Toward the Understanding of Benzannelated Annulenes: Synthesis and Properties of [a]-Ring Monobenzannelated Dihydropyrenes[1]

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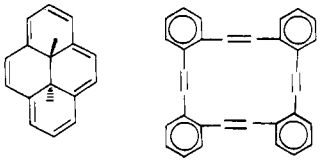
Abstract: The benzannelated dihydropyrenes **3** and **4** were synthesized from 1,3-bis(bromomethyl)naphthalene (**16**) and 1,3-bis(bromomethyl)-2-methylnaphthalene (**22**) (the latter obtained in 18% yield in seven steps from 2,3-dimethylnaphthalene) in 7.4% and 4.8% overall yields, respectively, using Stevens or Wittig rearrangement–Hofmann elimination sequences on the dithiacyclophanes **13** and **14**, followed by valence tautomerization of the resulting cyclophanedienes **11** and **12**. The dihydrobenzopyrene **3** rapidly dehydrogenates to benzo[a]pyrene (**21**), whereas the dimethyl derivative **4** is relatively stable. The internal protons of **3** and **4** show only about 50% of the shielding of the corresponding protons in the parent hydrocarbons **8** and **1**, respectively, and this effect is ascribed to bond localization caused by the benzannelating ring. The residual diatropicity of **3** or **4** is larger than that for the related less rigid **40** or **41**. Unlike the parent **1**, no evidence was found for a reversible valence isomerization of **4** to **12**. Coupling constants of the external protons of **4** were used to compare bond orders to calculated ones, and it was shown that both rings of **4** considerably perturb the delocalization of the other, in accordance with Günther's calculations. A comparison of the ^{1}H NMR spectra of **4** and benzo[a]pyrene (**21**) was made.

While many annulenes are now known,[3] few are as well suited for the study of effects associated with aromaticity as Boekelheide's[4] *trans*-15,16-dimethyldihydropyrene[5] (**1**). This annulene is stable and has a planar[6] 14π-electron periphery, but most important it has its internal bridges and substituents close to the "center of the ring current", which make them extremely sensitive[7] probes for changes in ring current and hence aromaticity.[8] Thus study of a phenomenon which changes the aromaticity of an annulene should have a much more pronounced magnetic resonance effect on internal groups, e.g., the internal methyl protons of **1**, which normally appear at δ −4.25, than for external groups, e.g., the external ring protons of **1**, or indeed any other annulene.

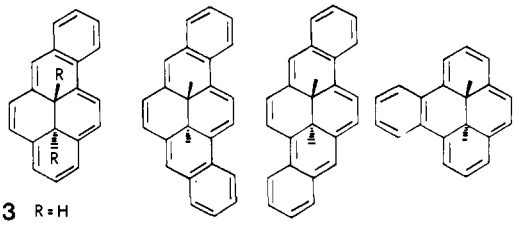


1 **2**

One such effect is benzannelation. At the outset of this work[9] many benzannulenes were known, e.g., **2**,[10] but unfortunately most were either nonplanar (with little or no delocalization in the macroring as a consequence) or else they did not have suitable probes from which useful conclusions concerning the delocalization in the macroring could be made. It was however generally recognized that fusion of several benzene rings onto an annulene appeared to reduce "aromaticity" of the macroring although at the same time imparting stability which allowed such molecules to at least be synthesized.[1]

The question then arose, was it possible to design a benzannulene which did show clear affects associated with aromaticity in the macroring, and then subsequently could a series of such compounds provide data which could be the input for an explanation of the behavior of such compounds? This and the following papers attempt to answer those questions.

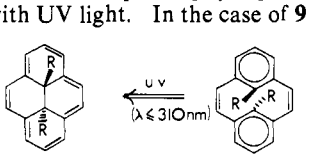
The first molecules that we chose to study were the benzannelated dihydropyrenes[11] **3** and **4**, which are reported in this paper. The subsequent accompanying papers report the dibenzannulenes **5** and **6** and the symmetrical monobenzannulene **7**, and the final paper unifies and provides an explanation of the results as well as making substantial predictions for as yet unknown molecules.



3 R = H
4 R = CH_3 **5** **6** **7**

Syntheses

Both dimethyldihydropyrene **1** and the parent dihydropyrene **3** have been shown to be synthetically accessible through their valence tautomers, the corresponding cyclophanedienes **9** and **10**, by irradiation with UV light. In the case of **9** ⇌ **1** the process



1 R = CH_3 **9** R = CH_3
8 R = H **10** R = H

is reversible and the position of equilibrium is sensitive to sub-

(1) Benzannelated Annulenes. 6. For part 5[2] see: R. H. Mitchell, *Isr. J. Chem.*, **20**, 594 (1980).
(2) For parts 4 and 3, respectively, see: (a) R. H. Mitchell and J. S. H. Yan, *Tetrahedron Lett.*, 1289 (1979); (b) R. H. Mitchell, R. J. Carruthers, and L. Mazuch, *J. Am. Chem. Soc.*, **100**, 1007 (1978).
(3) See, for example: F. Sondheimer, *Chimia*, **28**, 163 (1974); *Acc. Chem. Res.*, **5**, 81 (1972).
(4) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).
(5) *Chemical Abstracts* now calls **1**: *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene.
(6) A. W. Hanson, *Acta Crystallogr.*, **18**, 599 (1965).
(7) 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", Pergamon Press, Oxford, 1965, p 595.
(8) Strictly *diatropicity*, but the two words are often interchanged. For an interesting discussion see J. F. Labarre and F. Crasnier, *Top. Curr. Chem.* **24**, 33 (1971), and also R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 1722 (1979).
(9) For a preliminary report see: R. H. Mitchell and R. J. Carruthers, *Tetrahedron Lett.*, 4331 (1975), and also ref 2b.
(10) E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 4281 (1953); C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962). See ref 1 for a complete listing of other examples.
(11) Probable *Chemical* Abstracts name for **3**: *trans*-12b,12c-dihydrobenzo[a]pyrene.
(12) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1547 (1974).

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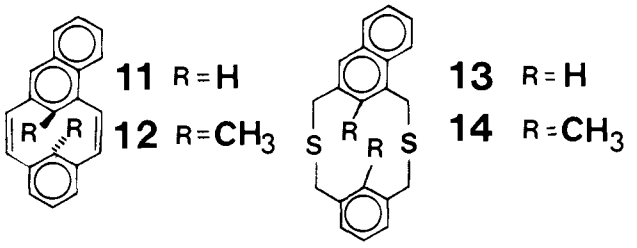
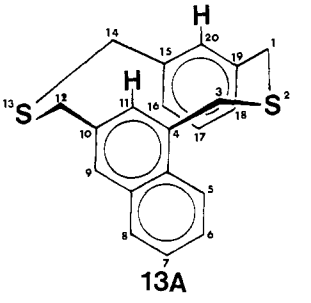
stituents on the ring.[13] The difference in free energy $\Delta G_f°_{298}$ for **1** and **9** is small however (ca. 11 kJ/mol) and is presumably a balance between the loss in delocalization energy of the two benzene rings of **9** and the gain in delocalization energy of the 14π-electron ring of **1** together with the formation of the new sp^3–sp^3 bond and the loss of strain energy in going from **9** to **1**. In the case of **10**, models indicate this strain to be less than that for **9**, and indeed **10** can be isolated in the crystalline state, whereas **9** spontaneously (even in the dark) reverts to **1**.[12,14] Synthesis of **3** and **4** by analogy would require tautomerization of the dienes **11** and **12**, respectively. It was not immediately obvious whether the isomerization would occur in this case and hence whether **3** and **4** would be accessible by this route, although our prediction was that they would: we expected little difference in strain energy between say **9** and **12**, but an easier loss of part of the delocalization energy of the naphthalene ring in **12** relative to the benzene in **9**.[15] This however would probably be partially offset by the reduction in gain of delocalization energy on formation of the benzannelated 14π ring of **4** relative to that on formation of **1**.[17]

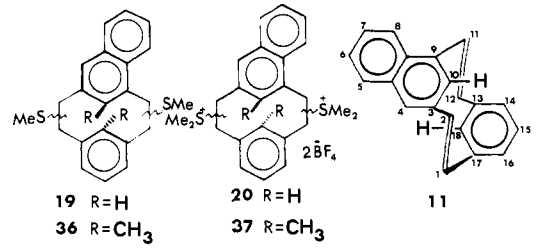
The advantage of proceeding through **11** or **12** was that these could be hopefully accessed through the thiacyclophanes **13** and **14** respectively, using a Stevens rearrangement (ring contraction)–Hofmann elimination sequence.[12]



