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Toward the Understanding of Benzannelated Annulenes: Synthesis and Properties of [*a*,*h*]- and [*a*,*i*]-Ring Dibenzannelated Dihydropyrenes[1]

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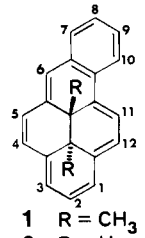
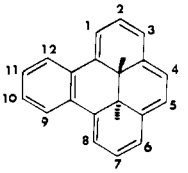
Abstract: The dibenzannelated [*a*,*h*]- and [*a*,*i*]dihydropyrenes **5** and **7** and dimethyldihydropyrenes **4** and **6** were synthesized from 1,3-bis(bromomethyl)naphthalene (**23**) and 1,3-bis(bromomethyl)-2-methylnaphthalene (**24**), respectively, using Wittig rearrangement–Hofmann elimination sequences on the corresponding dithiacyclophanes, followed by valence tautomerization of the resulting cyclophanedienes. The dihydropyrenes **5** and **7** could not be isolated, but rapidly dehydrogenated to dibenzo[*a*,*h*]- and -[*a*,*i*]pyrene. The dimethyldihydropyrenes **4** and **6** are relatively stable and their diatropicities are discussed in relation to each other and to other benzannulenes in terms of Kekulé structures and bond order calculations. It is shown that transoid fusion of the benzene rings on the annulene only somewhat perturbs the diatropicity of the annulene, whereas cisoid fusion strongly localizes the annulene macroring. Annulenes such as **6** which have transoid-fused benzenoid rings are also shown to display radicaloid properties.

In the previous accompanying papers,[1,2] we describe the syntheses and properties of the [*a*]- and [*e*]-ring benzannelated dihydropyrenes, **1** (R = CH_3), **2** (R = H), and **3**. This paper describes the dibenzannelated compounds[3] **4–7**.



1 R = CH_3
2 R = H



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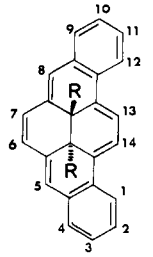
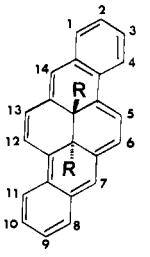
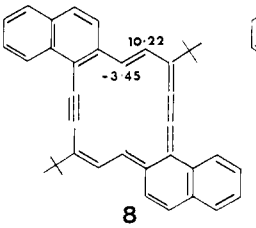


4 R = CH_3
5 R = H



6 R = CH_3
7 R = H

At the outset of this work,[4] though several dibenzannelated annulenes were known,[5] none showed any detectable aromaticity in the macroring. Given the success in preparing the monobenzannelated species **1–3** and their strong residual ring currents in the macroring,[1,2] it seemed likely that the dibenzannelated annulenes **4–7** would also show at least some residual macroring current as well. Impetus was given to our work when Nakagawa[6] reported the dinaphthannelated [14]annulene **8**, which clearly was diatropic from the chemical shifts of the internal and external macroring protons. The compound, however, was found to rapidly



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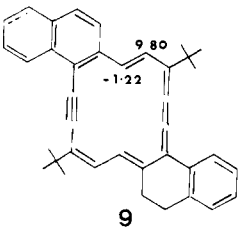
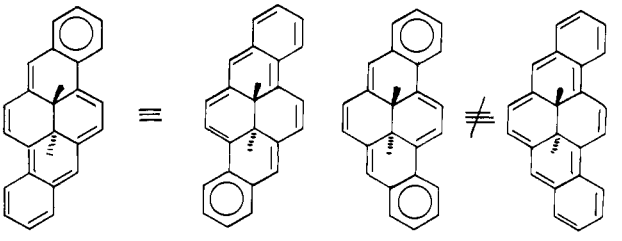


9

$\Delta\delta$ = 13·67 $\Delta\delta$ = 11·02

react with oxygen and could not be isolated in the solid state. Most interestingly though, **8** was considerably more diatropic than the mononaphthannelated derivative[7] **9**. Subsequently he reported[8] that this may be because the Kekulé structures that can be written for **8** are of identical π energy ("equivalent") but are not for **9**. The molecules that we were synthesizing, namely **4–7**, were to provide a striking verification of his hypothesis in that **6** (or **7**) can be written with two pairs of equivalent Kekulé structures, and hence should be strongly diatropic, whereas those of **4** (or **5**) have structures that are not equivalent, are of widely different energy (dominated by the two benzene rings), and thus would be predicted to be much less diatropic in the macroring. Nakagawa reported



6 **4**

studies in the [18]annulene series that would support the above suggestion, since he found that the dinaphthannelated derivative **10** (analogous to **4**)8 was *less* diatropic in the macroring than the mononaphthannelated species **11** (which is analogous to **1**). It would be desirable, however, to have the pair of isomers, such as **4** and **6**, that correspond to either **8** or **10**, for final comparisons in this series. Nakagawa also reported[9] the preparation of the

(1) Benzannelated Annulenes. 8. For part 7 see; R. H. Mitchell, J. S. H. Yan, and T. W. Dingle, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) R. H. Mitchell, R. J. Carruthers, L. Mazuch and T. W. Dingle, *J. Am. Chem. Soc.*, this issue.
(3) *Chemical Abstracts* would probably call **4** *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*rst*]pentaphene and **6** *trans*-13b,13c-dimethyl-13c,13b-dihydrodibenzo[*b*,*def*]chrysene.
(4) For a preliminary report see: R. H. Mitchell, R. J. Carruthers, and L. Mazuch, *J. Am. Chem. Soc.*, **100**, 1007 (1978).
(5) For a review see: R. H. Mitchell, *Isr. J. Chem.*, **20**, 594 (1980).
(6) M. Iyoda, M. Morigaki, and M. Nakagawa, *Tetrahedron Lett.*, 817 (1974).
(7) M. Iyoda, M. Morigaki, and N. Nakagawa, *Tetrahedron Lett.*, 3677 (1974).
(8) M. Iyoda and M. Nakagawa, *Chem. Lett.*, 815 (1975).

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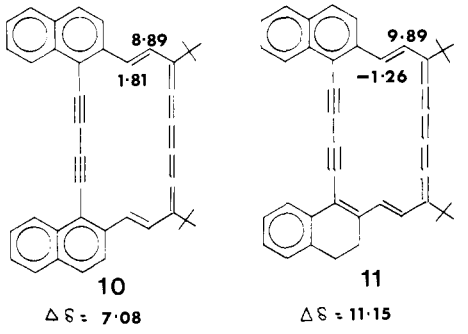
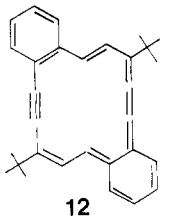
dibenzannelated annulene **12**, but unfortunately was not able to record its NMR spectrum. He reported that the deep blue **12** rapidly decomposed even at −78 °C.

We hoped that both **4** and **6** would be sufficiently stable for a detailed study of their properties to be made.



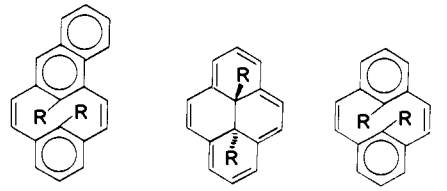
10 Δδ = 7·08 **11** Δδ = 11·15



12

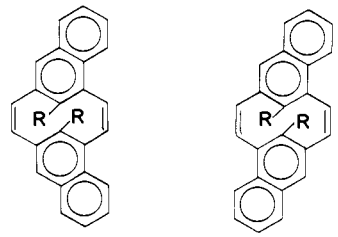
Synthesis

As we discussed in the previous paper,[1] the monobenzannelated annulene **1** was the product isolated in a synthesis leading to the cyclophanediene **13**. This was also the case for the parent dimethyldihydropyrene **14** obtained through **15**.[10] We therefore



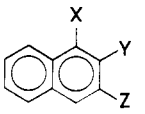
13 R = CH_3 **14** R = CH_3 **15** R = CH_3
18 R = H **19** R = H **20** R = H

hoped, but for the same arguments given[1] could not be sure, that **4** or **6** would be accessible from the analogous **16** and **17**. In the



16 R = CH_3 **17** R = CH_3
21 R = H **22** R = H

case of the compounds with internal −H substituents we were less certain. Experimentally it was more difficult to convert **18** into **2** than it was to convert **20** into the parent **19**. This difference between the internal −H and $-CH_3$ substituted series probably reflects slight differences in the relative energies of the cyclophanedienes, with the $-CH_3$ series being the more strained due compression of the $-CH_3$ substitutent and the opposite π cloud in the anti conformation. Nevertheless, because of the much easier accessibility of the unsubstituted bromide **23** over **24**, we decided to attempt the synthesis of the hydrogen series, **21** and **22** first.



	X	Y	Z
23	CH_2Br	H	CH_2Br
24	CH_2Br	CH_3	CH_2Br
25	CH_2SH	H	CH_2SH
26	[illegible]	H	[illegible]
38	Br	CH_3	CH_3
39	CN	CH_3	CH_3
40	CN	CH_3	CH_2Br
41	CHO	CH_3	CH_2Br
42	CH_2OH	CH_3	CH_2Br
43	CH_2SH	CH_3	CH_2SH

Dihydropyrenes 5 and 7. 1,3-Bis(bromomethyl)naphthalene[1] (**23**) was converted in 84% yield to the bisthiol **25**, through the bisisothiouronium salt **26** with use of thiourea and then base in the normal way.[10] The thiol, **25**, mp 38 °C, showed distinct ^1H NMR signals for each $-CH_2SH$ group and M^+ at *m/e* 220 confirming its structure. Coupling of **25** with the bromide **23** under high dilution conditions[11] with use of KOH in ethanol–benzene yielded 53% of a 1:1 mixture of the thiacyclophanes[12] **27** and **28**. These were separated by careful chromatography on silica gel, monitoring fractions by ^1H NMR, since almost identical R_f values were observed on TLC. The methylene bridge absorptions at δ 4.12 and 3.83 for **27** and at δ 4.16 and 3.79 for **28** were most useful for this purpose. Both thiacyclophanes were assigned the syn stereochemistry on the basis of the internal aryl hydrogens H-11, -22 which appear at δ 6.95 for both **27** and **28**, whereas anti conformers would have these protons shielded at ca. δ 5 by the opposite benzene ring.[13] The assignment of which isomer is **27** and which is **28** from their spectra is not trivial, though might be justified after the fact. We decided that the most unambiguous method of structure assignment was to carry each isomer through the sequence described below and to oxidize the final products **5** and **7** to the known dibenzopyrenes **29** and **30**. In the event the more soluble thiacyclophane, **27**, obtained as large colorless plates, mp 170–171 °C from cyclohexane, gave dibenzo[*a,h*]pyrene (**29**) and hence was assigned to the cisoid[14]-isomer **27**. The less soluble thiacyclophane, **28**, was obtained as a fine white powder from benzene, mp 188–189 °C, and gave dibenzo[*a,i*]pyrene (**30**) and thus must be the transoid-isomer **28**. Both isomers showed M^+ at *m/e* 372. The major difference in NMR spectra for the two isomers was the greater separation in chemical shift of the two types of methylene bridge protons and carbons in the transoid-isomer **28** (0.37 and 2.7 ppm, respectively) than in the cisoid-isomer **27** (0.29 and 1.6 ppm). The ring–ring π repulsion is possibly greater in **27** and **28** and results in a slightly different dihedral angle between the planes of the rings, which result in different torsional angles at the bridge methylene groups and hence different chemical shifts.

