 130.7, 128.5, 128.0, 126.3, 125.3 (all quaternary Ar-$\underline{C}$ and C-7, C-8, C-9, C-18, C-19 and C-20), 34.9, 31.1 (1, 3, 14 and 16 -$\underline{C}H_2$-S), 27.9, 25.5 (5, 6, 10 and 11 -$\underline{C}H_2$), 18.5 and 16.8 (Ar- $\underline{C}H_3$).

Anal. Calcd. for $C_{28}H_{28}S_2$: C 78.46, H 6.58

Found : C 76.70, H 6.12

41. *Wittig rearrangement of anti-dithiacyclophane 131A to 132A.*

n-BuLi (0.723 g, 11.29 mmol) in hexane (7.1 mL) was added using a syringe into a stirred solution of dithiacyclophane 131A (2.07 g, 4.84

mmol) in dry THF (150 mL) under N_2 at room temperature. After about 10 min, methyl iodide (1.5 mL, 24.2 mmol) was added until the deep reddish color was discharged, followed by water, aqueous HCl and dichloromethane. The layers were separated and the aqueous layer was extracted with dichloromethane (5 x 150 mL). The organic layers were combined, washed with water, dried and concentrated to yield a yellow-orange product. This was chromatographed over silica gel and elution with dichloromethane-pentane (3:7) gave 132A (2.18 g, 98.6%) as a mixture of stereoisomers, mp 95-128 °C; ^{1}Hmr, δ, (90 MHz), 7.9 - 6.9 (m, 6H, Ar-H), 4.2 - 1.8 (m, 14H, $-CH_2-CH_2-$, $-CH_2-CH-S$), 2.26, 2.1, 2.08 (singlets, total 6H, $-SCH_3$) and 1.05 - 0.53 (a series of singlets, 6H, Ar-CH_3); ms peaks (EI) at m/e (relative intensity) 456 (M^+, $C_{30}H_{32}S_2$, 64), 441 (19), 409 (1), 393 (19), 361 (15), 345 (16), 331 (19), 275 (21) and 202 (100).

42. *Anti-bis(sulfonium)salt 133A of the isomers of 132A.*

A solution of the mixture of 132A (1.97 g, 4.33 mmol) in dichloromethane (25 mL) was added dropwise with stirring to a suspension of $(MeO)_2CHBF_4$ (2.46 g, 80% as oil, 12 mmol) in dichloromethane (5 mL) held at - 30 °C under N_2. The mixture was then allowed to warm to room temperature and stirred for 20 h. Then ethyl acetate (40 mL) was added and the mixture was stirred for 1.5 h. It was filtered and the precipitate stirred with an additional portion of ethyl acetate (50 mL) for 2 h. This on filtration gave the bis(sulfonium) salts of 133A as a greenish-grey powder (2.48 g, 87%), mp 197-202 °C (dec.) losing dimethyl sulfide and turning deep red, on melting.

43. *Hofmann elimination of* 133A *to give* *trans*-*10b,10c-dimethyl-10b,10c,4,5,13,14-hexahydrodibenzo[cd,lm]perylene* 134A:

A mixture of *anti*-bis(sulfonium)salts 133A (2.47 g, 3.75 mmol) was added to potassium t-butoxide (1.47 g, 13.10 mmol) in freshly distilled dry THF (100 mL) under N_2. This was heated to reflux with stirring for 1 h. After the mixture had been cooled to room temperature, benzene (250 mL) was added and the mixture made acidic by the addition of dil.HCl. The aqueous layer was separated and extracted with benzene (3 x 250 mL). The organic extract was washed with water and dried to give a dark red product. This was chromatographed over deactivated silica gel (deactivated by adding 45 mL of water/ Kg of silica gel) using pentane as an eluant to yield mainly 134A (579 mg, 43%) as a dark red-brown powder. A sample of 134A was recrystallized from cyclohexane as dark reddish-black crystals, mp (dec.); ms peaks (EI) at m/e (relative intensity) 360 (M^+, $C_{28}H_{24}$, 100), 345 (100) and 330(33); each peak also showed 4 peaks of almost equal intensity corresponding to sequential loss of 4 H. ^{1}Hmr, δ, (90 MHz), 8.81 (d, 2H, J = 8.6 Hz, H-6 and H-12), 8.51 (d, 2H, J = 8.6 Hz, H-7 and H-11), 8.41 (d, 2H, J = 7.5 Hz, H-8 and H-10), 7.93 (t, 1H, J = 7.5 Hz, H-9), 7.23 (s, 3H, H-1, H-2 and H-3), 4.0 - 3.7 and 3.3 - 3.0 (ABCD- multiplet, 8H, $-\underline{CH_2}-\underline{CH_2}-$), -3.81 and -3.89 (s, each 3H, internal $\underline{CH_3}$); as eluted, 134A contained some 45 as evidenced by the ^{1}Hmr peak at δ -2.78 and this was apparently obtained by the partial dehydrogenation of 134A to give *trans*-*10b,10c-dimethyl-4,5,10b,10c-tetrahydrodibenzo[cd,lm]perylene* 45.

44. *Oxidation of 134A to 46 using potassium t-butoxide.*

Anhydrous potassium t-butoxide (150 mg, 1.34 mmol) was added to a solution of 134A (47 mg, 0.131 mmol) in dry THF (60 mL) and the mixture was heated under reflux under N_2 with stirring for 2 h. It was cooled to room temperature, benzene (50 mL) was added and the mixture acidified with dil.HCl. The layers were separated and the aqueous layer was extracted using benzene (2 x 50 mL). The organic layers were then combined, washed with water, aqueous sodium bicarbonate and water till neutral, dried and concentrated. The residue was preadsorbed on Celite and chromatographed over silica gel to give 46 (33 mg, 71%) as orange-red solid. A sample was recrystallized from methanol-benzene as dark red brown crystals, mp 198-199 °C; ^{1}Hmr, δ, (250 MHz), 9.74 (d, 2H, J = 8.13 Hz, H-6 and H-12), 9.54 (d, 2H, J = 9.27 Hz, H-5 and H-13), 8.94 (d, 2H, J = 8.13 Hz, H-7 and H-11), 8.79 (d, 2H, J = 7.57 Hz, H-8 and H-10), 8.33 (d, 2H, J = 9.27 Hz, H-4 and H-14), 8.28 (t, 1H, J = 7.55Hz, H-2), 8.27 (d, 2H, J = 7.55 Hz, H-1 and H-3), 8.05 (t, 1H, J = 7.57 Hz, H-9), - 4.14 and - 4.24 (s, each 3H, internal CH_3's); in the 90 MHz spectrum, the internal methyl groups were at δ -4.19 and - 4.28; ir(KBr), 1640 (m), 838 (s), 815 (m), 810 (s) and 630 (m) cm^{-1}; ms peaks (EI) at m/e (relative intensity) 356 (M^+, $C_{28}H_{20}$, 14), 341 (15), 327 (30), 326 (100) and 163 (43); ^{13}Cmr (62.9 MHz), δ, 136.9, 132.3, 131.5, 127.0, 125.4, 122.3 (C-3a, C-5a, C-5b, C-7a, C-10a, C-12a, C-12b, C-14a, C-14b and C-14c), 127.5, 126.4, 125.5, 124.4, 123.8, 123.3, 119.2 (C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8, C-9, C-10, C-11, C-12, C-13 and C-14), 30.6, 30.4 (C-10b and C-10c) and 14.3 (internal -CH_3's); UV, $\lambda_{max}^{cyclohexane}$ (ε) 254 nm (19,850), 272 (99,700), 306 (10,680), 396 (53,408), 416 (2 02,920),

446 (29,904), 465 (23,140) and 495 (26,344).