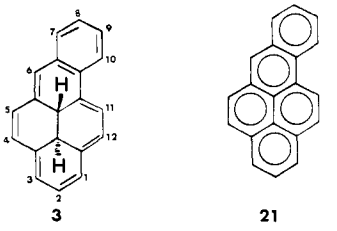
Thiacyclophane 13 and Dihydrobenzopyrene 3. The synthesis of **13** and hence **11** and **3** was attempted first because of the greater accessibility of the required 1,3-bis(bromomethyl)-naphthalene (**16**). Reaction of 1,3-dimethylnaphthalene with *N*-bromosuccinimide yielded 62% of **16**, mp 113–115 °C. Coupling of **16** and *m*-xylylenedithiol[12] (**17**) under high dilution conditions with KOH in ethanol–benzene yielded after chromatography 82% of thiacyclophane[19] **13**, mp 126–127 °C. The structure of **13** was established on the basis[20] of the base peak molecular ion at *m/e* 322 in its mass spectrum, and it was assigned the syn-stereochemistry **13A** on the basis of its ^{1}H NMR spectrum by comparison to the known[21] *syn*-cyclophane **18**, since the 11- and 20-aryl protons of **13A** appear at δ 6.94 and 6.73 (those for **18** are at δ 6.82),[21] whereas if **13** existed as the anti conformer they might be expected to be shielded by the opposite ring to ca. δ 5. Further the 16-, 17-, 18-aryl hydrogens can clearly be seen to be shielded at δ 6.73 by the adjacent ring, a common consequence of face-to-face benzene rings[12]. The ^{13}C NMR spectrum supports this, in that the methylene bridge carbons are at ca. δ 37 which is similar to those of *syn*-**14**, whereas those of *anti*-**14** are at ca. δ 31, shielded by the rings (see below).

Wittig rearrangement[22] of **13** occurred smoothly with *n*-butyllithium, followed by treatment with methyl iodide to yield quantitatively mixed isomers of **19**. These were used directly





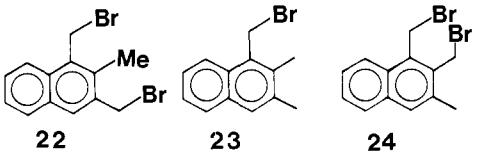
in a Hofmann elimination by reaction first with Borch reagent,[23] $(CH_3O)_2CHBF_4$, to yield the sulfonium salt **20**, and then treatment with potassium *tert*-butoxide in THF at 0 °C to effect elimination to the desired cyclophanediene **11**. In common[12] with the parent system **10**, exclusively *anti*-**11** was obtained, in 14.5% yield from **13** (or 7.4% overall). As eluted, after chromatography **11** was colorless, mp ~120 °C dec. However, the solid rapidly turns orange on its surface due to formation of **3** and subsequently converts to benzo[*a*]pyrene (**21**). The structure of **11** is clearly established by the molecular ion in its mass spectrum at *m/e* 254 and by its ^{1}H NMR spectrum which shows the internal 10-, 18-aryl protons as singlets at δ 8.09 and 8.03 (cf. **10** where they are at δ 7.90, deshielded from those of *anti*-[2.2]metacyclophane by the adjacent double bond and flattening of the ring).[12] Because of the rapid conversion of **3** to benzo[*a*]pyrene (**21**) a low-intensity spectrum of the latter was always observed with that of **11**.



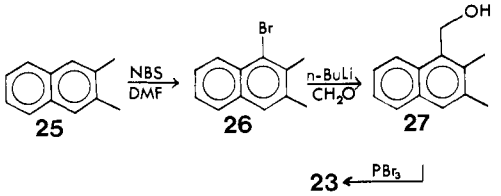
Irradiation of a solution of **11** in degassed THF-d_8 under vacuum with 254 nm (low-pressure mercury) light for ca. 4 h isomerized it to the benzannulene **3**, though some over-irradiation to **21** also occurred. Continued irradiation (~20h) or exposure of **3** to air cleanly converted it to **21**, identical in all respects with a commercial sample. The presence of the orange dihydropyrene **3**, however, was readily confirmed by the ^{1}H NMR signal of the internal hydrogens at δ −1.35, strongly shielded by being in the center of the π cavity. The external hydrogens appeared at δ 8.7 (m) and 8.4–7.0 (m) superimposed on a weak spectrum of **21**. In the UV spectrum of **3**, only those bands not obscured by benzo[*a*]pyrene's very intense bands could be observed at 440 nm (relative intensity 0.80), 466 (1.0), and 497 nm (0.83).

Dimethylcyclophane 12 and Dimethyldihydrobenzopyrene 4. The preparation of **3** had clearly shown that isomerization of **11** was possible and warranted preparation of dibromide **22**, the precursor to the dimethylbenzannulene **4**. However, unlike **3**, we expected **4** to be stable and hence able to be isolated in a pure state similar to **1**.

(13) H. R. Blattmann and W. Schmidt, *Tetrahedron*, **26**, 5885 (1970); W. Schmidt, *Helv. Chim. Acta*, **54**, 862 (1971).
(14) H. R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965).
(15) Nakagawa[16] estimates this to be 21 kcal/mol for naphthalene and 36 kcal/mol for benzene.
(16) A. Yasuhara, T. Satake, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, 895 (1975).
(17) For example, using the method of Hess and Schaad[18] the resonance energy of **4** is estimated to be 0.10β and that of **1** is 0.23β.
(18) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 (1971).
(19) For the nomenclature used in these systems see: F, Vögtle and P. Neumann, *Tetrahedron*, **26**, 5847 (1970).
(20) All new compounds unless otherwise stated showed analytical and spectral data in accord with the proposed structures.
(21) W. Anker, G. W. Bushnell, and R. H. Mitchell, *Can. J. Chem.*, **57**, 3080 (1979).
(22) R. H. Mitchell, T. Otsubo, and V. Boekelheide, *Tetrahedron Lett.*, 219 (1975).
(23) R. F. Borch, *J. Am. Chem. Soc.*, **90**, 5303 (1968); *J. Org. Chem.*, **34**, 627 (1969).

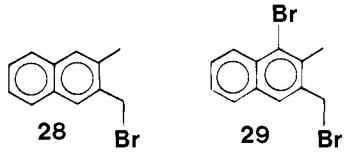


We anticipated that **22** would be formed on bromination of **23** with NBS, the second bromine entering the less hindered 3-methyl group. Unfortunately only 15% of **22**, mp 174–175 °C, was obtained, the major product being **24**, mp 95–98 °C. The two bromides were readily distinguished by their singlet $-CH_2Br$ resonances in their ^1H NMR spectra, which for the 1,2-isomer **24** were at δ 5.04 and 4.75 whereas for the 1,3-isomer **22** they were at δ 4.94 and 4.63. Their structures could not be unambiguously assigned until **23** was synthesized by an alternate and unambiguous route (see below). The monobromide **23** was obtained in three steps from commercial 2,3-dimethylnaphthalene (**25**): bromination of **25** in DMF with NBS[24] gave an 88% of 1-bromo-2,3-dimethylnaphthalene (**26**), in higher yield and purity then the literature method.[25] Reaction of **26** with *n*-butyllithium



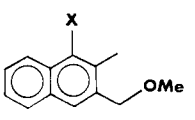
in ether–benzene at 20 °C followed by formaldehyde gave alcohol (IR 3270 cm^{-1}) **27**, mp 118–120 °C, in 45% yield. Reaction of this with PBr_3 in ether then gave **23**, mp 87–88 °C, in 96% yield. The overall yield of **22** from **25** was thus only 5.7%.

An alternate strategy was thus attempted whereby the steric effect of the bromomethyl group of **28** and the electronic effect of the methyl reinforce each other such that bromination of **28**[26] in $CHCl_3$ yielded 71% of **29**, mp 115–117 °C, with the desired substitution pattern. The structure of **29** was readily assigned by comparison of its ^1H NMR spectrum with that of **28**. The



$-CH_3$ group of **28** at δ 2.55 is deshielded by the adjacent bromine of **29** to δ 2.66, whereas the $-CH_2Br$ group at δ 4.61 remains almost the same as in **28** at δ 4.64.