Wittig rearrangement[11] of both **27** and **28** occurred smoothly with *n*-butyllithium, followed by treatment with methyl iodide to yield quantitatively **31** and **32** each as a mixture of stereoisomers, which preparatively were used directly in the next step. In the case of **32**, a single isomer, e.g., **32A**, could be obtained by crystallization from cyclohexane as white needles, mp 245 °C dec.

(9) A. Yasuhara, M. Iyoda, T. Satake, and M. Nakagawa, *Tetrahedron Lett.*, 3931 (1975).

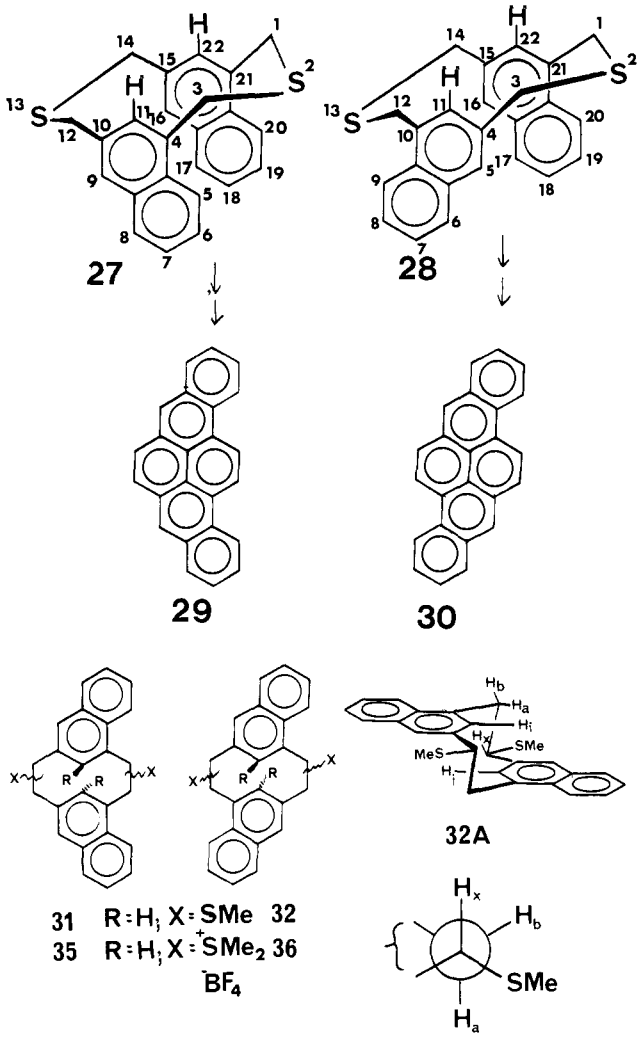
(10) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1547 (1974).

(11) (a) R. H. Mitchell, T. Otsubo, and V. Boekelheide, *Tetrahedron Lett.*, 219 (1975); (b) R. H. Mitchell, *Heterocycles*, **11**, 563 (1978).

(12) For the nomenclature used in these systems see: F. Vögtle and P. Neumann, *Tetrahedron*, **26**, 5847 (1970).

(13) W. Anker, G. W. Bushnell, and R. H. Mitchell, *Can. J. Chem.*, **57**, 3080 (1979).

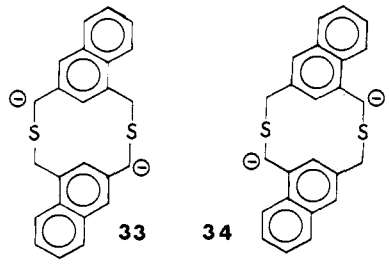
(14) Because syn and anti are used to specify the conformation of cyclophanes such as **27** and **28**, we will use cisoid and transoid to specify the orientation of the two benzene rings that are fused to the cyclophane. Thus **27** is a cisoid-syn compound, **6** is a transoid-trans compound and so on. See *J. Org. Chem.*, **35**, 2849 (1970).



Since the $-SCH_3$ ^1H NMR signals apppear as a singlet at δ 2.20, they must both be equivalent. They are probably pseudoequatorial because of (a) their chemical shifts, (b) a deshielded adjacent ring proton (singlet at δ 8.2), and (c) a normal[10] shielded resonance at δ 4.44 (singlet) for the internal aryl proton (again indicating both $-SCH_3$ groups are the same).[10] Moreover, the methine proton H_x shows a coupling constant of J_{xa} = 13 Hz which can only arise if H_x is in a pseudoaxial position.

The assignment of whether the $-SCH_3$ groups are attached to the α- or β-naphthyl positions is more difficult and can only be made by detailed comparison of chemical shifts (Figure 1) when clearly the β position is preferred,

Based on the ^1H NMR spectrum of the crude reaction mixture, this is the major isomer present and thus would appear to indicate that dianion **33** is preferred over **34**. This is consistent with the anticipated stability of the anions, based on steric arguments in which 1-naphthyl anions are destabilized by peri interactions.[15]



Hofmann eliminations on the salts **35** and **36** (prepared by treating **31** and **32** with the Borch[16] methylating reagent, $(C_2H_5O)_2CHBF_4$, were carried out with use of potassium *tert*-butoxide in THF at 0 °C, but the yields were very poor, probably because of competing Stevens rearrangements.[11b] The cisoid-diene **21** was only obtained in 1.4% yield from **35** together with dibenzo[*a*,*h*]pyrene (**29**) in 6% yield. Diene **21** was obtained as unstable yellow crystals, mp ~110 °C with decomposition, turning deep orange. This resolidified and then darkened above 280 °C. On standing in solution (and to a lesser degree in the solid state) **21** rapidly formed the dibenzopyrene **29**, which was readily identified by its characteristic UV spectrum[17,18] and mp 278 °C (lit.[18] mp 280 °C), This conversion appears to go faster than for the parent **20**, and it was not possible to achieve a reliable UV or mass spectrum of **21**. Its ^1H NMR spectrum showed all protons as a multiplet from δ 8.7–7.4. Irradiation of this sample sealed in degassed THF-d_8 under vacuum, with 253.7-nm light, gave no indication of substantial formation of dihydropyrene **5**, unlike the case of **20** → **19**, only the pyrene **29** being obtained. Presumably this occurred through **5**.

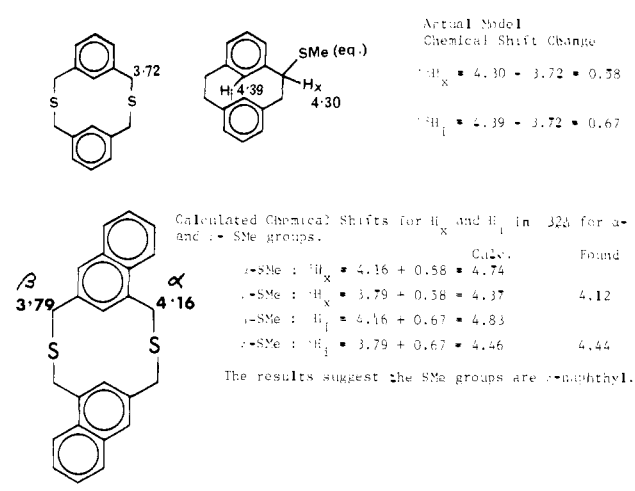


Figure 1. Chemical shift calculations for H_x and H_i of **32A** based on model data.[10]

Hofmann elimination of **35** gave the transoid-diene **22** in somewhat better yield (8,5%), together with 31% of dibenzo[*a*,*i*]pyrene (**30**), and thus in overall yield (~40%) was more comparable with the parent system (**20**, **19**).[10]

The diene **22** after chromatography was pale yellow, mp 186–196 °C, but rapidly turned orange on standing due to formation of **30**. This conversion also occurred in solution, and the pyrene **30** isolated showed identical UV spectrum[19] with that reported,[19,20] mp 310 °C (lit.[20] mp 308 °C) and M^+· at *m*/*e* 302.

The ^1H NMR spectrum of diene **22** showed a multiplet at δ 8.3–6.7 (clearly discernible from those of pyrene **30** at δ 9.3–7.7) and a doublet (J = 10.5 Hz) at δ 5.80. Because of overlap with the pyrene, it is difficult to be certain of the integration ratio of these peaks (15:1 found), and thus whether the doublet is real or an impurity. Perhaps it arises by disproportionation, which does occur in the mass spectrum of **22** (mol wt 304), where peaks at *m*/*e* 302–308 inclusive are found.

Irradiation of a solution of the diene **22** in degassed THF-d_8 under vacuum at 253.7 nm developed a green color. When the irradiation was carried out at −100 °C, the green color was much stronger. It faded either on warming the tube to room temperature or slowly on removing the light source (sample at −100 °C). Reirradiation, however, reproduced the green color.

We interpret this green color as being due to the dihydropyrene **7**. It is pertient to note that the parent **19** is green, as is the

(15) For a review see: V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(16) R. F. Borch, *J. Am. Chem. Soc.*, **90**, 5303 (1968); *J. Org. Chem.*, **34**, 627 (1969).

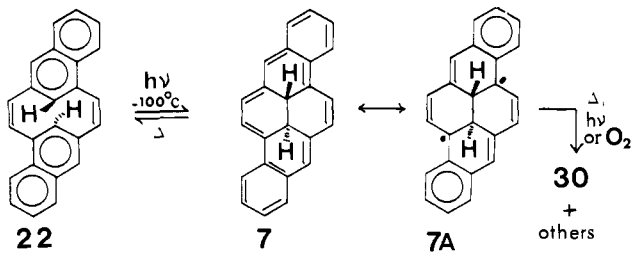
(17) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley and Sons, New York, spectrum No. 572.

(18) E. Clar, "Polycyclic Hydrocarbons", Vol. II, Academic Press, London, 1964, II, p 153.

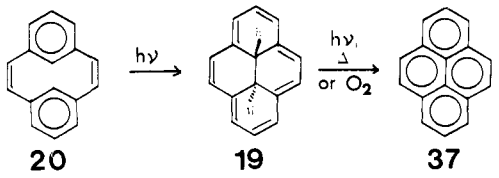
(19) Reference 17, spectrum No. 573.

(20) Reference 18, p 151.

dimethyldibenzo compound **6** (which we discovered much later). Despite intensive efforts, however, we were not able to obtain a ^{1}H NMR spectrum of **7** either at 20 °C or at −100 °C. At the



time we were not only disappointed but unable to understand why. Subsequently, we discovered that the dimethyl compound **6** behaves anomalously for a hydrocarbon, in that its ^{1}H NMR spectrum broadens and collapses on cooling (see below) and even at room temperature its peaks are much broader than normal. We interpret this behavior to be due to some radical contributors (see below) analogous to **7A**. The presence of **7A** would explain our inability to record a ^{1}H NMR spectrum and the extreme reactivity of the compound, It is interesting to note that **20** on irradiation forms **19** irreversibly and subsequently can be over irradiated, heated, or exposed to air to give only pyrene **37**.[10] In the case of the benzodiene **18**, conversion to **2** was difficult, though not apparently reversible.[2] It would appear that in the case of



22, the reverse reaction is now favorable, even more so than in the dimethyl parent (**15** → **14**). This must reflect the relatively small strain in **22** (in comparison to **17**) and the lower degree of aromaticity of **7** (in comparison to **19**).

While the preparation of the dienes **21** and **22** had been useful for structural assignments (via **29** and **30**), any understanding of the properties of the benzannulenes **5** and **7** would have to wait until the preparation of the dimethyl compounds **4** and **6** could be achieved. The latter should not suffer from the "oxidation to pyrene" problem and, based on previous examples,[1,2,10] should be reasonably stable, easily purified, and hopefully analyzed spectroscopically.