Anal. Calcd. for $C_{28}H_{20}$: C 94.34, H 5.66

Found : C 94.33, H 5.70

Note: When the dehydrogenation was carried out using potassium t-butoxide (2.6 g, 23 mmol) and a solution of 134A (335 mg, 0.93 mmol) in dry THF (200 mL), work-up after 8 h indicated that the oxidation was incomplete. Oxidation was continued by further addition of potassium t-butoxide (2.6 g) to the solution of the mixture in dry THF (200 mL) and heating the mixture under reflux in an atmosphere of N_2 for an additional 9 h. Usual work-up, followed by chromatography over silica gel, gave pure 46 (270 mg, 82%), identical with the product obtained earlier.

45. *Formation of trans-10b,10c-dimethyl-10b,10c-dihydrodibenzo[cd,lm]-perylene 46 by dehydrogenation of 134A with DDQ.*

A mixture of 134A (134 mg, 0.372 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 188 mg, 0.828 mmol) in dry benzene (100 mL) was heated under reflux with stirring for 3 h in an atmosphere of N_2. The solution was concentrated and chromatographed over silica gel using pentane to give 46 (4 mg, 3%), identical to the product obtained above as indicated by ^{1}Hmr.

46. *Partial dehydrogenation of 134A with DDQ to 45.*

A mixture of 134A (62 mg, 0.172 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 43 mg, 0.189 mmol) in dry benzene (40 mL) was boiled under reflux for 3 h under N_2. The solution was cooled,

concentrated and chromatographed over silica gel using pentane as an eluant to give a mixture of starting material 134A, the fully dehydrogenated 46 and the partially dehydrogenated 45 (50 mg) as a red-brown product. This was separated using preparative HPLC on a Varian Model 5000 Liquid chromatograph using MCH-10 column [reverse phase, CH_3CN-water (85:15)] to obtain pure 45 as a red-brown product, mp ∿ 120°C (dec.); ^{1}Hmr, δ, (90 MHz), 9.1 - 7.4 (m, 12H, Ar-H), 3.5 ('AB' multiplet, 4H, $-CH_2-CH_2$) and - 2.78 (s, 6H, internal CH_3's): ms peaks (CI) at m/e (relative intensity) 359 (MH^+, $C_{28}H_{22}$, 100) and 343 (12); ^{1}Hmr, δ, (250 MHz), 9.08 - 7.47 (m, 12H, Ar-H), 4.48 - 4.35, 3.65 - 3.32 (m, 4H, $-CH_2-CH_2$) and - 2.76 (s, 6H, internal CH_3's); ^{13}Cmr, (62.9 MHz), δ, 138.6, 138.1, 137.2, 133.4, 132.4, 131.0, 129.4, 128.6, 128.2, 125.9, (all quaternary Ar-C excluding C-10b and C-10c), 127.1, 126.4, 126.2, 125.3, 125.1, 125.0, 123.6, 122.6, 122.1, 122.0, 121.9, 118.0 (all aryl CH's), 30.1, 29.9, 25.3 (13 and 14 $-CH_2$, C-10b and C-10c), 16.3 and 16.0 (internal CH_3's); UV, $\lambda_{max}^{cyclohexane}$ (ε) 232 nm (12,615), 260 (5,796), 376 (31,879), 409 (10,910), 484 (3,068) and 514 (2,386).

47. *A. Syn-bis(sulfonium) salt of dithiacyclophane* 131B.

A solution of 131B (210 mg, 0.49 mmol) in dichloromethane (7 mL) was added slowly with stirring to a suspension of $(CH_3O)_2CHBF_4$ (278 g, 80% as oil, 1.37 mmol) in dichloromethane (2 mL) held at - 30 °C under N_2. When the addition was complete, the mixture was allowed to warm to room temperature and was stirred for another 5 h. After addition of ethyl acetate (5 mL) to dissolve excess methylating reagent and stirring for 0.5 h, the solid product was collected by filtration to give the

salt of 131B (306 mg, 99%) as a white, granular powder.

B. *Stevens rearrangement of sulfonium salts to give* 132B.

The *syn*-bis(sulfonium)salts obtained above (306 mg, 0.48 mmol) were added to a suspension of sodium hydride (35 mg, 1.46 mmol) in dry THF (60 mL) under N_2 and stirred for 45 h. This was acidified using aqueous HCl and extracted using dichloromethane (4 x 50 mL). The organic layer was washed, dried and chromatographed over silica gel using dichloromethane-pentane (2:8) to give 132B (81 mg, 37%) as a mixture of stereoisomers; ^{1}Hmr, δ, (90 MHz), 7.00 (s, Ar-H), 6.4 - 6.2 (m, Ar-H), 5.2 - 4.7 (m, -S-CH-CH_2), 4.0 - 2.0 (m, -CH_2-CH-S, -CH_2-CH_2), 2.32, 2.31 and 2.12 (s, -SCH_3 and internal CH_3's); ms peaks (CI) at m/e (relative intensity) 457 (MH^+, $C_{30}H_{32}S_2$, 100), 441 (63), 409 (20), 393 (57), 378(13), 361 (39), 345 (32), 330 (28), 291 (29), 275 (18) and 202 (37).

48. A. *Syn-bis(sulfonium)salt* 133B.

A solution of the mixture of isomers 132B (80 mg, 0.175 mmol) in dichloromethane (5 mL) was added with stirring to a suspension of $(MeO)_2CHBF_4$ (99 mg, 80% as oil, 0.49 mmol) in dichloromethane (2 mL) held at - 30 °C under N_2. The mixture was allowed to warm to room temperature and was stirred for an additional 4 h. Then ethyl acetate (10 mL) was added, the mixture stirred for 0.5 h and the solvent decanted. Fresh ethyl acetate (10 mL) was added to the residue and it was stirred for an additional 10 h. The resulting crystalline product was collected, dried under vacuum and gave 133B (97 mg, 84%) as a free-flowing white powder.

B. *Hofmann elimination of* 133B *to give* *cis*-*10b,10c-dimethyl-10b,10c,4,5,13,14-hexahydrodibenzo[cd,lm]perylene* 134B.

Anhydrous potassium t-butoxide (57 mg, 0.51 mmol) was added to a stirred suspension of *syn*-bis(sulfonium)salts 133B (97 mg, 0.147 mmol) in dry THF (60 mL). After the mixture had been stirred for 1 h under N_2 at room temperature, benzene (100 mL) was added and the mixture made acidic by the addition of dil.HCl. The organic layer was washed, dried and concentrated. This was chromatographed over silica gel using pentane as the eluant and gave 134B (16 mg, 30%) as brownish-black crystals, mp 164-167 °C; ^{1}Hmr, δ, (90 MHz), 8.99 (d, 2H, J = 9.0 Hz, H-6 and H-12), 8.68 (d, 2H, J = 9.0 Hz, H-7 and H-11), 8.18 ('AB_2' doublet, 2H, J = 5.7 Hz, H-8 and H-10), 7.50 ('AB_2' triplet, 1H, J = 5.7 Hz, H-9), 7.17 (s, 3H, H-1, H-2 and H-3); 4.2 - 2.7 (m, 8H, $-CH_2-CH_2-$), -1.82 and -1.89 (s, each 3H, internal CH_3's); ms peaks (CI) at m/e (relative intensity) 361 (MH^+, $C_{28}H_{24}$, 35), 345 (94), 343 (64), 330 (79), 328 (93) and 326 (100); ^{1}Hmr also indicated some of the corresponding 'phenanthrene' compound as seen by the singlets at δ - 0.99 and - 1.04 (s, each 3H, internal CH_3's).