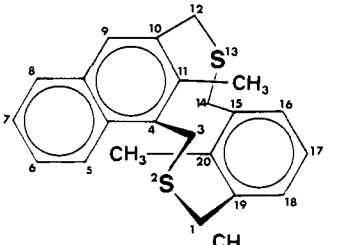
Elaboration of the nuclear bromine of **29** required protection of the side chain bromine, hence **29** was first converted into ether **30** (mp 70–72°C), using sodium methoxide in DMF (73% yield), and then to the nitrile **31** (mp 68–69 °C, IR 2220 cm^{-1}), using CuCN in *N*-methyl-2-pyrrolidinone, in 82% yield. The nitrile was then reduced to the aldehyde **32** (mp 72–73 °C, IR 1682 cm^{-1}; –CHO signal in ^1H NMR spectrum δ 10.86) in 99% yield, using diisobutylaluminum hydride in benzene. Reduction of **32** with $NaBH_4$ in THF gave 95% yield of **33** (mp 80–81 °C, IR 3420

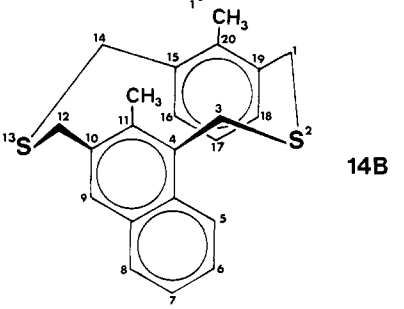


30 X= Br
31 X= CN
32 X= CHO
33 X= CH_2OH

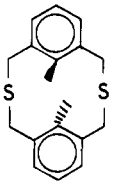
cm^{-1}), which on treatment with refluxing concentrated aqueous HBr for 4 h gave 89% of **22**, identical with the previous sample. The overall yield of **22** from **25** was thus improved to 17.8%. An attempt to shorten this route by reaction of **30** with activated[28] magnesium and then formaldehyde to yield **33** (followed by reaction with HBr) gave only a 30% yield on this step, reducing the overall yield to 7.8%.

Coupling of the bromide **22** and 2,6-bis(mercaptomethyl)-toluene[12] (**34**) proceeded smoothly, as for **13**, to give a 60% yield of **14** as syn and anti isomers, which could be separated by multiple chromatography on silica gel. The less soluble anti-isomer **14A**





(obtained in ca 55% yield) crystallised easily from benzene and had mp 188–190 °C. Its structure was established by chemical ionization mass spec, MH^+ at *m/e* 351, and by its ^1Hmr spectrum which showed the internal 11-CH_3 at δ 1.42 and the 20-CH_3 at δ 0.92 (cf *anti*-**35**, -CH_3 at δ 1.30)[12]. In contrast, the 11-CH_3



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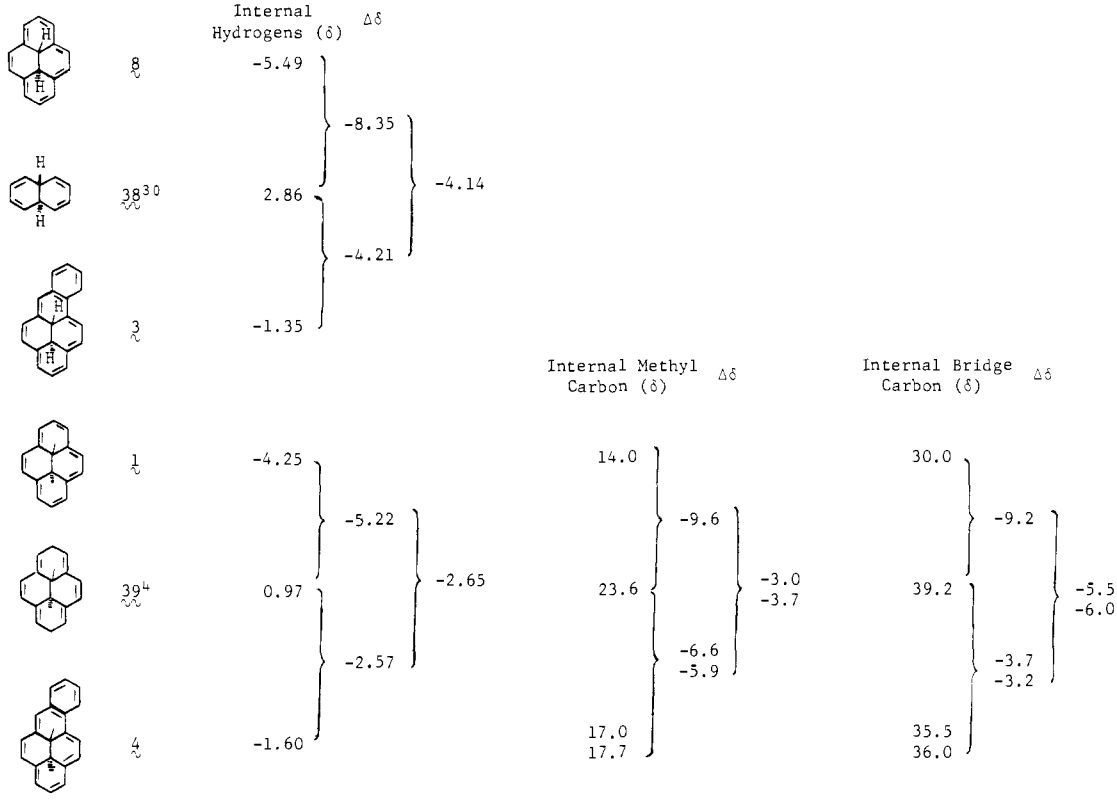
(δ 2.62) and 20-CH_3 (δ 2.45) of the syn isomer **14B** like those of *syn*-**35** (δ 2.54) were normal for an aryl methyl. The syn isomer **14B** (ca. 5% yield) was obtained pure only with difficulty, mp 136–137 °C. The 9- (δ 6.97), 16- (δ 6.16), 17- (δ 5.71), and 18- (δ 6.03) aryl hydrogens of this isomer all appeared shielded by the opposite syn ring, unlike *anti*-**14A** in which all aryl H appeared between δ 8.2 and 7.0. The methylene bridge protons of *anti*-**14A** appeared as separate AB quartets at δ 4.20 (3-CH_2–), 3.77 (1, 14-CH_2–), and 3.41 (12-CH_2–), whereas the 1,12,14-CH_2– of *syn*-**14B** overlapped between δ 4.1 and 3.6. In each of **13A**, **14A**, and **14B** one of the $-CH_2S-$ carbons appeared shielded. We have assigned this to the α-naphthyl carbon from the results of Grant et al.,[29] who have examined a whole series of methyl-substituted naphthalenes. The effect is interesting in that it is the reverse of what is observed for protons. The shielded anti methyls of **14A** can also be observed in the carbon spectrum at δ 15.3 and 14.9, whereas those for *syn*-**14B** are at δ 17.6 and 17.3.

Wittig rearrangement of **14A** with *n*-butyllithium in THF followed by methyl iodide quench gave mixed isomers of **36** which

(24) R. H. Mitchell, R. V. Williams, and Y. H. Lai, *J. Org. Chem.*, **44**, 4733 (1979).
(25) R. T. Arnold and R. Liggett, *J. Am. Chem. Soc.*, **64**, 2875 (1942).
(26) 1-(Bromomethyl)-2-methylnaphthalene (**28**) was prepared in ca. 50% yield from 2,3-dimethylnaphthalene and NBS in the modified Buu-Hoi[27] procedure used above for **23**. The product required four recrystallizations from cyclohexane to obtain pure: mp 101–103 °C (lit.[27] mp 103 °C); ^1H NMR (60 MHz) δ 7.9–7.3 (m, 6, ArH), 4.64 (s, 2, $-CH_2Br$), and 2.55 (s, 3, $-CH_3$).
(27) J. Lecocq and M. M. Buu-Hoi, *C. R. Hebd. Seances Acad. Sci.*, **224**, 471 (1971).
(28) R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974).
(29) D. K. Dalling, K. H. Ladner, D. M. Grant, and W. R. Woolfenden, *J. Am. Chem. Soc.*, **99**, 7142 (1977).
(30) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).
(31) R. DuVernet and V. Boekelheide, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 2961 (1974).

Table I. Chemical Shift Data for Dihydropyrenes ($CDCl_3$ Solution)



after conversion to the sulfonium salt **37**, as shown previously, underwent Hofmann elimination with potassium *tert*-butoxide to give a 48% yield (from **14A**) of orange dimethyldihydrobenzo[*a*]pyrene (**4**), mp 115–116 °C. That **4** was the product actually isolated, rather than the cyclophane-diene **12**, was evidenced from the ^1H NMR spectrum which showed the internal $-CH_3$ protons, highly shielded at δ −1.60, and by the presence of the shielded bridging carbons at ca. δ 36 in the ^{13}C NMR spectrum.

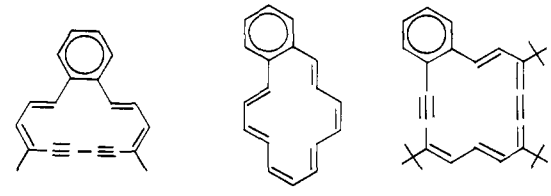
Indeed no evidence for any substantial (>4%) formation of **12** could be found even on prolonged irradiation of **4** with light from a 500W tungsten lamp, unlike the case of **1** ⇌ **9**· in which a 1:1 mixture could be obtained.[14] This probably confirms our original guess that the change of delocalization energy of a naphthalene (i.e., benzannelated benzene) relative to a benzene, when each forms its *o*-quinonoid species, is more significant than the difference of delocalization energy between a benzannelated annulene and the corresponding annulene.