Dimethyldihydrodibenzopyrenes 4 and 6. We have previously described[2] a preparation of the dibromide **24**. Because of the extensive chromatography that this route involved, we attempted to improve the synthesis as follows: reaction of 1-bromo-2,3-dimethylnaphthalene[2] (**38**) with CuCN in *N*-methyl-2-pyrrolidinone gave 79% of 2,3-dimethyl-1-naphthonitrile (**39**), mp 83.5–84.5 °C, The free-radical bromination of **39** (20-g scale) gave about 20% of the desired 3-bromomethyl **40** pure, mp 131–133 °C, by direct crystallization, and thus although a lesser yield was obtained than desired, it did not require expensive purification techniques. The structure of **40** was readily confirmed by its $M^{+\cdot}$ at *m/e* 261/259 and the ^{1}H NMR spectrum which showed the 3-CH_2Br group at δ 4.60 and the 2-CH_3 group at δ 2.77. The −CH_2Br resonance is normal for a β substitutent (cf **24**, 4.63),[2] whereas next to the nitrile it would have been deshielded by about 0,2 ppm (cf. **39**). Further proof was provided by its ultimate conversion to **24**. The nitrile was then subjected to the usual sequence, DIBAL to give aldehyde **41**, mp 120–121 °C, $NaBH_4$ to give alcohol **42**, and then concentrated aqueous HBr to give the desired bromide **24** (57% yield over the three steps), identical with an authentic sample. The overall yield from 2,3-dimethylnaphthalene was thus about 8%, though in a simply executed rapid sequence.

The bromide **24** was converted to the dithiol **43**, in the same manner as for **23** → **25**, in 85% yield and gave colorless needles,

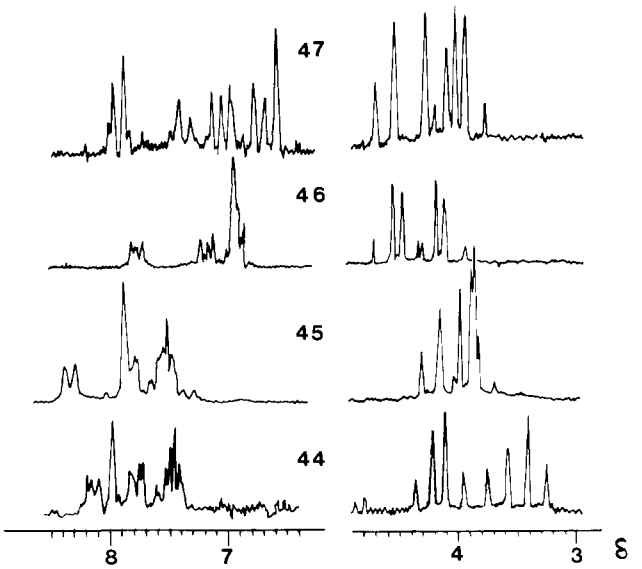


Figure 2. ^{1}H NMR spectra (90 MHz $CDCl_3$) of the aryl and methylene bridge proton regions of the dimethyldithiacyclophanes **44–47**.

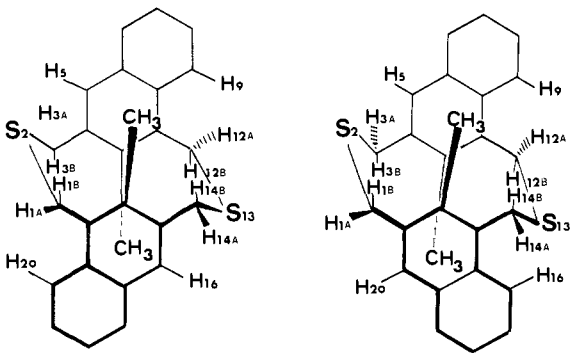
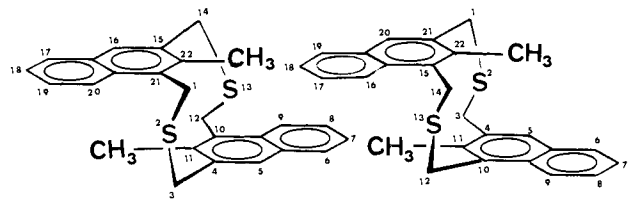


Figure 3. Preferred conformations of the *anti*-dithiacyclophanes **44** and **45**.

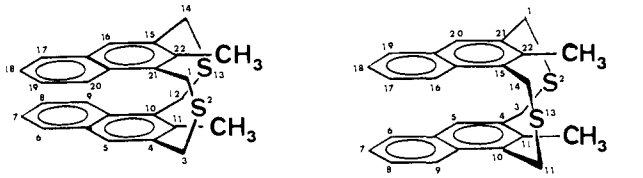
mp 88–89 °C, with readily distinguished −CH_2S− ^{1}H NMR signals at δ 4.04 (α) and δ 3.75 (β) and −SH signals at δ 1.68 (α) and δ 1,64 (β).

Coupling of the thiol **43** and bromide **24** proceeded smoothly to give, after chromatography, a 75% yield of the desired thiacyclophanes as a mixture of the four possible isomers **44–47**. The transoid-anti-isomer **44** was by far the least soluble, and extraction of the isomer mixture with boiling dichloromethane left behind this isomer, which could then be subsequently crystallized from benzene as white needles, mp 296–298 °C. The other isomers were far more difficult to separate and required several chromatographs on silica gel followed by fractional crystallization to obtain pure compounds. The anti-isomers **44** and **45** were readily distinguished from the syn-isomers **46** and **47** by the chemical shifts of the internal −CH_3 groups, which were shielded for **44** (δ 1.00) and **45** (δ 0.98) as expected[1,2,10] and normal for **46** (δ 2.69) and **47** (δ 2.62), However, although by ^{1}H NMR distinction of **44** from **45** (and **46** from **47**) was easy, assignment was not (cf. **27** and **28** above). We thus present the aryl and methylene bridge proton regions of the four ^{1}H NMR spectra in Figure 2.

Anti-Isomers 44 and 45. The assignment of which isomer is **44** and which is **45** can probably only be achieved unambiguously by X-ray crystal structure determination or by ^{33}S NMR. The more symmetric *transoid*-**44** should have one ^{33}S resonance, whereas *cisoid*-**45** should have two. In the absence of these data, however, we have made the assignments as follows. The much less soluble isomer, mp 296–298 °C, was assigned the transoid-structure **44** (compare **28**, also much less soluble). The more

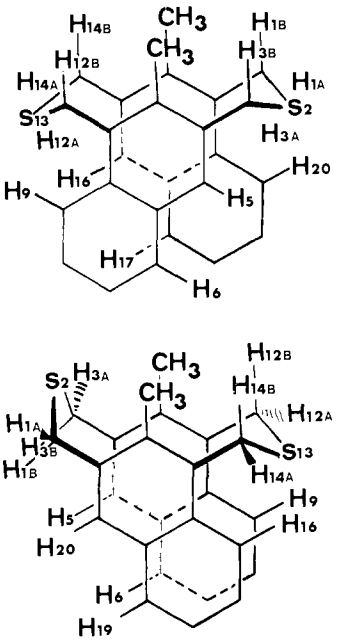


44 45



46 47

soluble cisoid isomer is thus the one of mp 290–292 °C. These original assignments were also made by a careful analysis of the ^{1}H NMR spectra, with the help of molecular models, and this is given below.[21] They were finally confirmed when **4** and **6** were later synthesized and could be unequivicably assigned on the basis of the high-field (250 MHz) ^{1}H NMR spectra of their aryl protons. About equal amounts (30% yield each) of each isomer were obtained. The assignments of the *syn*-cyclophanes were also made by ^{1}H NMR,[21] and lead to the lesser soluble (when pure), higher melting (282-283 °C) isomer to be *transoid*-**46** (compare **44**) and then the lower melting (175-176 °C) isomer to be *cis-coid*-**47**. These need to be confirmed either by X-ray crystallography or ^{33}S NMR.



46

47

Figure 4. Preferred conformations of the *syn*-dithiacyclophanes **46** and **47**.

The yields of **46** and **47** were ~6% and ~9%, respectively. The ratio of anti:syn product for **46**:**44** and **47**:**45** was thus about 5:1 to 3:1. This seems to be a somewhat lower ratio than for the parent system (7:1).

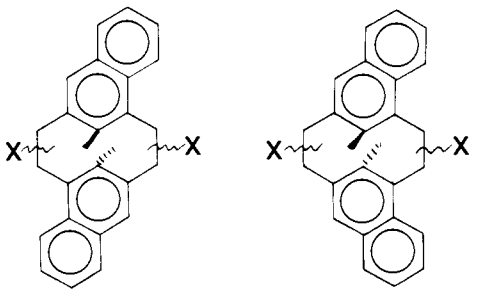
The ^{13}C NMR results of interest are given in Table I. The bridge methylene assignments are based on the results of Grant et al.,[22] who found that in ^{13}C NMR, the α-naphthyl carbon is shielded. Several points arise from the data of the whole series. The carbon of an internal methyl group of an *anti*-cyclophane is shielded with respect to its position in a *syn*-cyclophane by ca. 2.3–2.8 ppm. This can be compared with the corresponding shielding of the analogous protons of ca. 1.2–1.7 ppm and presumably reflects in part the fact that the carbon must be situated closer to the center of the magnetic field than the protons, though the difference is too large based on ring current calculations[21] and so probably includes a steric contribution. We hope further work will clarify these observations. It is of further interest to note that the bridge methylene carbons of the *syn*-cyclophanes are *deshielded* with respect to those of the *anti*-cyclophanes by ca. 5 ppm, an effect which is much larger than the analogous proton effect (ca. 0.4 ppm). This may be useful diagnostically in the future when internal substituents are present that are not suitable as NMR probes themselves.

Wittig rearrangement[11a] of both **44** and **45** with *n*-butyllithium in THF followed by methyl iodide quench gave mixed isomers of **48** and **49**, respectively, in essentially quantitative yields, which after conversion to the sulfonium salts **50** and **51**, respectively, as previously described, underwent Hofmann elimination with potassium *tert*-butoxide at 0 °C in THF. Purification of **6** or **4** by chromatography had to be carried out with use of deactivated silica gel with a minimum contact time and by using N_2-purged solvents (avoiding chlorinated hydrocarbons) and subsequent conversion into the solid state for storage. Even so, the yields in this step were very variable (20–80% yields), particularly for **6**. In some cases all material was lost on the surface of silica or alumina, possibly by ion–radical formation.[23]