49. *Dehydrogenation of* 134B *to give* 46C.

A mixture of 134B (16 mg, 0.04 mmol) and 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ, 30 mg, 0.13 mmol) in dry benzene (40 mL) was heated under reflux for 2 h under N_2. The solution was cooled, concentrated and chromatographed over silica gel using pentane as the eluant to give 46C (3.8 mg, 28%) as a pale green solid; ^{1}Hmr, δ, (250 MHz), 9.71 (d, 2H, J = 8.8 Hz, H-6 and H-12), 9.31 (d, 2H, J = 9. 1 Hz, H-5 and H-13),

8.96 (d, 2H, J = 8.8 Hz, H-7 and H-11), 8.45 (d, 2H, J = 9.1 Hz, H- 4 and H-14), 8.39 (dd, 2H, J = 7.4 Hz, H-8 and H-10), 8.22 - 8.18 (m, 3H, H-1, H-2 and H-3), 7.96 (t, 1H, J = 7.4 Hz, H-9), - 1.85 and - 2.14 (s, 3H each, internal $\underline{CH}_3$'s); UV, $\lambda_{max}^{cyclohexane}$ (ε) 263 nm(5,461), 276 (4,854), 310 (2,832), 322 (3,155), 368 (sh, 3,317), 386 (9,142), 407 (30,543), 432 (8,090), 437 (9,102), 468 (4,975) and 494 (3,236).

50. *Anti- and Syn- dithiacyclophane* 135A *and* 135B.

A solution of the bromide 105D (1 g, 2.46 mmol) and 1,3-bis-(mercaptomethyl)-2-methylnaphthalene 91A (0.576 g, 2.463 mmol) in N_2-degassed benzene (900 mL) was added dropwise over 82 h with vigorous stirring under N_2 to a deoxygenated solution of potassium hydroxide [prepared by dissolving potassium hydroxide (1.69 g, 85%, 25.6 mmol) in water (96 mL) and adding ethanol (800 mL)]. The reaction mixture was then evaporated to dryness. Water and aqueous HCl were added. This was extracted using benzene (5 x 150 mL). The combined organic extracts were washed, dried and concentrated. This was chromatographed over silica gel and eluted using dichloromethane-pentane (2:8). Eluted first was the *anti*-isomer 135A (0.73 g, 62%) which on recrystallization from benzene-cyclohexane gave white needles, mp 226-227 °C; ^{1}Hmr, δ, (90 MHz), 8.26 (d, 1H, H-9), 7.95 (s, 1H, H-5), 7.78 (dd, 1H, H-6), 7.6 - 7.4 (m, 2H, H-7 and H-8), 7.14 (s, 3H, H-18, H-19 and H-20), 4.5 - 2.5 (m, 16H, $-\underline{CH}_2-\underline{CH}_2$, $-\underline{CH}_2-S-\underline{CH}_2$), 1.50 and 0.72 (s, each 3H, Ar-$\underline{CH}_3$); ^{1}Hmr, δ, (250 MHz), 8.29 (d, 1H, J = 8.4 Hz, H-9), 7.97 (s, 1H, H-5), 7.81 (dd, 1H, J = 7.9 Hz, H-6), 7.60 - 7.40 (m, 2H, H-7 and H-8), 7.17 - 7.12 (A_2B multiplet, 3H, H-18, H-19 and H-20), 4.40 -

2.70 (m, 16H, $-\underline{CH}_2-\underline{CH}_2$, $-\underline{CH}_2-S-\underline{CH}_2$), 1.55 and 0.76 (s, 3H each, $Ar-\underline{CH}_3$); ms peaks (CI) at m/e (relative intensity) 479 (MH^+, $C_{32}H_{30}S_2$, 49), 478 (87), 446 (34), 412 (3), 309 (8), 277 (56), 245 (88), 229 (30) and 201 (100); ^{13}Cmr, (62.9 MHz), δ, 138.1, 138.0, 135.6, 135.3, 135.2, 132.7, 132.2, 131.0, 130.9, 130.3, 129.0, 128.9 (all quaternary Ar-C), 130.2, 128.2, 126.8, 126.1, 125.8, 125.2, 125.0, 123.9 (all C-H's i.e., C-5, C-6, C-7, C-8, C-9, C-18, C-19 and C-20), 32.4, 28.6 (1,3, 12 and 14 $-\underline{CH}_2-S$), 28.0, 26.4, 26.0(C-16,17,21 and 22), 16.3 and 15.4 ($Ar-\underline{CH}_3$).

Anal. Calcd. for $C_{32}H_{30}S_2$: C 80.29, H 6.31, S 13.40

Found : C 79.95, H 6.05

Eluted next was the *syn*-isomer 135B (130 mg, 11%) which was obtained as colorless crystals. Recrystallization from benzene-cyclohexane gave pure 135B, mp 204-206 °C; ^{1}Hmr, δ, (90 MHz), 8.00 (d, 1H, H-8), 7.5 - 6.7 (m, 7H, Ar-H excluding H-8), 4.8 - 3.5 (m, $-\underline{CH}_2-S-\underline{CH}_2-$, 8H), 3.2 - 2.0 (m, 8H, $-\underline{CH}_2-\underline{CH}_2$), 2.63 and 2.49 (s, each 3H, internal $\underline{CH}_3$'s); ^{1}Hmr, δ, (250 MHz), 8.01 (d, 1H, J = 8.5 Hz, H-9), 7.80 - 7.60 (m, 1H, H-6), 7.39 (s, 1H, H-5), 7.22 - 6.76 (m, 5H, H-7, H-8, H-18, H-19 and H-20), 4.80 - 3.53 (m, 8H, $-\underline{CH}_2-S-\underline{CH}_2$), 3.15 - 2.03 (m, 8H, $-\underline{CH}_2-\underline{CH}_2$), 2.65 and 2.51 (s, 3H each, internal $\underline{CH}_3$'s i.e $Ar-\underline{CH}_3$); ms peaks (CI) at m/e (relative intensity) 479 (MH^+, $C_{32}H_{30}S_2$, 42), 446 (25), 412 (14), 277 (53), 245 (74), 229 (28) and 201 (100); ^{13}Cmr,(62.9 MHz), δ, 135.4, 134.7, 134.5, 134.2, 132.6, 132.2, 131.9, 131.2, 131.0, 130.3,129.4, 128.5, 128.3, 126.3, 125.6(all quaternary Ar-C), 127.9, 127.4, 126.2, 125.0, 124.9, 124.6, 124.5, 124.2 (all aryl C-H), 35.7, 31.6, 31.0, 28.6, 28.0, 25.9, 25.2 (1,3,12 and 14 $-CH_2-S$ and 16,17,21 and 22

$-\underline{CH}_2$), 18.8 and 18.1 ($Ar-\underline{CH}_3$).