Discussion

From Table I it can be seen that benzannelation of **8** to give **3**, or **1** to give **4**, causes remarkably large downfield shifts for the internal protons (4.14 ppm for 8 → **3**) and for the internal methyls (2.65 ppm for **1** → **4**) in their ^1H NMR spectra and similarly for the internal carbon atoms of **1** → **4** in their ^{13}C NMR spectra.

This effect is much too large to be a diamagnetic deshielding of the internal substituents by the benzo ring, since such a deshielding can be estimated,[32] using the results of Bovey and Johnson,[7] to be only of the order of 0.05 ppm for the methyl protons of **4**, for example, and thus is most likely a real reduction in the diatropicity of the macroring. Relative to the model compounds **38** and **39**, the shielding (Table I, Δδ) of the internal protons of **3** and **4** is only ca. 50% of the corresponding values of **8** and **1**, respectively, the two sets of compounds showing remarkable agreement in this respect. This is also the case for the average shielding of the internal carbon atoms, though the deviations are greater here, possibly due to small changes in geometry on benzo fusion, which affect the chemical shifts of the carbon atoms much more than the protons.[33]

The residual diatropicity in the macrorings of **3** and **4** appears to be considerably larger than that for **40** or **41**, which are related but not very rigid molecules, and about the same as for **42**, which



40 **41** **42**

	40	**41**	**42**
Δδ(Parent)	11.0 (ref. 34)	8.5 (-60°C) (ref. 35)	11.0 (ref. 37)
Δδ(Benzannulene)	2.1 (ref. 34)	1.9 (ref. 36)	7.6 (ref. 37)

[Δδ = δ(outer protons) − δ(inner protons)].

has the advantage, like **3**, of being both rigid and relatively planar. In addition, as we predicted earlier, the effects on the inner protons on benzannelation are considerably greater than on the outer protons. However, the outer protons can provide information of a different kind. Günther et al.[38] have shown that the π electronic

(32) The methyl protons are estimated from models to be about 3.6 ring radii from the center of the benzo ring in plane and about 2 ring radii above the plane.

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

(34) R. T. Weavers and F. Sondheimer, *Angew. Chem., Int. Ed. Engl.*, **13**, 139 and 141 (1974).

(35) F. Sondheimer, *Acc. Chem. Res.*, 81 (1972).

(36) U. E. Meissner, A. Gensler, and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, **15**, 365 (1976).

(37) K. Sakano, S. Akiyama, M. Iyoda, and M. Nakagawa, *Chem. Lett.*, 1019 and 1023 (1978).

(38) (a) D. Cremer and H. Günther, *Ann.*, **763**, 87 (1972). (b) H. Günther, A. Shyoukh, D. Cremer, and K. Risch, *ibid.*, 150 (1978). (c) H. Günther, M. Günther, D. Mondeshka, and H. Schmickler, *ibid.* 165 (1978). (d) *Chem. Ber.*, **112**, 71 (1979).

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

Table II. Calculated[40] Bond Orders ($P_{\mu,\nu}$), Alternance Parameter (Q), and Coupling Constants ($^3J_{\mu,\nu}$) for **41** (and hence **4**) and Experimental Values for **4**

μ,ν	$P_{\mu,\nu}$	Q	$^3J_{\mu,\nu}$(calcd), Hz	$^3J_{\mu,\nu}$(calcd) [corrected for steric effect], Hz	$^3J_{\mu,\nu}$(exptl),[a] Hz
9, 10	0.711	1.162	7.99	8.29	8.21
8, 9	0.612	1.165	7.04	7.04	6.75
7, 8	0.713		8.01	8.09	7.96
5, 4	0.731	1.324	8.18	8.27–8.35	8.89
12, 11	0.552		6.46	6.76–6.84	6.64
3, 2	0.573	1.251	6.66	6.74	6.54
2, 1	0.717		8.05	8.13	8.86

[a] Because of the limited number of data points, probably ±0.4 Hz.

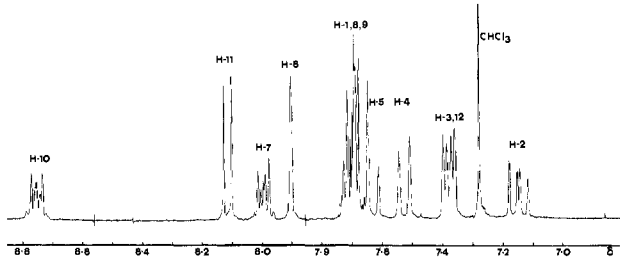
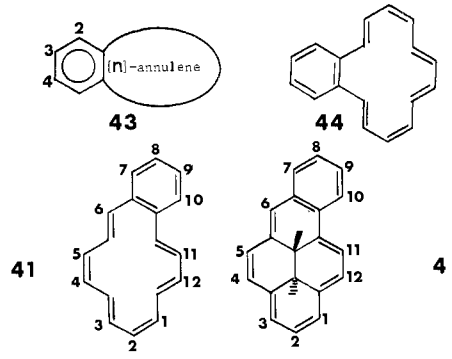


Figure 1. The 250 MHz (Brucker WM250) ^{1}H NMR spectrum of **4** (aryl protons only) in $CDCl_3$.

structure of annulenes can be probed to some extent by examination of the coupling constants of the protons on the benzannelating ring. He defines the *alternance parameter*, Q, as the quotient of the bond orders ($P_{\mu,\nu}$) of the 2,3 and 3,4 bonds of the benzo[n]annulene **43**, i.e., $Q = P_{2,3}/P_{3,4}$. For [$4q + 2$] π-electron systems, using SCF bond orders, Q is calculated to be >1.04. The actual bond orders are somewhat sensitive to the geometry of the annulene ring and for **44** the calculations give $P_{2,3} = 0.706$, $P_{3,4} = 0.617$, and hence $Q = 1.143$. It is thus suggested that the 14-π electron system of the annulene considerably perturbs the benzene ring, causing considerable localization of the bonds. An experimental comprehension of these results is provided by measurement of the coupling constants (Hz) of the bonds concerned, where the relationship[38a]

$$P_{\mu,\nu}(\mathrm{SCF}) = 0.104(^3J_{\mu,\nu}) - 0.120 \quad (1)$$

has been found to hold. Though Günther did not calculate the values for the geometry of **4** (i.e., **41**), Table II gives the results



of our calculations,[40] from which we would expect to find $J_{9,10}$ to be about 1 Hz larger than $J_{8,9}$. In fact because of steric compression of the 10–11 and 6–7 protons, coupling constant corrections[39] of ca. +0.30 Hz (phenanthrene type) and ca. +0.08 Hz (naphthalene type) should be added to those calculated from eq 1 to give the estimated corrected calculated values shown in Table II. Figure 1 shows the 250-MHz ^{1}H NMR spectrum of **4**. The bay protons H-10, -11 would be expected to be at lowest field by comparison with other polycyclic systems,[42] and indeed H-10 appears as the most deshielded multiplet at δ 8.75, with H-11 appearing as a clear doublet at δ 8.11 with a coupling constant of 6.64 Hz. This is in excellent agreement with that calculated, since the magnitude of the steric correction cannot necessarily be expected to be exactly the same as those quoted for phenanthrene and naphthalene above because from the known[6] geometry of **1** atoms 11 and 12 can be expected to be more out of plane. H-7 appears next as the multiplet at δ 7.99, with the two remaining protons H-8, -9 of the ABCD multiplet appearing at ca. δ 7.69 and 7.70. Computer simulation[43] of these multiplets using the coupling constants given in Table II gave the best fit to the experimental spectrum, but unfortunately they can only be considered satisfactory to ca. ±0.3 Hz since not enough lines were present to clearly iterate the meta and para coupling constants,[44] which then affect the ortho values obtained. Nevertheless very satisfactory agreement is found with the calculated values of Table II, and the correct order is observed with $J_{9,10}$ being at least 1 Hz larger than $J_{8,9}$ as previously predicted above.

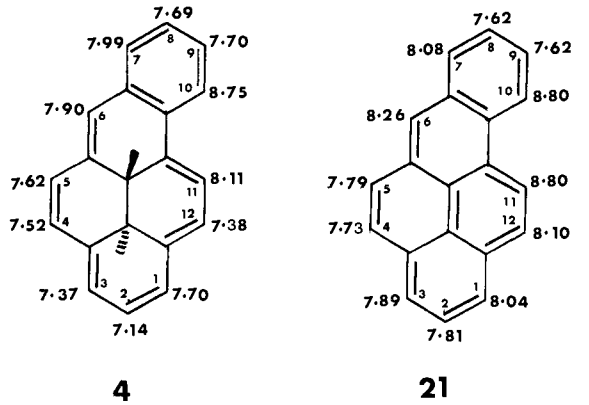


Figure 2. Chemical Shift values (δ) of **4** and **21**.