(21) Assignment of stereochemistry of **44** and **45** based on ^{1}H NMR. Figure 3 attempts to display a preferred conformation of each isomer which minimizes any interaction between the α-bridge methylene protons and the *peri*-naphthalene hydrogens.[15] This requires that in **44**, for example, H-1A is out of the naphthalene plane to avoid interaction with H-20, and thus H-1B must be in the plane pointing toward the shielding region of the opposite ring. Since H-1 (and H-12) are α-naphthyl substitutents, they are therefore deshielded with respect to H-3 and H-14. Thus H-1A, -12A are at δ 4.28 and H-1B, -12B at δ 4.08. Then H-3B,14B point to the other rings and are thus at δ 3.37 and H-3A, -14A are at δ 3.67. Analogous arguments can be made for **45** to minimize the H-9–H-12A interaction, but then H-16–H-14B do interact, so this isomer must skew more to avoid this. The net assignment then puts H-12A, -14A most deshielded (α-naphthyl) at δ 4.19 and H-12B, -14B at δ 3.91 with the β-naphthyl protons H-1A, -3A at δ 3.90 and H-1B, -3B at δ 3.82. The net effect of this assignment is then: (i) on average H-3B, -14B must be more shielded than H-1B, -3B, since only one of the latter can be shielded by the opposite ring at any one time (this accounts for the greater chemical shift difference between the bridge methylenes in the transoid isomer than in the cisoid isomer (a result also found from the known **27** and **28**)); (ii) as a consequence *on average*, the isolated protons H-5(16) in *transoid*-**44** are closer to the deshielding S-2(13) than their counterparts H-5,20 are to S-2, and thus should appear at greater chemical shift, which they do, δ 7.97 vs. δ 7.84; (iii) similarly the only other easily assigned ring hydrogens H-9(20) of **44** are less close to S-13(2) on average than H-9, -16 are to S-13 of **45** and hence the latter should be the more deshielded, which they are; δ 8.30 vs. δ 8.12. Similar arguments can be attempted for the syn-isomers **46** and **47**, the believed preferred conformer of each being shown to Figure 4. In each case the peri interactions are kept at a minimum such that for example in **46** H-12A is out of the plane in which H-9 lies, and similarly H-3A is out of plane with H-5. Since H-1B, -3B, -12B, and -14B all lie in the deshielding region[22a] of the opposite ring the shifts can be assigned an α-naphthyl (H-1B, -12B at δ 4.57, H-1A, -12A at δ 4.39) and a β-naphthyl (H-3B, -14B at δ 4.19 and H-3A, -14A at δ 4.05). In **47**, H-12A, -14A are out of the planes of H-9 and -16, respectively, to minimize the peri interaction, while H-1A, 3A are out of the ring planes to minimize interaction with the methyl groups. The assignments than are H-12B, -14B at δ 4.48, H-12A, -14A at δ 4.22, H-1B, -3B at δ 4.01, and H-1A, -3A at δ 3.87. As a consequence, consider the most shielded β-naphthyl protons H-1A, -3A of **47** and H-3A, -14A of **46**; the latter clearly should be deshielded by the unsubstituted ring of the opposite naphthalene more than the former, which in our assignment they are by 0.18 ppm. As a second consequence only in the transoid conformer **46** should H-5, -6, -16, -17 (all α-naphthalene hydrogens) be strongly shielded (~0.7 ppm) by the opposite ring (which they appear to be at δ 7.1–7.3), whereas the β-naphthalene protons H-7, -8, -18, -19 should remain normal or marginally shielded by the opposite ring. This would appear to be the case on comparison of **46** and **44**, and only H-9, -20 (α-type) are left deshielded. On the other hand, *cisoid*-**47** also has its β-naphthalene protons shielded, and thus of the two isomers should show the *most* shielded hydrogens, which it does at δ ~6.5.

(22) (a) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); J. W. Emsley, F. Feeney, and L. H. Sutcliffe in "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergammon Press, Oxford, 1965, p 595; (b) D. K. Dalling, K. H. Ladner, D. M. Grant, and W. R. Woolfenden, *J. Am. Chem. Soc.*, **99**, 7142 (1977).

(23) B. D. Flockhart, I. M. Sesay, and R. C. Pink, *J. Chem. Soc., Chem. Commun.*, 439 (1980).



48 X=SMe **49**

50 X= $\overset{+}{S}Me_2$ $\bar{B}F_4$ **51**

***transoid*-Dihydropyrene 6.** This was obtained as dark blue crystals, mp 196–197 °C, which give a green liquid, immediately turning brown. Solutions of **6** rapidly decompose when exposed to O_2 or light, especially when chlorinated solvents are used. In the solid state, at ca. −30 °C in the dark, **6** seems reasonably stable. The color and ^1H NMR spectrum left no doubt that **6** was the dihydropyrene and not the cyclophanediene **17**, in that the internal methyl protons appeared at δ −3.58. In fact, as with **1**,[1] no evidence for any substantial (>3%) formation of **17** could be found even on prolonged irradiation of **6** with incandescent light.

***cisoid*-Dihydropyrene 4.** This was obtained as green crystals from cyclohexane, mp 218–220 °C. It was readily distinguished from **6** by its ^1H NMR spectrum in which the internal methyl signal is at δ 0.02. Solutions of **4** were very much more stable to O_2 and $h\nu$ than was **6**, though it was still readily decomposed on silica. It was thus not at all easy to separate mixtures of **4** and **6**, and thus separation is recommended at the thiacyclophane stage. Like **6**, no evidence was found of its conversion to **16** with light. The structures of **4** and **6** were fully confirmed by ^{13}C NMR (see below), $M^{+\cdot}$ at *m/e* 332 (with ready loss of both methyl groups), and analysis.

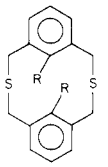
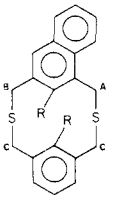
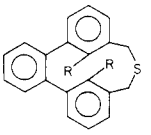
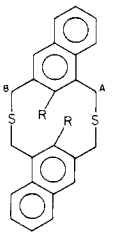
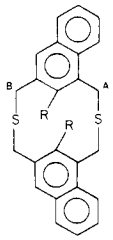
Discussion

The difference in diatropicity as measured by the chemical shifts of the internal methyl groups of **4** and **6** is quite outstanding and should be compared with the data obtained previously,[1,2] Table II.

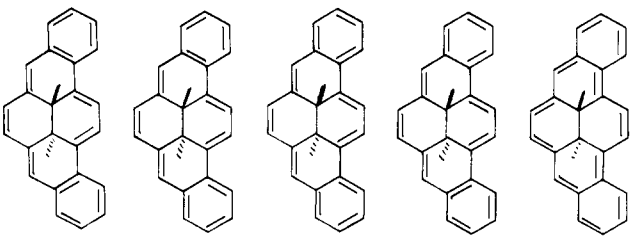
A steady decrease in diatropicity of the macroring is observed on passing from parent **14**, to monobenzo-**1**, to dibenzo-**4**. This is reflected in the shielding of not only the internal protons, but also the internal methyl carbons and bridge carbons, and this shielding falls off quite dramatically as estimated by the percent $\Delta\delta$ of the parent [$\Delta\delta = \delta_{annulene} - \delta_{model}$(**52**)]. Such a change in $\Delta\delta$ is far too great[1,21] just to be a diamagnetic shielding by the added benzene rings and must represent a real reduction in ring current and delocalization in the macrorings of **1** and **4** relative to **14**. Because of the extreme sensitivity of ^{13}C shifts to other factors,[25] exactly the same values of percent $\Delta\delta$ for ^1H and the two types of ^{13}C cannot be expected; however, the general order of agreement is excellent.

Consideration of the data obtained for *transoid*-annulene **6** reveals that it is strongly diatropic, which is dramatically different from **4**. Such a result implies that a strong ring current and hence good delocalization must occur in **6**. Pictorially this can be rationalized by consideration of the different Kekulé structures involved. In **4A–4D**, two benzene delocalizations can always be present, and regardless of the benzene rings, the macroring is always localized. Only when **4E** contributes does the macroring become delocalized, but now at the expense of both benzene ring

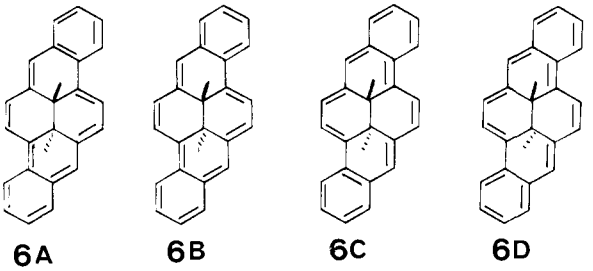
Table I. Selected ^{13}C NMR Data for Several Thiacyclophanes (δ)

conformation			chemical shift values, δ, ($CDCl_3$), of $-CH_2S-$	$-CH_3$
	R = H	syn	38.3	
	R = CH_3	syn	37.3	17.7
		anti	32.0	15.1
	R = H	syn	38.0 (B), 37.4 (C), 35.6 (A)	
	R = CH_3	syn	37.9, 37.1, 35.7 (B, C), 30.0 (A)	17.6, 17.3
		anti	32.3, 31.4, 31.0 (B, C), 27.1 (A)	15.3, 14.9
	R = CH_3	anti	30.7	17.4
	R = H	syn	37.7 (B), 35.0 (A)	
	R = CH_3	syn	38.3 (B), 30.7 (A)	18.3
		anti	31.5 (B), 27.0 (A)	15.5
	R = H	syn	37.5 (B), 35.9 (A)	
	R = CH_3	syn	35.9 (B), 30.0 (A)	18.0
		anti	31.6 (B), 27.9 (A)	15.3

delocalizations; clearly **4A–4D** dominate, which results in only a small ring current (delocalization) in the macroring. In the case of **6**, however, every structure contains one benzene ring with **6A** being equivalent to **6C** and **6B** to **6D**. If all four structures were



4A **4B** **4C** **4D** **4E**



6A **6B** **6C** **6D**

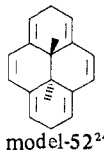
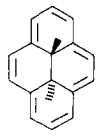
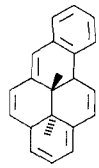
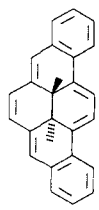
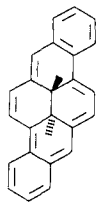
of identical energy then delocalization in the macroring would

(24) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1965 (1967); R. DuVernet and V. Boekelheide, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 2961 (1974).

(25) See, for example: F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, 1978, p 27.

(26) It is recognized that both the number of π electrons and the ring area affect the actual shielding involved, but in the case of **14** and **6B**, for example, these factors approximately cancel each other.

Table II. Chemical Shift Data for Dimethyldihydropyrenes ($CDCl_3$ Solution)

	internal hydrogens			internal methyl carbon			internal bridge carbon		
	δ	Δδ (annulene model), ppm	% Δδ of parent	δ	δΔ	% Δδ of parent	δ	Δδ	% Δδ of parent
 model-52[24]	+0.97			23.6			39.2		
 14	−4.25	−5.22	100	14.0	−9.6	100	30.0	−9,2	100
 1	−1.60	−2.57	49	17.0 17.7	−6.6 −5.9	69 61	35.5 36.0	−3.7 −3,2	40 35
 4	+0.02	−0.95	18	19.2	−4.4	46	39.5	+0.3	0
 6	−3.58	−4.55	87	15.9	−7.7	80	32.8	−6.4	70

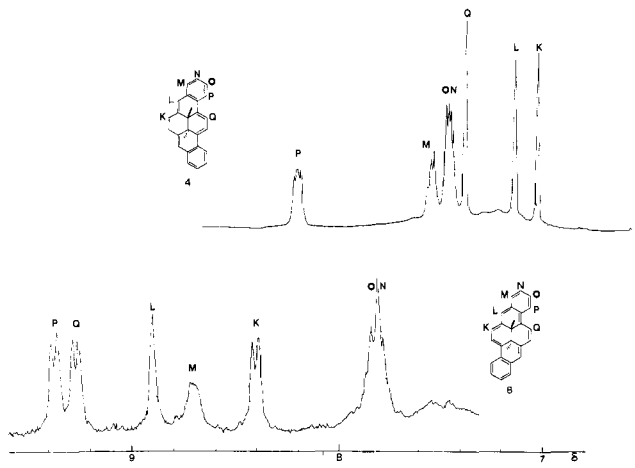
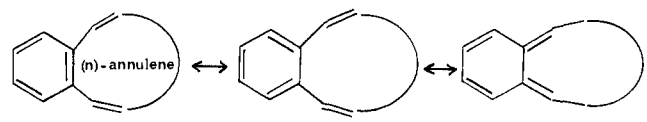


Figure 5. ^1H NMR spectra (250 MHz CD_2Cl_2) of the external protons of the dibenzannulenes **6** and **4**.