Anal. Calcd. for $C_{32}H_{30}S_2$: C 80.29, H 6.31, S 13.40

Found : C 79.70, H 6.32,

51. *Wittig rearrangement of anti-dithiacyclophane* 135A *to* 136A.

n-BuLi (220 mg, 3.44 mmol) in hexane (1.43 mL) was added using a syringe to a stirred solution of dithiacyclophane 135A (705 mg, 1.48 mmol) in dry THF (100 mL) under N_2 at room temperature. The initially colorless solution became dark red-brown after about 10 min of stirring, when methyl iodide (0.46 mL, 7.38 mmol) was added until the solution became pale red. This was worked up by the addition of water, aqueous HCl and dichloromethane. The aqueous layer was extracted with dichloromethane (5 x 75 mL). The organic layers were combined, washed with water, dried and concentrated to give a red product. This was then chromatographed over silica gel and elution with dichloromethane-pentane (3:7) gave 136A (0.436 g, 58.5%) as a mixture of stereoisomers; ^{1}Hmr, δ, (90 MHz), 8.4 - 7.0 (m, Ar-H), 5.93, 5.79 (s, ?), 4.4 - 2.5 ($-\underline{CH}_2-\underline{CH}_2$ and $-\underline{CH}_2-\underline{CH}-S$), 2.30 -2.14 (a series of singlets, $-S\underline{CH}_3$), and 1.62 - 0.97 (a series of singlets, 6H total, $Ar-\underline{CH}_3$).

52. *Hofmann elimination of* anti-*cyclophane* 136A *to* trans-*12c,12d-dimethyl-12c,12d,4,5,15,16-hexahydrobenzo[rst]naphtho-[8,1,2-cde]-pentaphene* 138A.

A solution of the mixed isomers of 136A from the Wittig rearrangement of 135A (435 mg, 0.86 mmol) in dichloromethane (10 mL) was added to $(MeO)_2CHBF_4$ (608 mg, 80% as oil, 3.0 mmol) stirred at - 30 °C under N_2. This mixture was then stirred for 20 h without further cooling, ethyl

acetate (10 mL) was added and stirring continued for 0.5 h. This was then filtered and the precipitate triturated with ethyl acetate (30 mL) for 20 h. Filtration gave the sulfonium salt 137A (503 mg, 82%) as a greenish grey powder, mp> 310 °C.

This salt was suspended in dry THF (50 mL) under N_2 and then potassium t-butoxide (278 mg, 2.48 mmol) was added. This was heated to reflux under N_2 with stirring for 1 h. After cooling, aqueous HCl and benzene (100 mL) were added. The aqueous layer was extracted with benzene (3 x 125 mL). The dark red organic layer was washed with water, sodium bicarbonate solution, water, dried and concentrated to give a red-brown product. This was pre-adsorbed on Celite and chromatographed using pentane as eluant to give 138A (36 mg, 12%) as a dark red product; ^{1}Hmr, δ, (90 MHz), 8.8 - 7.0 (m, 12H, Ar-H), 4.0 - 2.8 (m, 8H, $-CH_2-CH_2$), - 1.41 (s, 6H, internal CH_3's); a small singlet at δ -1.35 was also observed, probably due to the dehydrogenated product 47.

53. *12c,12d-Dimethyl-12c,12d-dihydrobenzo[rst]naphtho[8,1,2-cde]-pentaphene 47 by oxidation of 138A.*

Anhydrous potassium t-butoxide (246 mg, 2.2 mmol) was added to a suspension of 138A (36 mg, 0.09 mmol) in dry THF (70 mL) and the mixture was heated under reflux in an atmosphere of N_2 with stirring for 6 h. It was cooled to room temperature and the mixture was then acidified with dil.HCl. The layers were separated and the aqueous layer was extracted with benzene (3 x 75 mL). The organic layers were combined, washed with water, aqueous sodium bicarbonate and water till neutral, dried and concentrated. It was preadsorbed on Celite and chromatographed over silica gel using pentane as an eluant to give 47

(29 mg, 70%) as a dark red product, mp 219-221 °C; ^{1}Hmr, δ, (90 MHz), 8.9 - 7.2 (m, 16H, Ar-H), - 1.35 and - 1.41 (s, each 3H, internal CH_3's); ^{1}Hmr, δ, (250 MHz), 8.8 - 7.4 (m, 16H, Ar-H), - 1.32 and - 1.37 (s, each 3H, internal CH_3's); ms peaks (CI) at m/e (relative intensity) 407 (MH^+, $C_{32}H_{22}$, 100), 406 (68) and 213 (92); ^{13}Cmr, (62.9 MHz), δ, 137.5, 135.4, 134.4, 133.1, 132.7, 130.6, 128.6, 127.3 (all quaternary Ar-C excluding C-12c and 12d), 128.4, 127.5, 127.4, 127.3, 127.2, 126.5, 124.7, 124.4, 124.2, 123.5, 123.0, 121.6, 117.4, 117.1 (all aryl C-H) , 37.2, 36.9 (internal carbons C-12c and C-12d), 29.7 (?) , 17.8, 17.6 (internal CH_3's); UV, $\lambda_{max}^{cyclohexane}$ (ε) 226 nm (26,643); 264 (13,956), 296 (11,419), 410 (69,147), 427 (96,806), 505 (5,075), 535 (6,724) and 575 (5, 075).

54. *A. Bis(sulfonium)salt of syn-dithiacyclophane* 135B.

A solution of the dithiacyclophane 135B (128 mg, 0.268 mmol) in dichloromethane (15 mL) was added to a stirred suspension of $(MeO)_2CHBF_4$ (160 mg, 80% as oil, 0.79 mmol) in dichloromethane (5 mL) held at - 30°C under N_2. After the addition, the mixture was allowed to warm to room temperature and stirred for an additional 20 h. It was concentrated to half its volume on a rotary evaporator and ethyl acetate (20 mL) was then added and the mixture stirred for 1 h. The white powder was filtered off, washed with ethyl acetate (10 mL) and dried under vacuum to give the sulfonium salts of 135B (141 mg, 77%), mp >. 300 °C (dec.).

B. Stevens rearrangement of the bis(sulfonium) salt to 136B.

The *syn*-bis(sulfonium)salts of 135B (141 mg, 0.207 mmol) was added to a suspension of NaH(915 mg, 0.625 mmol) in dry THF (80 mL) under N_2 and stirred at room temperature for 10 h. This was acidified

using aqueous HCl and extracted with benzene (3 x 75 mL). The organic layer was washed, dried and concentrated to yield a mixture of stereoisomers of 136B (105 mg, quant.); ^{1}Hmr, δ, (90 MHz), 8.92 (d, 1H, Ar-H), 7.8 - 6.6 (m, 7H, Ar-H), 5.5 - 4.8, 4.0 - 1.8 including major singlets at 2.55, 2.40 and 2.22 (-SCH$_3$, -CH-S-CH$_3$ and internal CH$_3$'s).

55. *Hofmann elimination of syn-cyclophane 136B to cis-12c,12d-dimethyl-12c,12d,4,5,15,16-hexahydro[rst]naphtho[8,1,2-cde]-pentaphene 138B.*

A solution of the mixed isomers of 136B from the Stevens rearrangement of 135B (108 mg, 0.213 mmol) in dichloromethane (10 mL) was added to $(MeO)_2CHBF_4$ (150 mg, 80% as oil, 0.741 mmol) held at - 30 °C under N_2. This was concentrated to half its volume under reduced pressure and ethyl acetate (15 mL) was added and the stirring continued for 1.5 h. This was filtered and the precipitate washed with ethyl acetate (15 mL) The greenish-black powder was dried under vacuum to give the sulfonium salt 137B (76 mg, 50%).