Furthermore, in the same way that the macroring localizes the bonds in the benzene ring as stated by Günther, it is clearly seen that the benzene ring also localizes the bonds of the macroring. This we believe is the principal reason for the reduction in diatropicity observed for the internal protons and carbons on benzannelation. The remaining chemical shifts are shown below and compared in Figure 2 to those found[42] for benzo[*a*]pyrene (**21**): H-6 is the expected singlet, and the assignment of H-12 is made since it must have the same J value as H-11. H-5, -4 are the only remaining simple doublets. H-2 is easily assigned since it is coupled to H-1 and H-3. Only the latter are less obvious and the assignment made is based on comparison to **21** and on the calculated J values. Indeed the general similarity between the ^{1}H NMR spectra of **4** and **21** (Figure 2) is striking, the central 12b–12c π bond of **21** not appearing to affect the order of chemical shifts much, though all of the pyrene ring protons of **21** are deshielded from those of **4**, whereas the benzene ring protons are hardly affected. This to us indicated that the π-electron distribution in **4** was probably similar to that in **21** and thus we compared the π-bond orders[40] (Figure 3). To our surprise, whereas

(40) Bond orders were calculated by using Pariser–Parr–Pople (PPP) π-electron theory.[41] 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 −2.366 eV for nearest neighbors. All two-electron integrals, $\gamma_{\mu,\nu}$, were calculated by using the Mataga–Nishimoto relationship $\gamma_{\mu,\nu} = 1.4397/[R + (2.8794/(\gamma_{\mu,\mu} + \gamma_{\nu,\nu}))]$ eV with a value of 10.67 eV used for $\gamma_{\mu,\mu}$ for the carbon atom. These are the same parameters used by Cremer and Günther;[38a] therefore the results reported here are directly comparable to theirs. Other parametrizations give very similar values for the bond orders.

(41) See: J. N. Murrell and A. J. 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.

(42) K. D. Bartle, D. W. Jones, and R. S. Matthews, *Spectrochim. Acta, Part A*, **25A**, 1063 (1969).

(43) We thank Dr. Keith R. Dixon of this department for considerable help and for developing simple to use simulation programs.

(44) Actual best fit values were $J_{10,8} = 0.88$ Hz, $J_{10,7} = 0.5$ Hz, and $J_{9,7} = 1.5$ Hz.

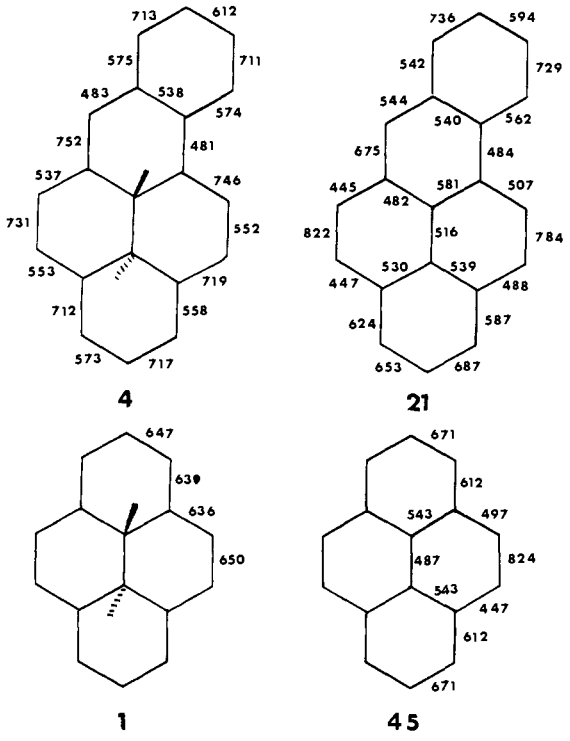
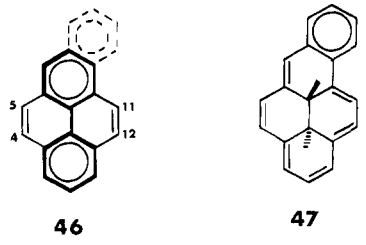


Figure 3. π-SCF[40] bond orders ($\times 10^3$) of **4** and **21**, and **1** and **45**.

most of the bond orders around the ring followed the same sequence in **4** and **21** (though of different magnitude), those around the 11–12 bond were reversed in order. This perhaps in part explains the different biological activities[45] of **4** and **21**. From Figure 3 it can be seen that both benzo[*a*]pyrene, (**21**) and pyrene (**45**) appear from bond order calculations to behave like a biphenyl with two alkene links in the 4–5 and 11–12 positions, **46**, whereas



the benzannulene **4** has alternate long and short bonds around the periphery of the 14-ring as shown in **47**. While calculation of the chemical shifts for the protons of polybenzenoid hydrocarbons[46] such as **21** and **45** and the annulenes[47] has received considerable attention in the past, attempts at annelated annulenes are as yet only in their infancy. Early results from Vogler,[48] e.g., for the benzannulene **44** (of **41**), predicted far too large values of $\delta\Delta$ (see p 16) but only the ring current contributions to chemical shift were taken into account, with no allowance for bond alternation effects. His more recent results[49] which use a quantum-mechanical approach[50] to calculate both the ring current and local anisotropy contributions give much better chemical shift values for both inner and outer protons for compounds such as **42**: $\delta\Delta_{calcd} = 9$ ppm, $\delta\Delta_{found} = 7.6$ ppm. It will be interesting to see if this method yields good results for bridged annulenes such as **4**.

Conclusions

We have successfully shown that benzannelated derivatives of **1** can be prepared and that a molecule such as **1** makes an excellent probe to measure effects associated with aromaticity. Indeed monobenzannelation of **1** reduces the shielding of the internal groups by ca. 50% of their values in **1**, yet leaves sufficient delocalization still present to warrant further investigation of polybenzannelated derivatives. The reduction in diatropicity of **1** on benzannelation is ascribed to bond localization caused by the effect of each ring on the other. This hypothesis should be easily tested by examination of other benzannelated derivatives of **1** and these results are discussed in the subsequent papers.

Experimental Section

All melting points were determined on a Kofler hot stage and are uncorrected. The ^{1}H NMR spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin-Elmer R12B (60 MHz) or R32 (90 MHz) spectrometer and are reported in ppm downfield from tetramethylsilane as internal standard. ^{13}C NMR spectra were determined in $CDCl_3$ on a Nicolet TT-14 Fourier transform spectrometer operating at 15.1 MHz. UV spectra were measured on a Carey 17 spectrophotometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7 or Finnigan 3300 mass spectrometer at 70 eV. Microanalyses were performed by this department. All evaporations were carried out under reduced pressure on a rotary evaporator at ca. 40 °C. Extracts were dried with anhydrous sodium sulfate.

1,3-Bis(bromomethyl)naphthalene (16). *N*-Bromosuccinimide (34.2 g, 0.195 mol) was added in three portions 90 min apart to a solution of 1,3-dimethylnaphthalene (Aldrich, 15 g, 96 mmol) in refluxing carbon tetrachloride (60 mL) and followed after each addition by a few milligrams of benzoyl peroxide. After a total reflux time of 4.5 h, the reaction was cooled and succinimide removed by filtration. The filtrate was washed once with water, dried, and evaporated. Recrystallization of the residue from cyclohexane (~130 mL) gave colorless crystals of product **16**: 18.8 g (62%); mp 113–115 °C; ^{1}H NMR (90 MHz) δ 8.3–7.4 (m, 5, ArH), 4.87 (s, 2, 1-CH_2Br), and 4.57 (s, 2, 3-CH_2Br); $M^+\cdot$ *m/e* 316, 314, 312 (10, 20, 10), 235, 233 (100, 100), 154 (95), and 153 (50). Anal. ($C_{12}H_{10}Br_2$) C, H.