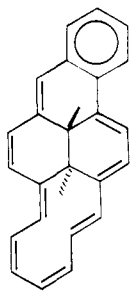
be complete and hence **6** would be maximally diatropic. In reality, probably **6A** is not of exactly the same energy as **6B** and hence the compound is strongly diatropic, though not as much as the parent **14**. Compound **6** might be though of as a monobenzo-[18]annulene, but careful examination of the Kekulé structures for any monobenzannulene reveals there are three possible structures, **52A–52C**, whereas for **6**, four are contributing.



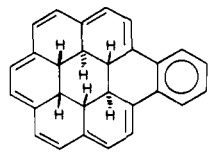
52A **52B** **52C**

Providing [*n*] is not too large in **52**, all three structures would contribute, and thus delocalization will occur, but not as much as would be expected for **6**. The larger [*n*] becomes, the less important **52C** becomes, and the more localized would be the macroring. Thus **6** should be more diatropic than the hypothetical monobenzo[18]annulene **53**. The closest model is Boekelheide's[27] benzohexahydrocoronene **54** in which the internal protons appear at δ −1,0 to −2,6. Since in the parent **55** they are at δ −6.5 to −8.0, clearly the ring current in **6** is much larger than in **54** (and hence the hypothetical **53**) lending considerable support to the idea that

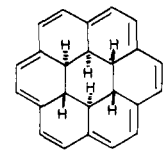
(27) T. Otsubo, R. Gray, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2449 (1978).
(28) C. W. Haigh and R. B. Mallion, *Mol. Phys.*, **18**, 751 (1970).
(29) K. D. Bartle, D. W. Jones and R. S. Matthews, *Spectrochim. Acta, Part A*, **25A**, 1063 (1969).
(30) This work. Values in parentheses calculated from C. W. Haigh and R. B. Mallion, *Mol. Phys.*, **18**, 767 (1970). Corrected for steric factor.



53



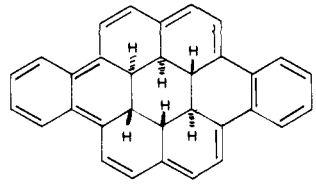
54



55

6, as far the macroring is concerned, should not be considered as a benzannulene, but is more like a perturbed annulene. This point will be examined further below.

With the data presented above, and additional fact[27] that the dibenzo derivative of **55**, namely **56**, is more diatropic (internal



56

protons at δ −3.5 to −5.3) than **54**, and Nakagawa's data discussed in the introduction, and elsewhere,[5] there can now be no doubt that analysis of the Kekulé structures of a benzannulene is a useful tool for qualitatively predicting relative diatropicities. In order to take the analysis now to a quantitative level, we have analyzed the spectral data in more detail. The following paper, for the whole series of compounds discussed, attempts to relate quantitatively diatropicity to delocalization, as calculated and measured by bond orders. We therefore now, as with the previous[1,2] examples **1** and **2**, attempt to relate calculated bond orders with experimentally determined ^{1}H NMR coupling constants.

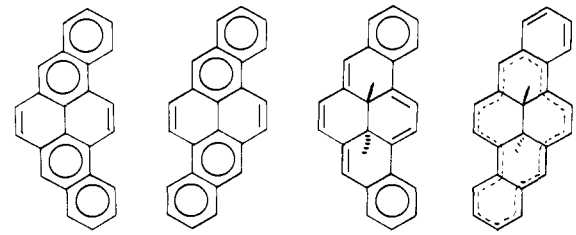
Figure 5 presents the 250-MHz ^{1}H NMR spectra for the external protons of **6** and **4**. Since these spectra can be assigned *unambiguously* to **6** and **4**, respectively (because of the two different types of symmetry), they confirm our assignments of the thiacyclophanes **44** and **45** made above. The assignments (Figure 6) were made as follows: As with hydrocarbons **1** and **2** the bay protons of **6**, H-4, -11 and H-5, -12, appear as doublets (J = 7.4 Hz each) at lowest field, δ 9.39 and δ 9.29, respectively. Since the whole spectrum shows peaks of relatively large line width (7 Hz, see below), further couplings are not well resolved, and hence this assignment, made by comparison to **1**, could be reversed. The singlet at δ 8.90 is readily assigned to H-7, -14, and then the only other simple doublet at δ 8.39 (J = 7.4 Hz) must be H-6, -13. This is also consistent with chemical shift data of **1**. The broad unresolved peak at δ 8.70 is then assigned to H-1, -8, leaving the most shielded protons H-2, -3, -9, -10 as the multiplet centered at δ 7.78.

In the case of **4**, the bay protons on the benzene ring H-1, -12 are most deshielded at δ 8.25 with the other bay protons H-13, -14 being the singlet at δ 7.40. The other singlet signals at δ 7.16 and 7.05 are assigned to H-5, -8 and H-6, -7, respectively, by comparison with the earlier examples, leaving H-2, -3, -10, -11 as the most shielded multiplet at δ 7.47 and H-4, -9 at δ 7,58. It is quite interesting to compare **14**, **1**, **6**, and **4** with their corresponding pyrenes **37**, **57**, **30**, and **29**, respectively (Figure 6). In the case of the parent **14** and the *transoid*-annulene **6**, strong ring currents give rise to strong deshielding of the macroring protons (cf. the results for the internal substituents discussed above), stronger in fact than for the pyrenes **37** and **30**. However, **1**, with its reduced macroring current, shows less deshielding of its macroring protons than the pyrene **57**, and finally the much reduced ring current of **4** relative to **6** discussed above and also shows up very clearly in the reduced deshielding of its macroring external protons relative to both **6** and **29**. These results are quite consistent with the calculated bond orders for **4** and **6** given in Figure 7. It can be seen that in **4** there should be considerably greater bond localization (and hence reduced ring current) than in **6**, in contrast to the pyrenes **29** and **30** which have approximately equal localizations, less than **4** greater than **6**. Indeed both pyrenes have bond orders consisten with **58** and **59** being the major structure contributors, whereas the dihydropyrenes **4** and **6** are better represented by **60** and **61**, in which **61**, as mentioned above, is really a perturbed annulene type structure for **6**.

Table III. Calculated[31] Bond Orders ($P_{\mu,\nu}$), Alternance Parameters (Q), and Coupling Constants ($^3J_{\mu,\nu}$) for 4 and 6

	μ,ν	$P_{\mu,\nu}$	Q	$^3J_{\mu,\nu}$ (calcd), Hz	$^3J_{\mu,\nu}$ (calcd)[a]	$^3J_{\mu,\nu}$ (exptl),[b]
4	1,2	0.694	1.103	7.83	8.13	~8.0
	2,3	0.629	1.107	7.20	7.20	~7.0
	3,4	0.696		7.85	7.93	~8.0
	5a,6	0.488	1.598			
	6,7	0.780				
	13,14	0.488	1.627			
	14,14a	0.794				
6	1,2	0.735	1.254	8.22	8.30	7–8
	2,3	0.586	1.252	6.79	6.79	
	3,4	0.734		8.21	8.51	
	4b,5	0.672	1.058			
	5,6	0.635		7.26	7.64	7.4
	12,13	0.635	1.022			
	13,13a	0.621				

[a] Corrected[31] for the steric effect. [b] See text.



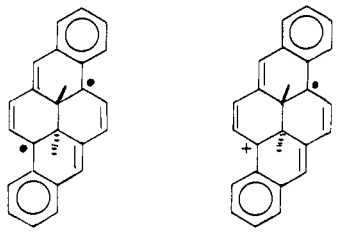
58 **59** **60** **61**

Coupling constants and alternance parameters can be derived from the calculated bond orders[31] (see Table III). Unfortunately with the limited number of data points used in recording the 250-MHz spectra of **4** and **6**, the experimental coupling constants could not be determined with sufficient accuracy to allow detailed comparison with the calculated results. This was particularly true for **6** which gave spectra with very broad lines (7 Hz line width) probably because of radicaloids being present. We do, however, hope to overcome these problems in the future. Similated spectra using the calculated values given in Table III, however, did give spectra very similar to those observed, providing confidence for our assignments.

The alternance parameters[32] (Q) given in Table III are worthy of comment. In **4** the Q values for the macrocyclic bonds are all large and in the examples given are ca. 1.6, the largest values found in this whole series. In **6** where values close to 1.0 are found, very little bond localization occurs in the macroring because of the opposing effects of the two benzene rings, unlike **4** where they reinforce each other. The results[1,2] for **1** and **3** are intermediate at about 1.3. Conversely, the benzene rings are most strongly localized in **6**, with a much lesser effect in **4**. The incentive to regain delocalization in the benzene rings of **6** much accounts for some of its unusual properties,[33] in particular the conversion to radicaloid species such as **62** and **63**.

We have already mentioned the broad lines in the ^{1}H NMR spectrum of **6**, (7 Hz, line width) whereas **4** is relatively normal (<2 Hz line width), which is consistent with the presence or

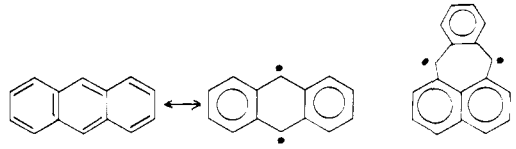
(31) See reference 1 for a detailed explanation of the calculations.
(32) D. Cremer and H. Gunther, *Justus Liebigs Ann. Chem.*, **763**, 87 (1972).
(33) R. H. Mitchell, R. V. Williams, T. W. Dingle, P. R. West, and R. J. Thompson, communication submitted.



62 63

formation of **62** and/or **63** from **6**. Moreover we also find that **6** reacts extremely rapidly with O_2, unlike **4**, and has unusual magnetic properties in the solid state. On attempting to measure the diamagnetic susceptibility exhaltation[34] of **1**, **3**, **4**, and **6**, which we anticipated would parallel the NMR results, we discovered that although **1**, **3**, and **4** were normal, the particular sample of **6** tested was paramagnetic with about 2 free-electron spins per mol.[35] Later we discovered that on cooling a ^1H NMR sample of **6**, the internal methyl signal, for example, broadened and almost collapsed at −70 °C in $(CD_3)_2CO$ but returned to normal on warming. In contrast the signal for **4** was still sharp at −95 °C. This behavior is also consistent with an increased concentration of species such as **62**/**63** as the temperature is lowered. Finally, calculations[33] indicate that **62** is of very similar energy to **6**, as is the case for corresponding radicaloids derived from **8**, **12**, and **56**, but not for the cisoid compounds such as **4** or **10**. This is supported by the UV data for **4** and **6** which have principal λ_{max} at 357 and 418 nm, respectively. The considerably longer wavelength λ_{max} for **6** indicates that its HOMO–LUMO gap must be much smaller than that for **4**, consistent with both calculations and probable involvement of **62**/**63**. However, more experimental work is underway to verify these suggestions.

Thus **4** can be considered as a true dibenzannulene, in which because of the powerful localizing power of the benzene rings the annulene only retains a portion of its normal ring current. In cases such as **6**, however, the benzene rings cannot both be delocalized and still retain a delocalized macrocyclic ring. The outcome then depends on the delocalization energy of the macrocyclic ring. In a 6π ring as in anthracene **64**, the diatropic form should be favored,[33] whereas a 7π ring as in **65** would favor the biradical.[36] In 14π and 18π rings such as **6**, **12**, or **56**, the balance is much closer and either form could predominate. We intend to explore further this aspect of the chemistry of benzannulenes.