The salt was suspended in dry THF (40 mL) under N_2 and anhydrous potassium t-butoxide (42 mg, 0.38 mmol) was added. This was stirred at room temperature for 2 h. Benzene (40 mL), water (20 mL) and water-dil.HCl (1:1, 30 mL) was added . The organic layer was separated and the aqueous layer was extracted well with benzene (3 x 50 mL). The organic layers were combined, washed well with water, dried and then concentrated to give a red product. This was preadsorbed on Celite and chromatographed over silica gel using pentane as eluant to give 138B (10 mg, 23%) as a red product; ^{1}Hmr, δ, (90 MHz), 8.8 - 7.0 (m,12H, Ar-H), 4.0 - 2.0 (m, 8H,-CH$_2$-CH$_2$), 0.05 and -0.08 (s, each 3H, internal

CH_3's); small singlets at δ 0.49 and 0.45 were also observed, possibly due the dehydrogenated product; ^{1}Hmr, δ , (250 MHz), 8.52 - 7.00 (m, 12 H, Ar-H), 3.8 - 2.6 (m, 8H, $-CH_2-CH_2$), - 0.08 and - 0.21 (s, 3H each, internal CH_3's); small singlets at δ 0.49 and 0.45 were also observed, possibly due to the dehydrogenated product; ^{13}Cmr, (62.9 MHz), δ, 140.0 -121.7 (quaternary Ar-C), 130.8, 127.0, 126.8, 126.6, 126.5, 126.2, 125.8, 124.9, 120.9, 120.7, 119.3 (aryl C-H's), 37.6, 31.3, 30.2, 29.9, 29.2, 28.5 (C-4, C-5, C-15 and C-16 CH_2's and C-12c, C-12d), 26.8 and 25.0 (internal CH_3's).

56. *~~cis~~-12c,12d-Dimethyl-12c,12d-dihydrobenzo[rst]naphtho-[8,1,2-cde] pentaphene* 47B *by oxidation of* 138B.

Anhydrous potassium t-butoxide (100 mg, 0.89 mmol) was added to a solution of 138B (10 mg, 0.02 mmol) in dry THF (30 mL) and the mixture was heated under reflux with stirring in an atmosphere of N_2 for 0.5 h. It was cooled to room temperature, benzene (40 mL) was added and the mixture acidified with dil.HCl. The layers were separated and the aqueous layer was extracted with benzene (2 x 30 mL). The combined organic layers were washed with water, aqueous sodium bicarbonate and water till neutral, dried and concentrated. The residue was preadsorbed on Celite and chromatographed over silica gel using pentane as an eluant to give 47B (3 mg, 30%) as a red product; ^{1}Hmr, δ, (250 MHz), 8.42 - 7.19 (Ar-H), - 0.10 and -0.14 (s, 3H each, internal CH_3's); UV, $\lambda_{max}^{cyclohexane}$ (ε) 252 nm(12,992), 262 (12,992), 283 (9,338), 295 (10,150), 335 (6,699), 352 (10,556), 403 (35,728), 466 (7,308), 473 (7,511), 487 (6,009) and 520 (5,481).

57. *anti- and syn-Dithiacyclophane* 139A *and* 139B.

A solution of the bromide 105D (2 g, 4.93 mmol) and the bis-thiol 105E (1.54 g, 4.93 mmol) in N_2-degassed benzene (900 mL) was added dropwise over 80 h to a deoxygenated solution of potassium hydroxide [prepared by dissolving potassium hydroxide (3.38 g, 85%, 51.23 mmol) in water (190 mL) and adding ethanol (1610 mL)]. The reaction mixture was then evaporated to dryness, water and aqueous HCl were then added. This was extracted using dichloromethane (9 x 150 mL). The organic extracts were combined, washed, dried and concentrated. This was chromatographed over silica gel using dichloromethane-pentane (3:7). Eluted first was the *anti*-isomer 139A (1.49 g, 54%) which on recrystallization from benzene-cyclohexane gave pale yellow crystals, mp. 289-291 °C, turning yellowish-orange; ^{1}Hmr, δ, (90 MHz), 7.12 ('A_2B' multiplet, 6H, Ar-H), 3.78 (s, 8H, $-CH_2-S-CH_2$), 3.4 - 2.5 (m, 16H, $-CH_2-CH_2$) and 1.32 (s, 6H, Ar-CH_3); ^{1}Hmr, δ, (250 MHz), 7.15 ('A_2B' multiplet, 6H, Ar-H), an 'AB' doublet with the 'A' doublet at 3.85 (d, 4H, J = 14 Hz, $-CH_2-S$), and the 'B' part at 3.80 (d, 4H, J = 14 Hz, $-CH_2-S$), 3.40 - 3.25, 3.05 - 2.80 (m, 16H, $-CH_2-CH_2$) and 1.34 (s, 6H, Ar-CH_3); ir (KBr), 3005 (w), 2950 (m), 2935 (s), 2890 (m), 2830 (m), 1468 (m), 1438 (s), 1428 (s), 1412 (m), 1208 (m), 1202 (m), 865 (w), 802 (m), 788 (m), 769 (s), 758 (s) and 730 (w); ms peaks (CI) at m/e (relative intensity) 557 (MH^+,$C_{38}H_{36}S_2$,100), 498 (96) and 447 (59); the major spectrum peak was at 278 (∿ 100 x MH^+); ^{13}Cmr, (62.9 MHz), δ, 139.2 (C-13 and C-26), 135.5, 131.1, 130.5, 129.1 (all other quaternary Ar-C), 126.9 (C-8 and C-21), 125.8 (C-7, C-9, C-20 and C-22), 28.7 (5,6, 10,11,18,19,23 and 24 - CH_2-CH_2), 26.4 (1,3,14 and 16 $-CH_2-S$) and

16.0 (Ar-$\underline{C}H_3$),

Anal. Calcd. for $C_{38}H_{36}S_2$: C 81.97, H 6.52, S 11.51

Found : C 80.17, H 6.30

Subsequent fractions gave a mixture of *syn*-139B and *anti*-139A (~1:1 ratio, 314 mg, 11.5%) from which the *syn*-isomer 139B could not be isolated pure. ^{1}Hmr, (90 MHz),δ, [by subtraction] gave 7.05 (s, Ar-$\underline{H}$), ~3.75 (s, -$\underline{C}H_2$-S), ~3.5 - 2.6 (m, -$\underline{C}H_2$-$\underline{C}H_2$) and 2.14 (s, internal -$\underline{C}H_3$'s).

58. *Rearrangement of dithiacyclophane* 139A.

A. Bis(sulfonium)salts of anti-dithiacyclophane 139A.

A solution of the dithiacyclophane 139A (1.146 g, 2.061 mmol) in dichloromethane (250 mL) was added to a stirred suspension of $(MeO)_2CHBF_4$ (1.241 g, 80% as oil, 6.13 mmol) in dichloromethane (20 mL) at -30 °C under N_2. After the addition, the mixture was allowed to warm to room temperature and stirred for an additional 20 h. It was concentrated to half its volume on a rotary evaporator and then ethyl acetate (40 mL) added to dissolve any excess methylating reagent present and the mixture was stirred for an hour. The white powder of the bis(sulfonium)salt of 139A was filtered, washed with ethyl acetate (30 mL) and dried under vacuum to give the salt (1.261 g, 81%), mp > 300 °C (dec.).