2,13-Dithia[3]metacyclo[3](1,3)naphthalenophane (13). A solution of the bromide **16** (6.28 g, 20 mmol) and *m*-xylylene dithiol (**17**)[12] (3.4 g, 20 mmol) in N_2-degassed benzene (600 mL) was added dropwise over 48 h with vigorous stirring under N_2 to a solution prepared by dissolving KOH (4 g, 85%, 60 mmol) in water (75 mL) and adding ethanol (1.5 L). The reaction mixture was then evaporated to dryness and water and dichloromethane were added. The organic layer was washed, dried, and evaporated to a crystalline residue, which was chromatographed over silica gel with benzene–pentane (3:7) as eluant to give pure **13**, 5.29 g (82%). Recrystallization from cyclohexane–benzene gave colorless needles: mp 126–127 °C; ^{1}H NMR (90 MHz) δ 7.95 (m, 1, 5-ArH), 7.7–7.3 (m, 4, 6-, 7-, 8-, 9-ArH), 6.94 (s, 1, 11-ArH), 6.73 (m, 4, 16-, 17-, 18-, 20-ArH), 4.12 (s, 2, 12-CH_2S–), 3.80 (s, 2, 3-CH_2S–), and 3.70 (s, 4, 1-, 14-CH_2S–); ^{13}C NMR δ 136.9, 136.6, 134.5, 133.9, and 129.9 (quaternary Ar–C), 131.8, 130.2, 128.1, 128.0, 127.3, 127.0, 126.7, 125.5, 125.3, and 123.7 (Ar–*C*H), 38.0 (12-CH_2S–), 37.4 (1-, 14-CH_2S–), and 35.6 (3-CH_2S–); $M^+\cdot$ *m/e* 322 (100). Anal. ($C_{20}H_{18}S_2$) C, H.

Wittig Rearrangement of Dithiacyclophane 13. *n*-Butyllithium (30 mmol) in hexane (15 mL) was injected into a solution of cyclophane **13** (4.19 g, 13 mmol) in dry THF (75 mL) under N_2 at 0 °C. After ~3 min, methyl iodide was added until the deep color discharged (~2 mL), followed by water, aqueous HCl and dichloromethane. The organic layer was washed, dried, and evaporated to yield **19** (quantitative) as a mixture of stereoisomers: ^{1}H NMR (60 MHz) δ 8.3–6.8 (m, 8, ArH), 5.4–4.3 (several s, 2 total, internal ArH), 4.3–2.0 (m, 6, >CH–CH_2–), 2.2–1.7 (several s, 6 total, –SCH_3). This product was used directly in the next step.

Hofmann Elimination of Cyclophane 19. *anti*-[2]Metacyclo[2](1,3)-naphthalenophane-1,11-diene (11). The mixed isomers of **19** from the Wittig rearrangement above (4.2 g, 12 mmole) in dichloromethane (20 mL) were added to $(CH_3O)_2CHBF_4$[23] (5 g, 85% oil, 26 mmol) at −30 °C under N_2. This mixture was then stirred for 4 h without further cooling. The resulting oily precipitate was triturated with ethyl acetate to yield after filtration and drying the bissulfonium salt **20**, 5.8 g (87%), ~190 °C dec. This salt was added to a solution of potassium *tert*-butoxide (5.9 g, 53 mmol) in dry THF (200 mL) under N_2 at 0 °C. After the solution was stirred for 30 min the cooling bath was removed, and after 4 h, ether, water, and aqueous HCl were added. The organic layer was washed, dried, and evaporated (<25 °C) to a dark oil. This was

(45) M. J. Ashwood-Smith, R. H. Mitchell, and A. Kennedy, *Mutat. Res.*, **57**, 123 (1978).
(46) See, for example: C. W. Haigh, R. B. Mallion, and E. A. G. Armour, *Mol. Phys.*, **18**, 751 (1970); M. Barfield, D. M. Grant, and D. Ikenberry, *J. Am. Chem. Soc.*, **97**, 6956 (1975), and the references quoted therein.
(47) R. C. Haddon, *Tetrahedron*, **28**, 3613 and 3635 (1972).
(48) H. Vogler and G. Ege, *Tetrahedron*, **32**, 1789 (1976).
(49) H. Vogler, *Tetrahedron*, **35**, 657 (1979).
(50) H. Vogler, *J. Am. Chem. Soc.*, **100**, 7464 (1978).

chromatographed on silica gel with pentane as eluant to yield **11**, 440 mg (14.5% from **13**), contaminated with some benzo[*a*]pyrene (**21**). Freshly eluted **11** is colorless, mp 120 °C (turning orange and then fading), but rapidly turns orange on its surface due to **3** and subsequently slowly converts to **21**; ^{1}H NMR (90 MHz, THF-d_8, obtained by subtraction of benzo[*a*]pyrene spectrum) δ 8.09, 8.03 (s, 10-, 18-ArH) and 7.7–6.3 (m, ArH); $M^{+\cdot}$ *m/e* 254 with strong variable peak at 252 (benzo[*a*]pyrene). Anal. ($C_{24}H_{14}$) C, H.

Irradiation of 11 to *trans*-12b,12c-Dihydrobenzo[*a*]pyrene (3). A sample of the diene **11** (~25 mg) was sealed under vacuum in ca. 1 mL of dry degassed THF-d_8 in an NMR tube. This was then irradiated with 2537 Å, light from a low-pressure mercury lamp with air cooling. The reaction was monitored by ^{1}H NMR and after ca. 4 h the dihydropyrene internal hydrogen peak at δ −1.3 had maximized. The sample was then orange-red. The ^{1}H NMR spectrum showed almost all the diene **11** was converted, though some **3** had over irradiated to benzo[*a*]pyrene (**21**). The dihydropyrene **3** showed peaks (90 MHz) at δ 8.7 (m) and 8.4–7.0 (m) and −1.35 (s, internal −H); UV (cyclohexane) λ_{max} (relative intensity) 440 nm (0.80), 466 (1.00) 497 (0.83) (any other peaks obscured by benzo[*a*]pyrene). Continued irradiation for about 20 h, or exposure of the 4 h irradiation product to O_2, or irradiation for 1 h in the presence of O_2 cleanly converted **3** into benzo[*a*]pyrene (**21**), identical by TLC, UV, ^{1}H NMR, and mp with a commercial sample.

1-Bromo-2,3-dimethylnaphthalene (23). This was prepared in ca. 50% yield from Br_2 and 2,3-dimethylnaphthalene (**25**) as described[25] but required several recrystallizations to purify from the 1,4-dibromide. Subsequently *N*-bromosuccinimide–dimethylformamide as the brominating agent was found[24] to give pure product in 88% yield.

1-Hydroxymethyl-2,3-dimethylnaphthalene (27). *n*-Butyllithium (0.12 mol in 75 mL of hexane) was added dropwise to a stirred solution of **26** (23.5 g, 0.10 mol) in dry benzene (200 mL) and dry either (300 mL) under argon at 20 °C. After this mixture had refluxed for 1 h, dry paraformaldehyde (15 g) was added and reflux continued for a further 1.5 h. The suspended solids were removed by filtration, and the filtrate was washed once with water (150 mL), dried, and evaporated. The resulting pale yellow solid was recrystallized twice from cyclohexane to yield colorless crystals of **27**, 8.3 g (45%): mp 118–120 °C; IR (KBr) 3270 cm^{-1}; ^{1}H NMR (60 MHz) δ 8.2–7.0 (m, 5, ArH), 5.12 (s, 2, $-CH_2O-$), 2.47 and 2.44 (s, 3 each, $-CH_3$), and 1.53 (s, 1, exchanged by D_2O, −OH); $M^{+\cdot}$ *m/e* 186 (97), 168 (100), and 157 (86). Anal. ($C_{13}H_{14}O$) C, H.

The yield could be increased by about 10% by heating the mother liquors from the above recrystallization with 20% NaOH solution to hydrolyze any formate esters formed, followed by chromatography on neutral alumina with pentane–ether (2:1) as eluant.

1-(Bromomethyl)-2,3-dimethylnaphthalene (23). A solution of PBr_3 (30 mL, 0.32 mol) in dry ether (500 mL) was added dropwise to a stirred solution of alcohol **27** (29.3 g, 0.16 mol) in dry ether (1500 mL). After 24 h, the mixture was concentrated to 500 mL, washed with H_2O and aqueous $NaHCO_3$, dried, and evaporated to give product **23**, 37.7 g (96%) pure by ^{1}H NMR. A sample was recrystallized from hexane as white needles: mp 87–88 °C; ^{1}H NMR (90 MHz) δ 8.2–7.3 (m, 5, ArH), 5.01 (s, 2, $-CH_2Br$), and 2.41 (s, 6, $-CH_3$); $M^{+\cdot}$ *m/e* 250, 248 (10 each), and 169 (100). Anal. ($C_{13}H_{13}Br$) C, H.