64 65

Conclusions

We have successfully shown that dibenzannelated derivatives of **14** can be prepared and are diatropic. We have also shown that the relative positions of benzannelation are of extreme importance in determining the diatropic properties of the macroring. When dibenzannelation takes place such that delocalizations of the benzene ring oppose each other, i.e., when all contributing Kekulé structures have similar π energy, then the macroring is strongly diatropic, but the possibility exists that a biradicaloid form will participate in which both benzene rings can be localized. When the benzene rings are placed such that both can be localized simultaneously, then the macroring diatropicity is minimized. Finally, the use of dimethyldihydropyrene **14** as a sensitive probe of aromaticity associated phenomena has been strikingly verified.

(34) H. J. Dauben, J. D. Wilson, and J. L. Laity, *J. Am. Chem. Soc.*, **91**, 1991 (1969).

(35) Not all samples are paramagnetic. This seems to depend upon the rate of crystallization. Both paramagnetic and diamagnetic samples have been obtained from cyclohexane, which range in color from green to blue. Dissolution of the crystals gave identical ^1H NMR spectra and TLC properties.

(36) J. Kolc and J. Michl, *J. Am. Chem. Soc.*, **95** 7391 (1973).

Experimental Section

1,3-Bis(mercaptomethyl)naphthalene (25). A solution of the bromide **23** (9.0 g, 28.7 mmol) and thiourea (5.0 g, 66 mmol) were stirred in 95% ethanol (150 mL) under reflux for 40 min. After the solution was cooled, three-quarters of the solvent was removed by evaporation, and after further cooling the precipitate of the bisisothiouronium salt **26** was collected, to give 11.3 g (84%) of white powder. A sample after drying showed mp 244–245 °C. Anal. ($C_{14}H_{18}Br_2N_4S_2$) C, H.

The salt was then heated under reflux with KOH (33 g, 85%, 0.5 mol) in water (150 mL) under N_2 for 4 h. After the mixture was ice cooled, 50% H_2SO_4 was added until the solution was acidic, and then the thiol was extracted into ether (1 L total). The ether was washed, dried, and evaporated to leave the bisthiol **25** as a stinking oil, 5.3 g (84% from bromide **23**), which solidified on standing: mp 38 °C; ^1H NMR (60 MHz) δ 8.1–7.0 (m, 6, ArH), 3.96 (d, J = 7.5 Hz, 2, 1-CH_2S), 3.66 (d, J = 7.5 Hz, 2, 3-CH_2S), 1.81 (t, J = 7.5 Hz, 1, 1-SH), and 1.73 (t, J = 7.5, 1, 3-SH); M^+, m/e 220 (60), 187 (100), 155 (36), 154 (80), 153 (57), and 152 (60). Anal. ($C_{12}H_{12}S_2$) C, H.

2,13-Dithia[3,3](1,3)naphthalenophanes 27 and 28. A solution of the bromide **23** (8.21 g, 26.1 mmol) and the thiol **25** (5.75 g, 26.1 mmol) in N_2-degassed benzene (1 L) was added dropwise over 60 h, with vigorous stirring under N_2, to a solution prepared by dissolving KOH (10 g, 85%, 0.15 mol) in water (150 mL) and adding ethanol (1.35 L). The reaction mixture was then evaporated to dryness and water and dichloromethane were added. The organic layer was washed, dried, and evaporated. The residue was preabsorbed on silica gel (~100 mL) and chromatographed over silica gel (~900 mL), using benzene–pentane (3:7) as eluant, to give first the cisoid-isomer **27** and second the transoid-isomer **28**. Mixed fractions were rechromatographed. Since almost no difference in R_f was observed on TLC, ^1H NMR was used to separate the various fractions. The total yield was 5.17 g (53%), approximately equal amounts of **27** and **28**. The more soluble *cisoid*-**27** was recrystallized from cyclohexane as large colorless plates: mp 170–171 °C; ^1H NMR (90 MHz) δ 8.05–7.85 (m, 2, 5-, 20-ArH), 7.55–7.35 (m, 2, 8-, 17-ArH), 7.35–7.10 (m, 3, 6-, 7-, 9-, 16-, 18-, 19-ArH), 6.95 (bs, 2, 11-, 22-ArH), 4.12 (s, 4, 1-, 3-CH_2S), and 3.83 (s, 4, 12-, 14-CH_2S); ^{13}C NMR (15.1 MHz) δ 134.0, 133.6, 131.6, 129.8 (quaternary aryl carbons), 130.3, 127.85, 127.2, 125.5, 125.1, 123.8 (aryl CH), 37.5 (12-, 14-CH_2S-),[22] and 35.9 (1-, 3-CH_2S-); M^+, m/e 372 (52), 217 (33), 187 (33), 186 (48), 185 (50), 184 (35), 156 (40), 155 (100), 154 (30), 153 (38), and 152 (34). Anal. ($C_{24}H_{20}S_2$) C, H.

The less soluble *transoid*-**28** was recrystallized from benzene as a fine white powder: mp 188–189 °C; ^1H NMR (90 MHz) δ 7.95 (d, J = 7 Hz, 2, 9-, 20-ArH), 7.50–7.35 (m, 2, 6-, 17-ArH), 7.35–7.20 (m, 4, 7-, 8-, 18-, 19-ArH), 7.18 (s, 2, 5-, 16-ArH), 6.95 (s, 2, 11-, 22-ArH), 4.16 (s, 4, 1-, 12-CH_2S-), and 3.79 (s, 4, 3-, 14-CH_2S); ^{13}C NMR (15.1 MHz) δ 134.4, 133.7, 131.7, 129.9 (quaternary aryl carbons), 130.7, 128.2, 127.0, 125.3 (double), 123.2 (aryl CH), 37.7 (3-, 14-CH_2-),[22] and 35.0 (1-, 12-CH_2-); M^+, m/e 372 (60), 217 (32), 187 (20), 186 (33), 185 (35), 184 (31), 156 (35), 155 (64), 154 (25), 153 (26), 152 (24), 143 (33), 142 (25), and 141 (100); MH^+, (CI) m/e 373 (67), 171 (90), and 155 (100). Anal. ($C_{24}H_{20}S_2$) C, H.

Wittig Rearrangement of *cisoid*-27. *n*-Butyllithium (11 mmol, in 5.5 mL of hexane) was added from a syringe to a solution of the cyclophane **27** (1.86 g, 5.0 mmol) in dry THF (60 mL) under N_2 at ~20 °C. After 3 min, methyl iodide (~11 mmol) was added to discharge the color of the dark solution and then water and dichloromethane and aqueous HCl were added. The organic layer was washed, dried, and evaporated to yield **31** as an oil, 2 g (quantitative) as a mixture of stereoisomers: ^1H NMR (60 MHz) δ 8.3–6.7 (m, ~10, ArH), ~4 (bs, ~2, internal ArH), 4.0–1.5 (m, ~6, >CH–CH_2–), and 1.9 and 1.8 (s, 6 total, –SCH_3). This material was used directly in the Hofmann elimination step.

Wittig Rearrangement of *transoid*-28. This was carried out exactly as described for *cisoid*-**27**, except that it was possible to crystallize a portion from cyclohexane as white needles, mp 245 °C dec, probably a single stereosiomer, e.g., **32A**: ^1H NMR (90 MHz) δ 8.3–7.2 (m, 10, ArH), 4.44 (bs, 2, internal ArH), 4.12 (bd, J = 13 Hz, 2, –CH_xSCH_3), 3.47 (bd, J = 11 Hz, 2, –CH_aH_b–), and 2.20 (s and m, 4, –SCH_3 and –CH_aH_b–); MH^+, (CI) m/e 400 (23), 353 (42), and 305 (100). Anal. ($C_{26}H_{24}S_2$) C, H.

Hofmann Elimination on *cisoid*-35: *anti*-[2,2]-*cisoid*-(1,3)-Naphthalenophane-1,11-diene (21). A solution of the mixed isomers of **31** from the Wittig rearrangement of *cisoid*-**27** (2 g, 5 mmol) in dichloromethane (60 mL) was added to $(CH_3O)_2CHBF_4$[16] (2.0 g, 80% oil, 14 mmol) stirred at −30 °C under N_2. This mixture was stirred for 3 h without further cooling and then ethyl acetate was added. Even after extensive trituration with ethyl acetate, the resultant oil would not crystallize. Vacuum drying yielded a glass, which was powdered to 1.45 g (48%) of salt **35**, which smelt strongly of $(CH_3)_2S$. A sample of this powder melted at ca. 140 °C, turned yellow at 200 °C, and then gave

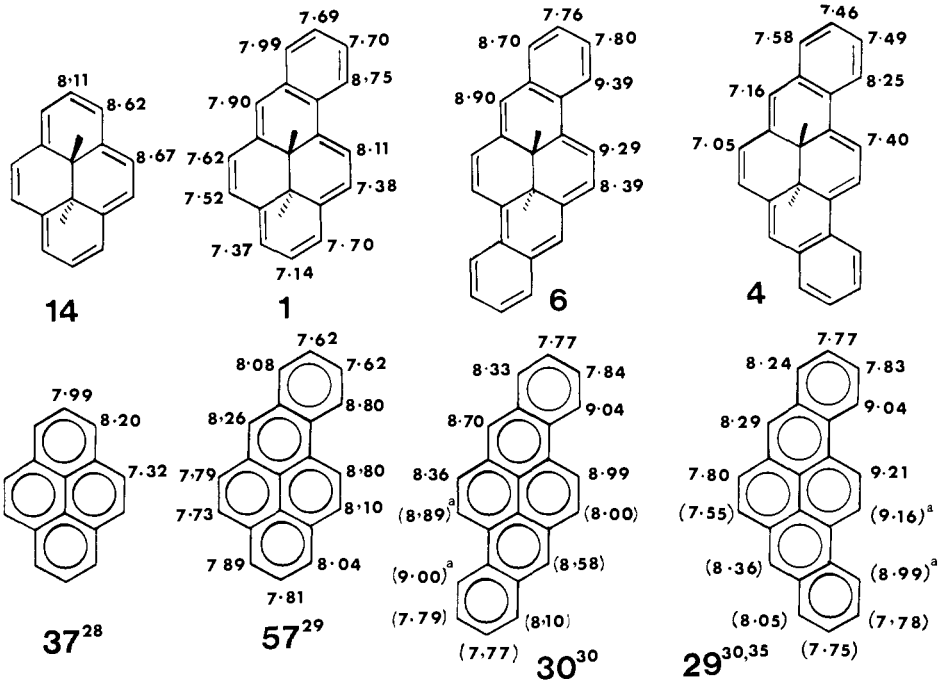


Figure 6. Selected ^1H chemical shift data for compounds **14**, **1**, **4**, **6**, **37**,[28] **57**,[29] **30**,[30] and **29**.[30,38]

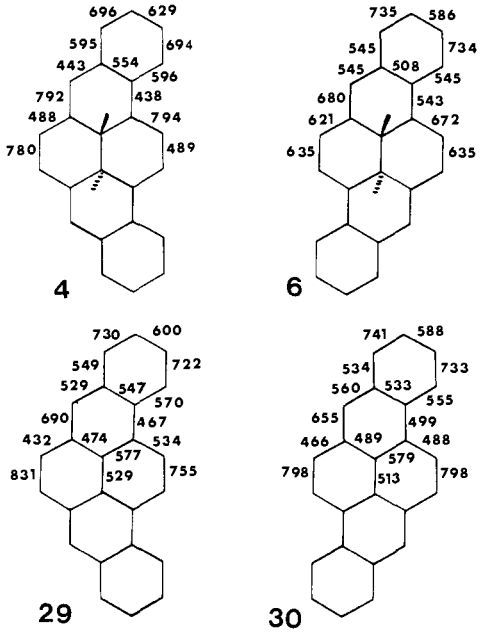


Figure 7. Calculated[31] π-SCF bond orders for benzannulenes **4** and **6** and pyrenes **29** and **30** (bond orders $\times 10^3$).

a vigorous evolution of $(CH_3)_2S$. The powder (1.4 g) was added to a solution of potassium *tert*-butoxide (1.5 g, 14 mmol) in dry THF (100 mL) at 0 °C under N_2 and was stirred for 3 h. After addition of water, ether, and aqueous HCl, the organic layer was washed, dried, and evaporated. The residual oil was chromatographed on silica gel, using pentane as eluant. Diene **21** (~10 mg, ~1.4%) was eluted first as unstable yellow crystals, mp ~110 °C dec turning deep orange, solidifying and darkening after 280 °C. On standing and in solution, the diene rapidly formed dibenzo[*a,h*]pyrene (**29**), which was also eluted next from the column (~40 mg, 6%) and readily identified by its characteristic UV spectrum,[17,18] and mp 278 °C (lit.[18] mp 280 °C); M^+, *m/e* 302. The diene **21** showed ^1H NMR (90 MHz, THF-d_8) δ 8.7–7.4 (m, all protons). Irradiation of this sample sealed under vacuum with 2537 Å light gave no indication of the formation of **5**, only dibenzopyrene **29** being formed.