B. Stevens rearrangement of the bis(sulfonium)salts to 140A.

The *anti*-bis(sulfonium)salts (1.261 g, 1.66 mmol) was added to potassium t-butoxide (0.56 g, 4.99 mmol) in dry THF under N_2 and stirred for 1 h at room temperature. This was acidified using dil.HCl

and extracted using dichloromethane (6 x 100 mL). The organic layers were combined, washed well with water, dried and concentrated to give 140A (914 mg, 94%) as a dark red product; ^{1}Hmr, δ, (90 MHz), 7.06 (A_2B multiplet, Ar-H), 3.9 - 2.5 (m, $-CH_2-CH_2$, $-CH_2-CH-S$), 2.28, 2.21 (s, $-SCH_3$) and 1,1 - 0.7 (a series of singlets, internal CH_3's).

59. *Hofmann elimination of anti-cyclophane 140A to trans-14c,14d-dimethyl-14c,14d,4,5,8,9,13,14,17,18-decahydrobenzo[rst]-dinaphtho[8,1,2-cde: 2',1',8'-klm]pentaphene 142A.*

A solution of the mixed isomers of 140A from the Stevens rearrangement of dithiacyclophane 139A (901 mg, 1.54 mmol) in dichloromethane (80 mL) was added to $(MeO)_2CHBF_4$ (924 mg, 80% as oil, 4.57 mmol) and stirred at - 30 °C under N_2. This was then stirred for 20 h without further cooling and then it was concentrated to half its volume. Ethyl acetate (40 mL) was added and stirring continued for 5 h. Filtration, followed by washing with ethyl acetate (10 mL), gave a pink red salt of 141A (687 mg, 57%).

The salt was suspended in dry THF (150 mL) under N_2 and potassium t-butoxide (351 mg, 3.13 mmol) was added. This was heated to reflux under N_2 with stirring for 1 h. After cooling, aqueous HCl and benzene (100 mL) were added. The aqueous layer was extracted with benzene (4 x 150 mL). The organic layers were combined, washed with water, sodium bicarbonate solution, water till neutral, dried and concentrated to give a red product. This was preadsorbed on Celite and chromatographed over silica gel using pentane as an eluant to give 142A (302 mg, 71%) as a red product; ^{1}Hmr, δ, (90 MHz), 10.0 - 7.1 (Ar-H), 4.0 - 2.7

(-$\underline{CH}_2$-$\underline{CH}_2$) and - 4.10 (s, 6H, internal $\underline{CH}_3$'s); small peaks at δ - 3.20, - 3.56, -3.68 and - 4.15 corresponding to the dehydrogenated product were also seen in the ^{1}Hmr spectrum of the product.

60. *Attempted synthesis of 48 by oxidation of 142A using potassium t-butoxide.*

Anhydrous potassium t-butoxide (1.725 g, 15.37 mmol) was added to a suspension of 142A (300 mg, 0.615 mmol) in dry THF (150 mL) and the mixture was heated under reflux under N_2 with stirring for 21 h. It was cooled to room temperature, benzene (150 mL) and dil.HCl were added. The layers were separated and the aqueous layer was extracted with benzene (5 x 150 mL). The organic layers were combined, washed well with water, sodium bicarbonate solution and water till neutral, dried and concentrated. It was preadsorbed on Celite and chromatographed over silica gel using pentane as eluant to give a dark red product, (25 mg, 8.4%); ^{1}Hmr of the product showed the aromatic H's at δ 9.94-7.98 in the 90 MHz spectrum and the internal $\underline{CH}_3$'s were seen at - 4.06 and - 4.11 (this actually corresponds to the saturated system); ^{13}Cmr, (62.9 MHz), δ, 139.9, 136.9, 133.0, 132.9, 132.4, 131.7, 129.0, 126.2 (all quaternary Ar-$\underline{C}$), 125.6, 125.2, 124.7, 124.4, 119.6, 118.1 (all $\underline{C}$-H's), 40.2 and 37.9 (C-14c and C-14d).

61. *Electrophilic substitution of 46.*

Nitration of 46 using cupric nitrate trihydrate:

Powdered cupric nitrate trihydrate (54 mg, 0.22 mmol) was added to a solution of 46 (72 mg, 0.202 mmol) in acetic anhydride (50 mL) at 0 °C. After stirring for 2 h, the dark greenish-red solution was

poured into ice-water mixture. This was stirred well and extracted using benzene (4 x 100 mL). The organic extracts were combined, washed with water, aqueous sodium bicarbonate solution, water, dried and then concentrated. The resulting bluish-red residue was chromatographed over silica gel using initially pentane to elute any unreacted starting material 46 (26 mg, 0.07 mmol) and then dichloromethane-pentane (2:8) to give a mixture of at least two nitro compounds, as indicated by ^{1}Hmr. This was separated by a preparative HPLC on a Varian Model 5000 Liquid chromatograph[silica-10 column, 50 cm long, 8 mm i.d., solvent system : dichloromethane-hexane (35:65)].

Eluted first was a dark red compound which on recrystallization from cyclohexane gave 147 as dark reddish-black crystals, mp 222-224 °C; ^{1}Hmr, (250 MHz), of the product indicated at δ 9.92 (s, 2H, Ar-H), 9.85 - 8.35 (a set of 9 doublets, 10H, Ar-H), 8.14 (t, 1H, Ar-H), - 3.99 and - 4.03 (internal CH_3's); ms peaks (CI) at m/e (relative intensity) 402 (MH^+, $C_{28}H_{19}NO_2$, 24), 223 (34) and 207 (100); UV, $\lambda_{max}^{cyclohexane}$ (ε) 254 nm (10,776), 298 (6,265), 373 (7,769), 442 (48, 019), 514 (9,524) and 557 (9,674).

Eluted next was 145, which was recrystallized from cyclohexane as dark red crystals, mp 228-230 °C; ^{1}Hmr, δ, (250 MHz), 10.54 (s, 1H, Ar-H), 9.9 - 8.3 (a set of 9 doublets, 10H, Ar-H), 8.55 (t, 1H, Ar-H), 8.13 (t, 1H, Ar-H), -3.92 and -4.00 (s, each 3H, internal CH_3's); ms peaks (CI) at m/e (relative intensity) 402 (MH^+, $C_{28}H_{19}NO_2$, 28), 223 (50) and 207 (100); UV, $\lambda_{max}^{cyclohexane}$ (ε) 254 nm (6,894),

315 (5,156), 428 (30,361), 440 (32,939), 470 (12,316), 508 (7,734), 571 (3,724) and 774 (1,145).

Eluted lastly was the third compound which was not identified.

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92. Dr. T. W. Dingle (Department of Chemistry, University of Victoria) provided the π-SCF bond orders used in this section.