***N*-Bromosuccinimide Bromination of 23.** *N*-Bromosuccinimide (27 g, 0.15 mol) was added in four portions at 90-min intervals to a solution of the bromide **23** (37 g, 0.15 mole) in CCl_4 (1500 mL) at reflux, followed by a few milligrams of benzoyl peroxide. When all the suspended solids floated (succinimide) the reaction was stopped (ca. 5 h), cooled, and filtered. The filtrate was evaporated and the residue was fractionally crystallized from cyclohexane. The less soluble 1,3-bis(bromomethyl)-2-methylnaphthalene (**22**) crystallizes out first in about 15% yield as white crystals, mp 174–175.5 °C (two recrystallizations). The mother liquors contain mostly the more soluble 1,2-bis(bromomethyl)-3-methylnaphthalene (**24**), mp ca. 95–98 °C. The latter compound was not obtained absolutely pure. The two bromides could be partially separated by chromatography on silica gel with pentane as eluant, with the 1,2-isomer **24** being eluted first. They are most readily distinguished by the singlet $-CH_2Br$ resonances in their ^{1}H NMR spectrum which for the 1,2-isomer **24** are at δ 5.04 and 4.75 and for the 1,3-isomer **22** are at δ 4.94 and 4.63. The structure of the latter was assigned unambiguously by the alternate synthesis described below.

1-Bromo-3-(bromomethyl)-2-methylnaphthalene (29). A solution of Br_2 (30.2 g, 0.189 mol) in $CHCl_3$ (70 mL) was added to a refluxing solution of 1-bromomethyl)-2-methylnaphthalene[26] (**28**) (44.0 g, 0.187 mol) in $CHCl_3$ (200 mL) over 1 h. Reflux was continued one further hour, and after being stirred overnight the solution was poured into 10% aqueous $Na_2S_2O_3$. The organic layer was washed, dried, evaporated, and crystallized from CCl_4 to yield white needles of **29**, 42 g (71%): mp 115–117 °C; ^{1}H NMR (60 MHz) δ 8.4–8.1 (m, 1, 8-ArH), 7.9–7.3 (m, 4, ArH), 4.61 (s, 2, $-CH_2Br$), and 2.66 (s, 3, $-CH_3$); $M^{+\cdot}$ *m/e* 316, 314, 312 (7, 14, 7), 235, 233 (100, 100), 154 (52), 153 (100), and 152 (80). Anal. ($C_{12}H_{10}Br_2$) C, H.

1-Bromo-3-(methoxymethyl)-2-methylnaphthalene (30). The bromide **29** (70 g, 0.223 mol) in DMF (400 mL) was added dropwise to a refluxing solution of sodium methoxide (prepared from 10 g (0.45 mol) of Na and 450 mL of dry methanol). After a further 3 h of reflux the reaction mixture was allowed to cool and the methanol was evaporated. Dichloromethane and water were added and the organic layer was washed well with 5% aqueous HCl and then water, dried, and evaporated to yield 43.1 g (73%, yields ranged from 65 to 85% on several runs) of solid **30**, sufficiently pure by ^{1}H NMR to be used directly in the next reaction. On some occasions filtration through a short column of silica gel in pentane–CH_2Cl_2 (1:1) was used to remove any remaining DMF. Crystallization from hexane gave white needles: mp 70–72 °C; ^{1}H NMR (60 MHz) δ 8.5–8.1 (m, 1, 8-ArH), 7.9–7.2 (m, 4, ArH), 4.58 (s, 2, $-CH_2O-$), 3.41 (s, 3, $-OCH_3$), and 2.60 (s, 3, $-CH_3$); $M^{+\cdot}$ *m/e* 266, 264 (13), 234, 232 (62), and 153 (100).

3-(Methoxymethyl)-2-methyl-1-naphthonitrile (31). Cuprous cyanide (29.2 g, 0.326 mol) was added to a stirred solution of the bromide **30** in *N*-methyl-2-pyrrolidinone (500 mL) and then the mixture was stirred at 180 °C for 18 h. After being cooled to about 90 °C, the mixture was poured into a concentrated NH_4OH solution and ice and dichloromethane was added. The large amounts of copper salt precipitated were washed well (in a blender) with more dichloromethane and then the combined organic extracts were washed well with water, dried, and evaporated. The residue was preabsorbed onto silica gel and filtered through a short column of the same with pentane–CH_2Cl_2 as eluant (1:1) to give 28 g (82%) of **31**, pure by ^{1}H NMR. Crystallization from cyclohexane gave colorless crystals: mp 68–69 °C; ^{1}H NMR (60 MHz) δ 8.3–7.2 (m, 5, ArH), 4.42 (s, 2, $-CH_2O-$) 3.40 (s, 3, $-OCH_3$), and 2.57 (s, 3, $-CH_3$); IR (CH_2Cl_2) 2220 cm^{-1}; $M^{+\cdot}$ *m/e* 211 (20), 196 (8), and 179 (100). Anal. ($C_{14}H_{13}NO$) C, H, N.

3-(Methoxymethyl)-2-methyl-1-naphthaldehyde (32). A solution of diisobutylaluminum hydride (Texas Alkyls, 20 g, 0.141 mol) in hexane (133 mL) was added dropwise over 1 h to a stirred solution of the nitrile **31** (23 g, 0.133 mol) in dry benzene (500 mL) at ca. 20 °C under N_2. After being stirred for a further 3 h, the mixture was cooled in an ice-bath and then anhydrous methanol (50 mL), methanol–water (1:1, 50 mL), and aqueous HCl (25 mL of concentrated acid:300 mL of water) were added cautiously. The organic layer was separated and the aqueous layer extracted with ether or benzene. The combined organic layers were washed, dried, and evaporated to yield aldehyde **32**, 28 g (99%), pure by ^{1}H NMR. A sample was crystallized from cyclohexane to give pale yellow crystals: mp 72–73 °C; ^{1}H NMR (60 MHz) δ 10.86 (s, 1, −CHO), 8.8–8.5 (m, 1, 8-Ar–H), 8.0–7.2 (m, 4, ArH), 4.50 (s, 2, $-CH_2O$), 3.39 (s, 3, $-OCH_3$), and 2.62 (s, 3, $-CH_3$); IR (CH_2Cl_2) 1682 cm^{-1}; $M^{+\cdot}$ *m/e* 214 (49), 182 (93), and 153 (100). Anal. ($C_{14}H_{14}O_2$) C, H.

1-(Hydroxymethyl)-3-(methoxymethyl)-2-methylnaphthalene (33). A solution of the aldehyde **32** (23 g, 0.131 mol) in THF (not dried, 150 mL) was added dropwise over 30 min to a stirred suspension of $NaBH_4$ (2.3 g, 0.06 mol) in THF (250 mL) at ca. 20 °C. After being stirred overnight the reaction mixture was poured onto ice and aqueous HCl was added slowly until the solution was acidic. The aqueous layer was saturated with NaCl and extracted with ether. The combined ether layers were washed, dried, and evaporated to yield the alcohol **33**, 27 g (95%), as a pale yellow oil, sufficiently pure by ^{1}H NMR to be used directly in the next reaction. A portion was recrystallized from cyclohexane as colorless needles: mp 80–81 °C; ^{1}H NMR (60 MHz) δ 8.1–7.8 (m, 1, 8-ArH), 7.8–7.2 (m, 4, ArH), 4.83 (s, 2, $-CH_2OH$), 4.33 (s, 2, $-CH_2OCH_3$), 3.25 (s, 3, $-OCH_3$), 2.62 (s, 1, −OH), and 2.29 (s, 3, $-CH_3$); IR (KBr) 3420 cm^{-1}, (CH_2Cl_2) 3600 cm^{-1}; $M^{+\cdot}$ *m/e* 216 (70), 184 (100). Anal. ($C_{14}H_{15}O_2$) C, H.

1,3-Bis(bromomethyl)-2-methylnaphthalene (22). A mixture of the alcohol **33** (22 g, 0.10 mol) and 48% aqueous HBr (400 mL) was heated under reflux for 4 h. After the mixture cooled, water and dichloromethane were added, and the organic layer was washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated to yield crude bromide **22**, 29 g (89%). This was recrystallized from benzene–cyclohexane to yield pure **22**: mp 175–176 °C; ^{1}H NMR (60 MHz) 8.2–7.2 (m, 5, ArH), 4.94 (s, 2, 1-CH_2Br), 4.63 (s, 2, 3-CH_2Br), and 2.50 (s, 3, $-CH_3$); $M^{+\cdot}$ *m/e* 330, 328, 326 (5, 10, 5), 249, 247 (55, 55), and 169 (100). Anal. ($C_{13}H_{12}Br_2$) C, H.

Reaction of Grignard Reagent of 30 with Formaldehyde and then HBr To Give 22. A solution of the bromide **30** (5 g, 19 mmol) in dry THF (75 mL) was added dropwise over 30 min to a refluxing suspension of activated[28] magnesium (prepared from 3.8 g of $MgBr_2$ and 1.5 g of K) in THF (100 mL) under N_2. After a further 90-min reflux, paraformaldehyde (4 g, dried over P_2O_5) was added, and reflux continued for 1

h. After being cooled, the mixture was poured over ice (**CAUTION**), and the organic layer was washed, dried, and evaporated. The residual oil was heated under reflux with 48% aqueous HBr (75 mL) for 3 h, cooled, and diluted with water and dichloromethane. The organic layer was washed, dried, and evaporated to yield an oil containing the desired **22**, together with **28**. Chromatography on silica gel with pentane–dichloromethane (8:2) as eluant gave pure **22**, 1.9 g (30%), identical with the previously obtained samples.