Hofmann Elimination of *transoid*-35: *anti*-[2,2]-*transoid*-(1,3)-Naphthalenophane-1,11-diene (22). This was carried out as described for **21** above, except that on trituration with ethyl acetate the salt **35** was obtained as a white powder (2 g, 66%), mp 260 °C dec, with vigorous evolution of $(CH_3)_2S$. After base treatment and chromatography the diene **22**, 85 mg (8.5%), gave crystals which rapidly turned yellow and showed mp 186–198 °C dec turning bright orange. Eluted second was dibenzo[*a,i*]pyrene (**30**): 310 mg (31%); mp 310 °C (lit.[20] mp 308 °C); identical UV spectrum to that reported; M^+, *m/e* 302.

The diene **22**, ^1H NMR (60 MHz) δ 8.3–6.7 (m, ~15) and 5.80 (d, J = 10.5 Hz, ~1), slowly formed dibenzopyrene **30** on standing in solution. The mass spectrum of the diene **22** showed peaks at 302–308 inclusive, with the largest peak at 306, suggesting disproportionation into dibenzopyrene and tetrahydrobenzopyrenes was occurring.

Irradiation of Anti-Diene 22: Dihydrodibenzannulene 7. A solution of the diene **22** (~4 mg) in degassed THF-d_8 was sealed under vacuum in an NMR tube and irradiated with 2537 Å light. A pale green color developed. When the irradiation was carried out at −100 °C a stronger green color formed which faded on warming to room temperature or more slowly when the light source was removed but the sample kept at −100 °C. Reirradiation reproduced the green color. Despite intensive effort on an XL-100 (Fourier transform) spectrometer, an ^1H NMR spectrum of the suspected (green) dibenzannulene **7** could not be obtained.

2,3-Dimethyl-1-naphthonitrile (39). Cuprous cyanide (9 g, 100 mmol) was added to a solution of the bromide **38**[2] (21.8 g, 93 mmol) in *N*-methyl-2-pyrrolidinone (140 mL) and then the mixture was stirred at 180 °C for 24 h. After 6 h, a further portion of CuCN (8 g, 90 mmol) was added. After being cooled, the mixture was poured into concentrated aqueous ammonia ("880", 150 mL) and water (50 mL) at 0 °C and after 1 h at this temperature was filtered. The solid thus obtained was extracted with dichloromethane several times in a blender. The extracts were washed, dried, and evaporated. The residual product was preabsorbed onto silica gel and filtered in CH_2Cl_2 through a short column of silica gel to give the nitrile, **39**, 13.3 g (79%), as colorless crystals from 95% aqueous ethanol: mp 83.5–84.5 °C; ^1H NMR (60 MHz) δ 8.2–7.9 (m, 1, 8-ArH), 7.8–7.2 (m, 4, ArH), 2.51 (s, 3, 2-CH_3), and 2.31 (s, 3, 3-CH_3); IR (KBr) 2210 cm^{-1} (-CN); M^+, *m/e* 181 (91), 166 (100), and 151 (11). Anal. ($C_{13}H_{11}N$) C, H, N. The above reaction could be scaled to five times the above with no change in yield.

3-(Bromomethyl)-2-methyl-1-naphthonitrile (40). *N*-Bromosuccinimide (18.63 g, 105 mmol) was added in four equal portions over 3 h to a refluxing, stirred solution of the nitrile **39** (18.94 g, 105 mmol) in CCl_4 (250 mL) under irradiation from a 500 W tungsten lamp. At each addition a few milligrams of benzoyl peroxide were added. After a further 3-h reflux period, the reaction was cooled and the succinimide removed by filtration. The filtrate was washed, dried, and evaporated. The residue was extracted with boiling cyclohexane and filtered hot. This process was repeated and the remaining solid residue was recrystallized from a larger volume of hexane to give pure **40**. A further portion of **40** could be obtained with difficulty by chromatography of the evaporated extracts over silica gel, to give a combined yield of nitrile 40 of 6.3 g (23%) as colorless needles: mp 131–133 °C; ^1H NMR (60 MHz) δ 8.2–7.4 (m, 5, ArH), 4.60 (s, 2, -CH_2Br), and 2.77 (s, 3, -CH_3); IR

(KBr) 2210 cm^{-1} (-CN); M^+, *m/e* 261, 259 (8), and 180 (100). Anal. ($C_{13}H_{10}BrN$) C, H, N.

Separation of the product isomers could not be achieved in this manner on scaling up.

3-(Bromomethyl)-2-methyl-1-naphthaldehyde (41). A solution of diisobutylaluminum hydride (11 mmol) in hexane (10.5 mL) was added dropwise under N_2 to a solution of the nitrile **40** (2.87 g, 11 mmol) in dry benzene (50 mL) with vigorous stirring at ca. 20 °C. After 2 h, the mixture was cooled to 0 °C and methanol (15 mL), methanol:water (1:1, 20 mL), and then concentrated aqueous HCl:water (1:2) were added cautiously until the mixture was slightly acidic. The mixture was extracted with ether and the extracts were washed, dried, and evaporated to give the aldehyde **41**, 2.90 g (99.8%), as off-white plates from cyclohexane: mp 120–121 °C; ^1H NMR (60 MHz) δ 10.96 (s, 1, -CHO), 8.8–8.5 (m, 1, 8-ArH), 7.93 (s, 1, 4-ArH), 7.85–7.2 (m, 3, ArH) 4.63 (s, 2, $-CH_2Br$), and 2.74 (s, 3, $-CH_3$); IR (KBr) 1675 cm^{-1} (-C=O); M^+, *m/e* 264, 262 (8), and 183 (100). Anal. ($C_{13}H_{11}BrO$) C, H.

3-(Bromomethyl)-1-(hydroxymethyl)-2-methylnaphthalene (42). The aldehyde **41** (4.01 g, 15 mmol) in THF (30 mL) was added dropwise to a stirred slurry of $NaBH_4$ (0.29 g, 7.6 mmol) in THF (not dried, 20 mL) at ca. 20 °C. After 18 h, 10% aqueous H_2SO_4 (not HCl or HBr)[37] was added until the solution was just acidic. It was then extracted with ether. The extract was washed (once), dried, and evaporated to give crude alcohol **42**, 2.84 g (67%), which was used directly in the bromination below: ^1H NMR (90 MHz) δ 8.3–8.1 (m, 1, 8-ArH), 7.9–7.2 (m, 4, ArH), 5.19 (s, 2, $-CH_2OH$), 4.70 (s, 2, $-CH_2Br$), 2.64 (s, 3, $-CH_3$), and 1.53 (s, 1, -OH).

1,3-Bis(bromomethyl)-2-methylnaphthalene (24). The crude alcohol **42** from above (28.4 g, 10.7 mmol) and concentrated 48% aqueous HBr (100 mL) were heated under reflux with vigorous stirring for 3 h. The mixture was cooled, poured into water, and extracted with dichloromethane. The extract was washed (H_2O, aqueous $NaHCO_3$, H_2O), dried, and evaporated. The residue was chromatographed on silica gel, using pentane:dichlormethane (8:2) as eluant, to yield the bromide **24**, 3.09 g (85%), identical with previously obtained authentic samples.

1,3-Bis(mercaptomethyl)-2-methylnaphthalene (43). A mixture of bromide **24** (20 g, 61 mmol) and thiourea (9.8 g, 130 mmol) were heated under reflux in 95% ethanol (400 mL) for 1.5 h and then the solvent was evaporated to leave ca. 80 mL. The white precipitate of bisisothiouronium salt was then collected. A small portion was dried, mp 265 °C. Anal. ($C_{15}H_{20}Br_2N_4S_2$) C, H. The salt was added to a N_2-degassed solution of KOH (106 g, 85%) in water (200 mL) and refluxed under N_2 for 4 h. While the solution was ice cooled, 50% aqueous H_2SO_4 was slowly added until the reaction mixture was acidic. Ether was then added and the organic layer was washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated to yield the thiol **43**, 12.1 g (85%), which on crystallization from cyclohexane yielded colorless needles: mp 88–89 °C; ^1H NMR (60 MHz) δ 8.0–7.1 (m, 5, ArH), 4.04 (d, *J* = 6.5 Hz, 2, 1-CH_2S), 2.75 (d, *J* = 7 Hz, 2,3-CH_2S–), 2.46 (s, 3, $-CH_3$), 1.68 (t, *J* = 6.5 Hz, 1, 1-SH), and 1.64 (t, *J* = 7 Hz, 1, 3-SH); IR (KBr) 2545 cm^{-1} (-SH); M^+, *m/e* 234 (100), 201 (80), and 167 (100). Anal. ($C_{13}H_{14}S_2$) C, H.

11,22-Dimethyl-2,13-dithia[3,3](1,3)naphthalenophanes 44, 45, 46, and 47. A solution of the bromide **24** (15.8 g, 48.2 mmol) and the thiol **43** (11.3 g, 48.2 mmol) in N_2-degassed benzene (1 L) was added dropwise over 72 h with vigorous stirring under N_2 to a solution prepared by dissolving KOH (9.6 g, 85%, 150 mmol) in water (200 mL) and adding ethanol (1.3 L). The reaction mixture was then evaporated to dryness and water and dichloromethane were added. The organic layer was washed, dried, and evaporated. The residue was filtered through a short column of silica gel, using benzene:pentane (1:1) as eluant, to give 14.5 g (75%) of the mixed isomers of dimers **44–47**. Extraction of this mixture with hot CH_2Cl_2 dissolved the more soluble isomers and left relatively pure transoid-anti-isomer **44**, which could be subsequently recrystallized from benzene. The total mother liquors were preabsorbed onto silica gel from CH_2Cl_2 and chromatographed several times on silica gel, using benzene–pentane (3:7) as eluant, to obtain the pure isomers. The elution order was *transoid-anti*-**44** followed by *cisoid-anti*-**45**, *transoid-syn*-**46**, and then *cisoid-syn*-**47**; however, if too much *transoid-anti*-**44** is present, the lower solubility of this isomer tends to slow up its elution to mix into all fractions. The transoid-anti-isomer **44**, ~5.8 g (~30%), was recrystallized from benzene as white needles: mp 296–298 °C; ^1H NMR (90 MHz) δ 8.3–7.2 (m, 10, ArH), 4.28 and 4.08 (ABq, *J* = 13.3 Hz, 2 each, 1-, 12-CH_2–, see text), 3.67 and 3.37 (ABq, *J* = 14.6 Hz, 2 each, 3-, 14-CH_2–, see text), and 1.00 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 137.0, 135.7, 132.6, 132.1, 128.6 (Ar quaternary C), 129.6, 128.1, 126.2, 125.1, 123.5 (aryl *C*H), 31.5 (3-, 14-CH_2S–),[22] 27.0 (1-, 12-CH_2S–), and 15.5 ($-CH_3$); M^+, *m/e* 400 (14), 266 (2), 201 (32), 199 (31), 198 (36), 185 (24), 184 (28), 169 (47), 168 (100), 167 (52), and many lower *m/e* peaks. Anal. ($C_{26}H_{24}S_2$) C, H.