93 (a) Bond orders were calculated using Pople-Pariser-Parr (PPP) π-electron theory[93b] Idealized geometries (C-C bond length =140 pm, CCC bond angle 120°) were used. The resonance integral, $\beta_{\mu,\nu}$, was assigned a value of - 2.366eV for nearest neighbors. All two electron integrals, $\gamma_{\mu,\nu}$, were calculated using Mataga-Nishimoto relationship

$$\gamma_{\mu,\nu} = \frac{1.4397}{R + \frac{2.8794}{\gamma_{\mu,\mu} + \gamma_{\nu,\nu}}} \text{ eV}$$

with a value of 10.67 eV used for $\gamma_{\mu,\mu}$ for the carbon atom. Other

parametrization gave very similar values for bond orders; (b) See J. N. Murrell and A. N. Harget in "Semi-empirical Self Consistent Field -Molecular Orbital Theory of Molecules", John Wiley, London, (1972), Chapter 2 for a discussion of π-electron theory.

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95. It could be argued that in 40 the bonds q, s and e which are close to or a part of the benzannelating ring might be affected by ring fusion and introduce anisotropy effects. To account for this, equation (4) has been derived by neglecting bonds q, s and e in the calculation of $\Delta r'$, the average bond order deviation:

$$\Delta\delta' = 5.297 - 0.0292\,\Delta r' \quad \ldots\ldots \quad (4)$$

However, such exclusion would be rather unproductive when considering highly annelated systems.

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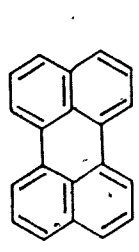
APPENDIX

KEY TO SELECTED NUMBERED STRUCTURES



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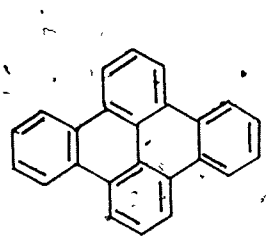

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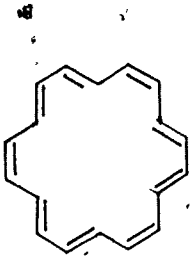

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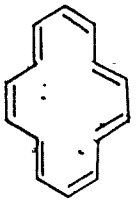
6[6]



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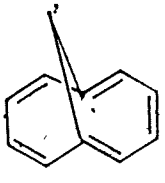

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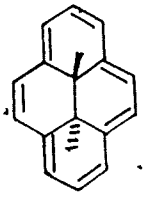
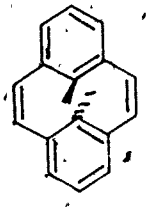
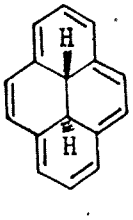


25[63a,85a]



25A[100]



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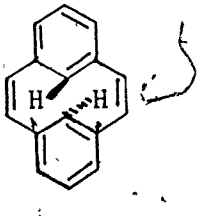

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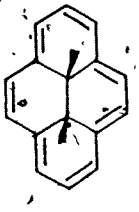

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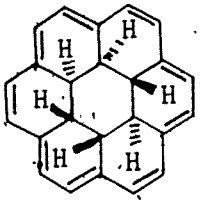

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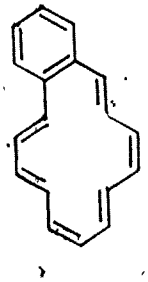

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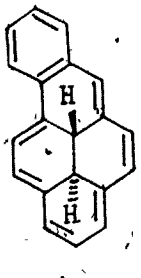

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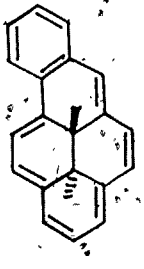

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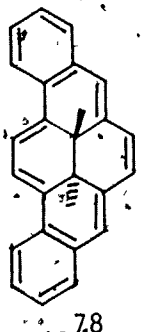

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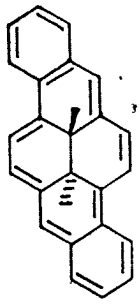

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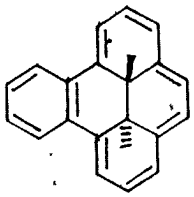

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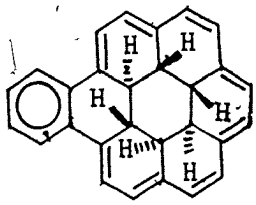

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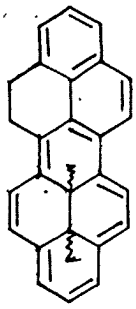

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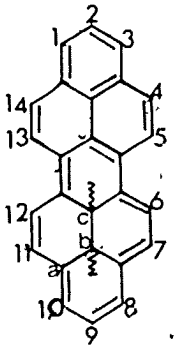

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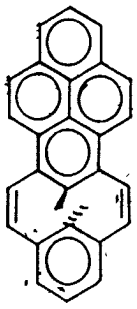

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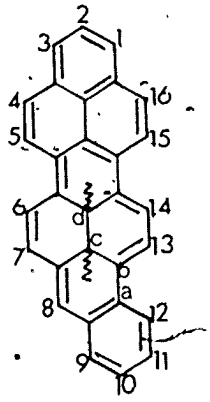
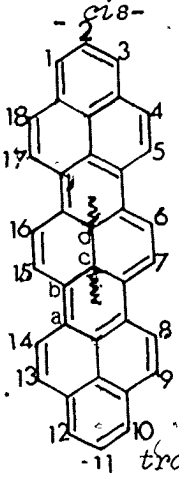


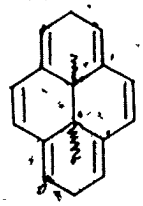
trans-47

cis-47B



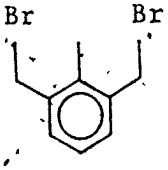
trans-48

cis-48B

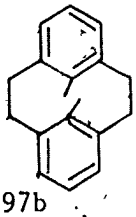


trans-59[63a, 85a, 85b]

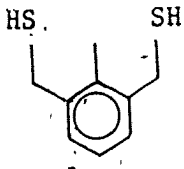
cis-59A



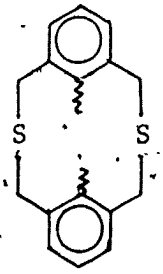
64[85a]



66[97b]

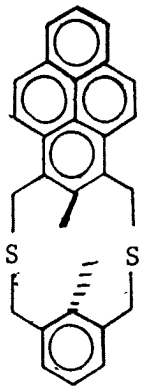


71[85a]

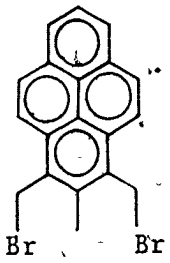


anti-72

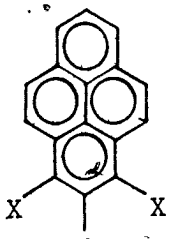
syn-72A



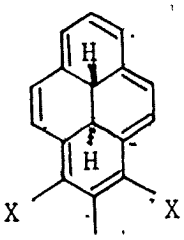
anti-73



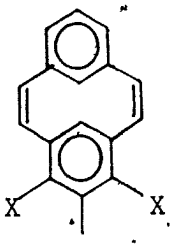
74



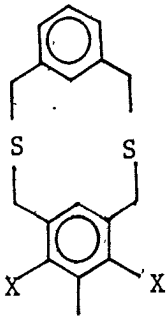
75, X = Br
75A, X = CN
75B, X = CHO
75C, X = CH_2OH
75D, X = CH_2SH