11,20-Dimethyl-2,13-dithia[3]metacyclo[3](1,3)naphthalenophane (14). A solution of the bromide **22** (6.50 g, 19.8 mmol) and 2,6-bis(mercaptomethyl)toluene (**34**)[12] (3.65 g, 19.8 mmole) in N_2-degassed benzene (800 mL) and THF (200 mL) was added dropwise over 70 h with vigorous stirring under N_2 to a solution prepared by dissolving KOH (4.4 g, 85%, 67 mmol) in water (300 mL) and adding ethanol (2.7 L). The reaction mixture was then evaporated to dryness and water and dichloromethane were added. The organic layer was washed, dried, and evaporated to give a yellow oil. This was preabsorbed and chromatographed on silica gel with benzene–pentane (1:4) as eluant. The anti-isomer **14A** was eluted first followed by the syn-isomer **14B**. This step had to be repeated several times to separate all of the isomers. The anti isomer **14A**, 3.8 g (55%), was recrystallized from benzene to give colorless crystals: mp 188–190 °C; ^{1}H NMR (90 MHz) δ 8.16 (broad d, J = 8 Hz, 1, 5-Ar-H), 7.9–7.0 (m, 7, ArH), 4.20 (ABq, $\Delta\nu$ = 11.2 Hz, J = 13.5 Hz, 2, 3-CH_2), 3.77 (ABq, $\Delta\nu$ ~11 Hz, J ~14 Hz, 4, 1-, 14-CH_2), 3.41 (ABq, $\Delta\nu$ = 15.5 Hz, J = 15.5 Hz, 2, 12-CH_2), 1.42 (s, 3, 11-CH_3), and 0.92 (s, 3, 20-CH_3); ^{13}C NMR δ 138.7, 137.0, 136.6, 135.4, 135.1, 132.0, and 131.7 (quaternaty Ar–C), 130.3, 129.8, 129.5, 128.0, 126.0, 125.5, 125.0, 123.5, and 123.2 (Ar–*C*H), 32.3, 31.4, 31.0 (1, 12, 14-CH_2S), 27.1 (3-CH_2S), 15.3 and 14.9 (–CH_3); IR (KBr, major bands) 720, 760, 775, 790, 870, 885, and 1025 cm^{-1}; MH^+· (CI) m/e 351 (100). Anal. ($C_{22}H_{22}S_2$) C, H.

The syn-isomer **14B**, 350 mg (ca. 5%), was extremely difficult to crystallize pure and was obtained as a white powder from cyclohexane–pentane: mp 136–137 °C; ^{1}H NMR (90 MHz) δ 7.95 (broad d, J = 9 Hz, 1, 5-Ar–H), 7.6–7.2 (m, 3, 6-, 7-, 8-ArH), 6.97 (s, 1, 9-ArH), 6.16 (broad d, J = 8 Hz, 17-ArH), 4.37 (Abq, $\Delta\nu$ = 36.6 Hz, J = 15 Hz, 2, 3-CH_2–), 4.1–3.6 (three overlapping ABq, 6, 1-, 12-, 14-CH_2–), 2.62 (s, 3, 11-CH_3), and 2.45 (s, 3, 20-CH_3); ^{13}C NMR 135.7, 135.5, 135.2, 134.1, 134.0, 132.6, 131.7, 130.3 (quaternary Ar–C), 129.7, 129.5, 128.0, 127.0, 125.4, 124.5, and 123.2 (double intensity) (Ar–*C*H), 37.9, 37.1, 35.7 (1-, 12-, 14-CH_2–), 30.0 (3-CH_2–), 17.6 and 17.3 (–CH_3); MH^+· (CI) m/e 351 (100). Anal. ($C_{22}H_{22}S_2$) C, H.

Wittig Rearrangement of *anti*-Cyclophane 14A. *n*-Butyllithium (10 mmol) in hexane (4.5 mL) was injected into a solution of *anti*-cyclophane **14A** (1.50 g, 4.3 mmol) in dry THF (50 mL) under N_2 at 0 °C. After 3 min, methyl iodide was added until the deep color was discharged, followed by water, aqueous HCl, and dichloromethane. The organic layer was washed, dried, and evaporated to yield **36** (quantitative) as a mixture of isomers: ^{1}H NMR (60 MHz) δ 8.4–6.8 (m, 8, ArH), 4.3–1.7 (m, 6, $-CH_2-CH<$), 2.25, 2.20, (s, ~6 total, $-SCH_3$), and 0.93, 0.78, 0.22 (s, ~6 total, internal Ar-CH_3); M^+· m/e 378 (40), 331 (50), and 283 (100). This product was used directly in the next step.

Hofmann Elimination of 36 to *trans*-12b,12c-Dimethyl-12b,12c-dihydrobenzo[*a*]pyrene (4). The mixed isomers of **36** from the Wittig rearrangement above (1.46 g, 3.86 mmol) in dichloromethane (10 mL) were added to $(CH_3O)_2CHBF_4$[23] (2 g of 80% oil, 10 mmol) at −30 °C under N_2. This mixture was then stirred for 4 h without further cooling. The resulting only precipitate was triturated with ethyl acetate to yield after filtration and drying the white bissulfonium salt **37**, 1.93 g (86% yield from thiacyclophane **14A**), mp 186–196 °C dec. This salt was stirred under N_2 in dry THF (50 mL) at 20 °C and potassium *tert*-butoxide (1.7 g, 15 mmol) was added. The mixture was brought to reflux for 30 min, cooled in ice and water, and aqueous HCl and ether added. The organic layer was washed, dried, and evaporated. The residue was chromatographed on silica gel with pentane as eluant. The orange-purple fractions were collected and on evaporation gave **4** (0.52 g (56%)), which on recrystallization from cyclohexane–methanol gave dark orange crystals: mp 115–116 °C; ^{1}H NMR (60 MHz) δ 8.9–6.9 (m, 12, ArH) and −1.60 (s, 6, $-CH_3$); for 250 MHz spectrum see text; ^{13}C NMR 139.2, 138.7, 137.0, 133.7, 130.3 (quaternary Ar–C), 128.5, 127.0, 126.2 (>1 C), 125.5, 123.6 (>1 C), 123.5 (>1 C), 122.0, 121.2, 117.0 (Ar–*C*H), 36.0, 35.5 (bridge >C<), 17.7 and 17.0 (internal –*C*H$_3$); MH^+ (CI) m/e 283 (100), 267 (15), and 252 (13); UV (cyclohexane) λ_{max} (log ϵ_{max}) 630 nm (sh, 1.77), 600 (sh, 1.92), 508 (3.26), 478 (3.39), 453 (3.32), 430 (sh, 3.20), 388 (3.90), 364 (sh, 4.10), 350 (4.43), and 337 (sh, 4.30). Anal. ($C_{22}H_{18}$) C, H.

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Toward the Understanding of Benzannelated Annulenes: Synthesis and Properties of an [*e*]-Ring Monobenzannelated Dihydropyrene[1]

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Abstract: The benzo[*e*]-annelated dimethyldihydropyrene **2** was synthesized in 9.9% yield in nine steps from *o*-dibromobenzene by using either a Wittig rearrangement–Hofmann elimination sequence on the benzo[3.2]thiametacyclophane **9** or, alternatively, a benzyne-induced Stevens rearrangement of **9** followed by oxidation to the sulfone **22** and then base catalyzed sulfinate elimination to **2**. The benzannulene **2** was shown to undergo electrophilic substitution reactions (nitration, acylation) and reversible photoisomerization with the cyclophanediene **8**. The rate of this isomerization was slower than that for the nonbenzannelated **6**. Methylation of the sulfone **22** provided a novel entry to the bridge-substituted derivative 4-methyl-**2** and also to a cyclophane with an exo methylene group on the bridge, **36**. The shielding of the internal protons of **2** is discussed in terms of bond localization, as are the observed coupling constants for its external protons. The ^{1}H NMR spectrum is compared to that of benzo[*e*]pyrene, and the analysis supports Günther's hypothesis that cofusion of the two rings results in considerable bond localization in each. The coupling constant analysis also indicates that the benzo ring localizes the 14π ring more than vice versa.

In the previous paper,[1] we described the synthesis and properties of the [*a*]-ring benzannelated dihydropyrene **1**. While considerable information concerning the π-electron structure of **1** could be obtained from its ^{1}H NNR spectrum, the asymmetry present

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