The cisoid-anti-isomer **45**, ~5.8 g (~30%), was recrystallized from cyclohexane as colorless crystals: mp 290–292 °C; ^1H NMR (90 MHz) δ 8.4–7.2 (m, 10, ArH), 4.19 and 3.91 (ABq, *J* = 14 Hz, 2 each, 1-, 3-CH_2S–, see text), 3.90 and 3.86 (ABq, *J* = 14 Hz, 2 each, 12-, 14-CH_2S–, see text), and 0.98 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 136.9, 134.6, 132.2, 131.8, 128.7 (Ar quaternary C), 130.4, 128.0, 125.8, 125.0, 123.9 (aryl *C*H), 31.6 (1-, 3-CH_2S–),[22] 27.9 (12-, 14-CH_2S–), and 15.3 ($-CH_3$); MH^+, (CI) *m/e* 401 (100), (EI) very similar to **44**. Anal. ($C_{26}H_{24}S_2$) C, H.

The transoid-syn-isomer **46**, ~1.2 g (~6%), was recrystallized from cyclohexane as colorless crystals: mp 282–283 °C; ^1H NMR (90 MHz) δ 7.9–7.6 (m, 2, 9; 20-ArH), 7.4–6.8 (m, 8, ArH), 4.57 and 4.39 (ABq, *J* = 14.5 Hz, 2 each, 1-, 12-CH_2–, see text), 4.19 and 4.05 (ABq, *J* = 15 Hz, each, 3-, 14-CH_2–, see text), and 2.69 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 133.5, 133.3, 132.1, 131.7, 130.5 (aryl quaternary C), 129.3, 127.3, 124.8, 124.5, 123.5 (aryl *C*H), 38.3 (3-, 14-CH_2–),[22] 30.7 (1-, 12-CH_2–), and 18.3 ($-CH_3$); MH^+, (CI) *m/e* 401 (2), 354 (9), 265 (65), and 263 (100), (EI) very weak M^+, at *m/e* 400. Anal. ($C_{26}H_{24}S_2$) C, H.

The cisoid-syn-isomer **47**, ~1.7 g (~9%), was recrystallized from cyclohexane as colorless plates: mp 175–176 °C; ^1H NMR (60 MHz) δ 8.0–6.4 (m, 10, ArH), 4.48 and 4.22 (ABq, *J* = 15 Hz, 2 each, 12-, 14-CH_2S–, see text), 4.01 and 3.87 (ABq, *J* = 16 Hz, 2 each, 1-, 3-CH_2–, see text) and 2.62 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 133.8, 133.6, 131.8, 131.4, 130.7 (aryl quaternary C), 128.6, 127.1, 125.1, 124.2, 122.1 (aryl *C*H), 35.9 (1-, 3-CH_2S–),[22] 30.0 (12-, 14-CH_2S–), and 18.0 (-CH_3); M^+, at *m/e* 400 (weak). Anal. ($C_{26}H_{24}S_2$) C, H.

Wittig Rearrangement of *transoid-anti*-Cyclophane 44. *n*-Butyllithium (19 mmol in 8 mL of hexane) was added from a syringe to a solution of the cyclophane **44** (2.50 g, 6.24 mmol) in dry THF (100 mL) under N_2 at ~20 °C. After 5 min, methyl iodide (~19 mmol) was added to discharge the color of the dark solution. After a further 5 min, water and dichloromethane were added. The organic layer was washed, dried, and evaporated and left a light yellow foul-smelling solid, **48**, in quantitative yield as a mixture of stereoisomers: ^1H NMR (60 MHz) δ 8.5–7.0 (m, ArH), 4.5–1.2 (m, bridge CH–), 2.2 (s, $-SCH_3$), 0.5, 0.4 (s, $-CH_3$ of different isomers). The material was used directly in the Hofmann elimination step.

Hofmann Elimination of *transoid-anti*-Cyclophane 48 to Dibenzannulene 6. A solution of the mixed isomers of **48** from the Wittig rearrangement of **44** (1.5 g, 3.5 mmol) in dichloromethane (50 mL) was added to $(CH_3O)_2CHBF_4$[16] (2 g, 80% oil, ~10 mmol) stirred at −30 °C under N_2. This mixture was then stirred for 3 h without further cooling and ethyl acetate (50 mL) was added. Further stirring and trituration with ethyl acetate gave after filtration the sulfonium salt **50** (1.43 g, 65%) as a yellow powder. This salt (2.3 mmol) was suspended in dry THF (200 mL) under N_2 and cooled to 0 °C and potassium *tert*-butoxide (2 g, 18 mmol) was added. After the solution was stirred for 3 h at 0 °C and then for 1 h without further cooling, aqueous HCl and dichloromethane were added. The dark green organic layer was washed, dried, and evaporated (20 °C) without delay. The residue was chromatographed on deactivated silica gel (5% H_2O), using pentane as eluant, and the product was crystallized from either benzene–cyclohexane or cyclohexane as rapidly as possible, since solutions of **6** fairly rapidly decompose.

The dark blue crystals of **6** so obtained, ~600 mg (80%, yields in this step were very variable ranging from 25 to 80%), showed mp 196–197 °C (the blue crystals give a green liquid, which rapidly turns brown): ^1H NMR (250 MHz) δ 9.39 (d, *J* = 7.4 Hz, 2, 4-, 11-ArH), 9.29 (d, *J* = 7.4 Hz, 2, 5-, 12-ArH), 8.90 (s, 2-, 7-, 14-ArH), 8.70 (m, 2, 1-, 8-ArH), 8.39 (d, *J* = 7.4 Hz, 2, 6-, 13-ArH), 7.78 (m, 4, 2-, 3-, 9-, 10-ArH), and −3.58 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 137.0, 132.6, 127.8, 119.5 (quaternary aryl –C), 129.9, 126.0, 125.6, 124.7, 124.4 (aryl –CH), 32.8 (internal >C<)8 and 15.9 (v weak, $-CH_3$); M^+, *m/e* 332 (25), 317 (50), and 312 (100); UV (cyclohexane) λ_{max} (log ϵ_{max}) 734 nm (2.50), 716 (2.85), 683 (sh, 3.54), 653 (3.91), 615 (sh, 3.78), 572 (sh, 3.46), 418 (5.16), 397 (4.97), 380 (4.60), 359 (4.49), 339 (sh, 4.27), 298 (4.00), 279 (4.20), and 232 (4.77). Anal. ($C_{26}H_{20}$) C, H.

***cisoid-trans*-Dibenzannulene 4. (a) Wittig Rearrangement of 45.** This was carried out as described above for **44**. From 1.71 g (4.27 mmol) of **45** there was obtained 1.83 g (quant) of **49** as a mixture of stereoisomers, which was used directly in the next step. **(b) Hofmann Elimination of 49.** This was carried out exactly as described for **48** above. From 1.83 g (4.27 mmol) of **49** there was obtained 810 mg (57%) of dark green **4**.

(37) Mixtures of bromomethyl- and chloromethylnaphthalenes were obtained.

(38) P. Mahathalung, Ph.D. Thesis, 1978, Boston College Graduate School. University Microfilms No. 7803801, Ann Arbor, Mich.

Recrystallization from cyclohexane gave green crystals: mp 218–220 °C; ^{1}H NMR (250 MHz) δ 8.25 (m, 2, 1-, 12-ArH), 7.58 (m, 2, 4-, 9-ArH), 7.48 (m, 4, 2-, 3-, 10-, 11-ArH), 7.40 (s, 2, 13-, 14-ArH), 7.16 (s, 2, 5-, 8-ArH), 7.05 (s, 2, 6-, 7-ArH), and 0.02 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 138.5, 136.2, 131.6, 129.5 (quaternary aryl C), 128.2, 127.7, 127.2, 127.1, 124.4, 123.2, 116.7 (aryl CH), 39.5 (bridge >C<), 19.2 ($-CH_3$); MH^+, (CI) *m/e* 333 (100), 317 (20), 302 (13); UV (cyclohexane) λ_{max} (log ϵ_{max}) 733 nm (1.21), 716 (1.43), 703 (sh, 1.57), 683 (sh, 2.01), 654 (2.37), 615 (2.25), 567 (1.96), 460 (sh, 3.70), 435 (sh, 3.82) 417 (4.04), 397 (4.15), 360 (4.97), 343 (4.83), 284 (sh, 4.13), 272 (4.31), 258 (4.30), and 207 (4.66). Anal. ($C_{26}H_{20}$) C, H.

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Toward 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[1]

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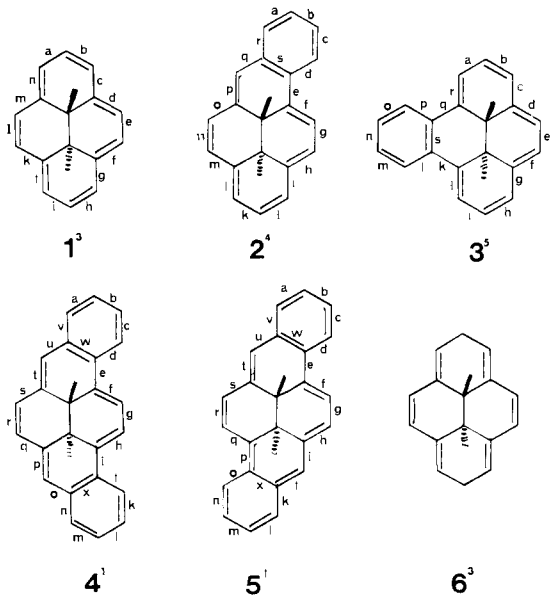
Abstract: A linear relationship between the chemical shift shielding of the internal protons of the series of benzannelated dihydropyrenes **1–5** and the average deviation of π-SCF bond order of the macrocyclic ring from the Hückel [14]annulene value of 0.642 has been determined empirically. A similar relationship was obtained for selected internal and external protons of the series of Nakagawa's benzannelated dehydro[14]annulenes **28–30**. The equations thus determined have been used to predict 18 known and 29 unknown chemical shifts of other benzannelated annulenes. Most of the known shifts agree with those calculated to <0.5 ppm. These results suggest that bond localization caused by benzo- or other aromatic ring annelation is the principal determinant of the strength of the macrocyclic ring current in these compounds.

In the three accompanying preceding papers, we have described the syntheses and properties of the benzannelated dihydropyrenes[2] **2–5**. These properties have been comparedd to each other and to those of the parent dihydropyrene[2] **1**. We have shown that the diatropicity order as evidenced by the shielding of the internal methyl protons (and carbons) is in the order **1 < 5 < 2, 3 < 4** and we have interpreted this in terms of bond localizations as predicted by consideration of simple Kekulé structures,

In this paper we wish to show that the diatropicity of these systems can be correlated quantitatively (though empirically) by means of simple π-SCF bond order calculations and that the results can be used predictively in this as well as other systems.



(1) Benzannelated Annulenes. 9. For part 8, see: R. H. Mitchell, R. V. Williams, and T. W. Dingle, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) For *Chemical Abstract* names and numbering see the preceding papers.[1,4,5] Since we require to identify each bond we have chosen to use the lettering system given in this paper.

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