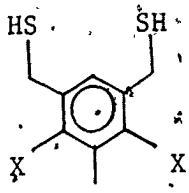
76, X = Br
76A, X = CN



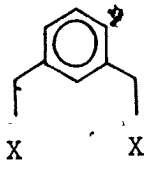
77, X = Br
77A, X = CN



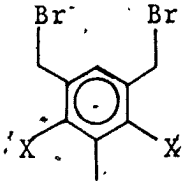
78, X = Br
78A, X = CN



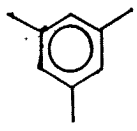
79, X = Br
79A, X = CN



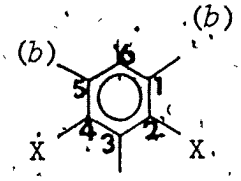
80, X = Br
81, X = SH



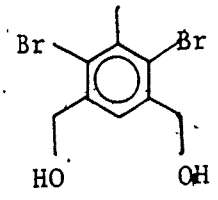
82, X = Br
82A, X = CN



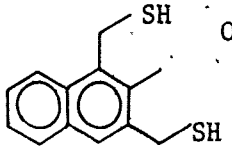
83



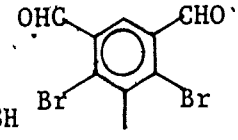
84, X = Br
84A, X = CN



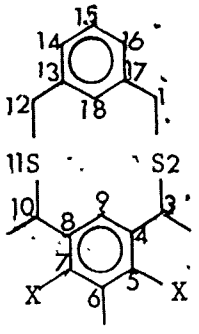
87



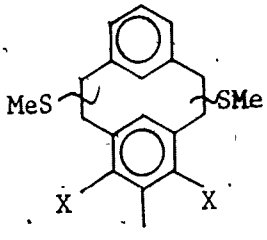
91A



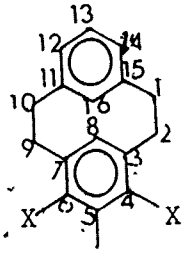
94



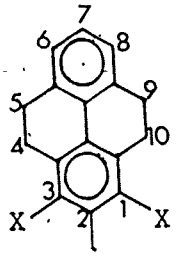
99, X = Br



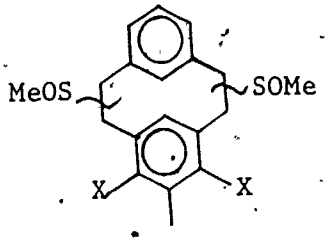
100



104



105

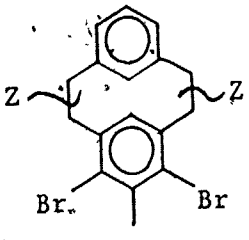


107

X = Br, 100, 104, 105, 107 X = CN, 100A, 104A, 105A, 107A

X = CHO, 100B, 104B, 105B, 107B X= CH_2OH, 100C, 104C, 105C, 107C

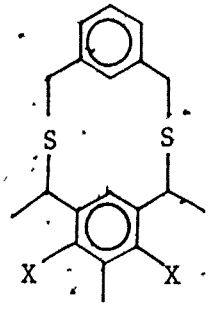
X = CH_2Br, 100D, 104D, 105D X= CH_2SH, 100E, 104E, 105E



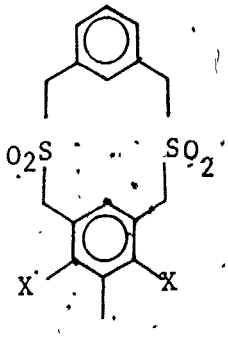
108, Z = Sφ

109, Z = $SO_2\phi$

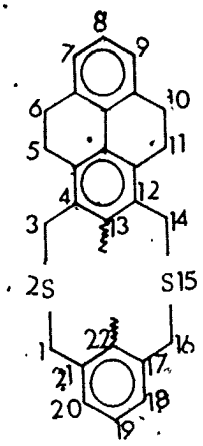
110, Z = SOφ



115, X= CN

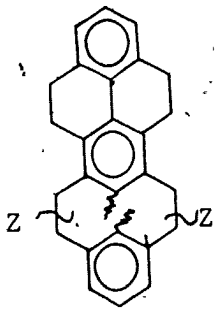


126, X= Br



anti-131A

syn-131B



Z = SMe

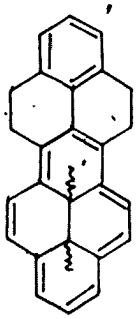
anti-132A

syn-132B

Z = $\overset{+}{S}Me_2$

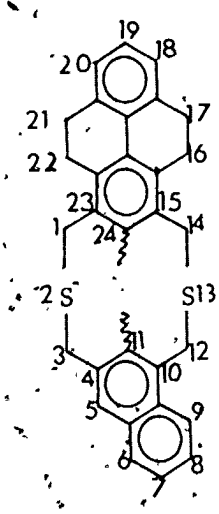
anti-133A

syn-133B



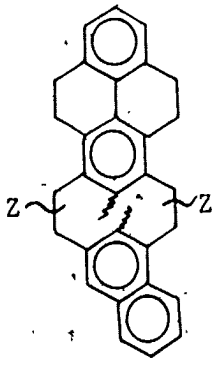
trans-134A

cis-134B



anti-135A

syn- 135B

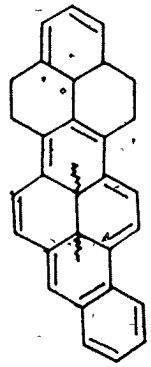


Z = SMe

anti-136A

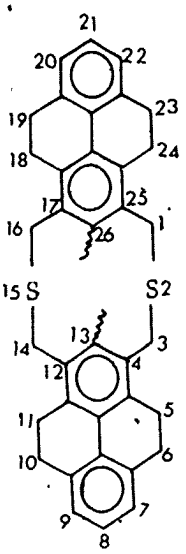
syn-136B

Z = $\overset{+}{S}Me_2$ *anti*-137A , *syn*-137B



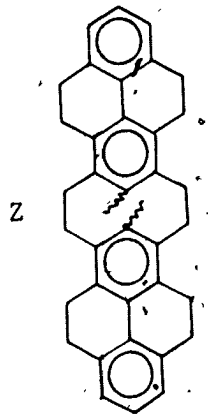
trans-138A

cis-138B



anti-139A

syn-139B

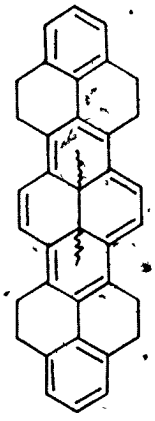


Z ≠ SMe *anti*-140A

syn-140B

Z = $\overset{+}{S}Me_2$ *anti*-141A

syn-141B



trans-142A

cis-143

VITA

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UNIVERSITY OF BOMBAY, BOMBAY, INDIA	1970 to 1972
UNIVERSITY OF VICTORIA, VICTORIA, CANADA	1977 to 1981

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

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M.Sc	1972	UNIVERSITY OF BOMBAY, BOMBAY, INDIA

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Publications:

1 Synthesis of diatropic highly benzannelated annulenes. R. H. Mitchell and R. Mahadevan, in press.

2 Towards the understanding of benzannelated annulenes: a simple correlation of the diatropicity of several benzannelated dihydropyrenes in terms of bond order deviations with predictions for other benzannulenes. R. H. Mitchell, R. V. Williams, R. Mahadevan, Y. H. Lai, and T. W. Dingle, in press.

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SYNTHESIS OF SOME PYRENE ANNELATED MACROCYCLIC SYSTEMS

Author .....

Signature

RAMANATHAN MAHADEVAN

.....

September 30, 1981

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Date