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, $\Delta\nu \sim 11$ Hz, $J \sim 14$ 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}; $MH^{+\cdot}$ (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); $MH^{+\cdot}$ (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, $\sim$6 total, $-SCH_3$), and 0.93, 0.78, 0.22 (s, $\sim$6 total, internal Ar-CH_3); $M^{+\cdot}$ 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 –CH_3); $MH^{+\cdot}$ (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.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support, and Dr. Keith Dixon of this department for help with the simulation of NMR spectra.

Registry No. 1, 956-84-3; **3**, 58746-77-3; **4**, 66093-76-3; **8**, 27786-82-9; **11**, 58746-76-2; **13A**, 72150-49-3; **14A**, 66093-79-6; **14B**, 80734-46-9; **16**, 36015-77-7; **17**, 41563-69-3; **19**, 58751-24-9; **20**, 80680-00-8; **21**, 50-32-8; **22**, 66093-80-9; **23**, 80665-22-1; **24**, 80665-23-2; **25**, 581-40-8; **26**, 5334-79-2; **27**, 80665-24-3; **28**, 39171-57-8; **29**, 80665-25-4; **30**, 80665-26-5; **31**, 80665-27-6; **32**, 80665-28-7; **33**, 80665-29-8; **34**, 41563-67-1; **36**, 80680-03-1; **37**, 80680-02-0; **41**, 58673-25-9; 1,3-dimethylnaphthalene, 575-41-7.

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

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Contribution from the Department of Chemistry, University of Victoria, Victoria, British Columbia, V8W 2Y2 Canada. *Received November 26, 1980*

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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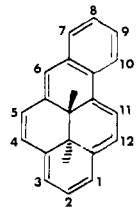

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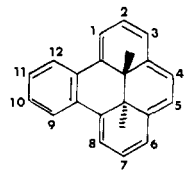

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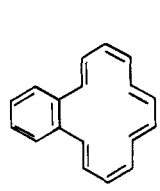
in this molecule, which causes H-7,8,9,10 to appear as an ABCD multiplet, makes the analysis difficult and not very precise. The coupling constants between these protons could only be estimated to ±0.3 Hz, and hence only general agreement between measured and calculated bond orders could be obtained. The symmetrical [*e*]-ring benzannelated dihydropyrene[2] **2** should not suffer from this disadvantage, and analysis of the ^{1}H NMR spectrum should be much easier.

We also were interested in the question as to whether the position at which benzo fusion occurred on an annulene made any difference to its properties, since at the time of starting this work[3] no indication was available as to whether it would or would not. Subsequently calculations made by Vogler and Ege[4] suggested



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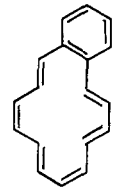

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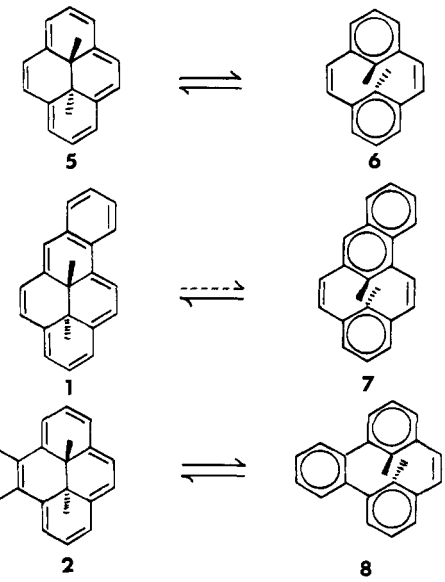
that the difference between **3** and **4**, for example, might not be very great, though earlier work by Cremer and Günther[5] suggested that differences could be expected in bond order in benzannulenes, depending upon the geometry of the molecule, and hence implied that differences in ^{1}H NMR spectra might result. Very recently Staab et al.[6] attempted to synthesize **3**, but obtained instead **4**, hence the question cannot be decided for **3** or **4**; however, no such rearrangement is possible for **1** or **2**, and thus an answer should be possible.

A further reason for wishing to synthesize **2** was to investigate whether valence tautomerization between it and the cyclophanediene **8** was possible. The parent hydrocarbon **5** readily undergoes reversible photoisomerization[7] with **6**, whereas in the previous paper[1] we have shown that although **1** is synthetically accessible from **7** (as **5** is from **6**), no reverse reaction could be detected. We have accounted for this principally by suggesting that the energy balance between disturbing the π systems of the naphthalene and benzene rings of **7** and forming the new π system of **1**, the formation of the new sp^3–sp^3 bond, together with the release of strain energy in going from **7** to **1** favors the formation of **1**; for **5** $\rightleftarrows$ **6**, however, this balance in energies must be closer, probably because of the larger[8] amount of energy required to



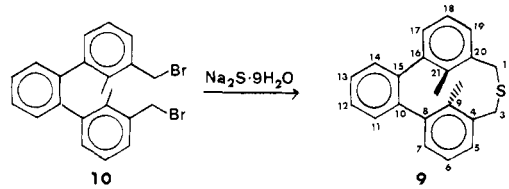
5 6 1 7 2 8

disturb the two benzene rings of **6** to form **5**. Still, however, **5** is the thermodynamically more stable isomer. In the case of **2** $\rightleftarrows$ **8** the prediction is less obvious. Three benzene ring delocalizations have to be disturbed in **8** to get **2**, which should make **8** more favorable than **2** relative to **7** or **6**. However, if significant extra strain is introduced in **8** by fusion of the additional benzene ring, this may not be the case. In summary, however, we anticipated that the cyclophanediene form, **8**, would be more accessible from **2** relatively, than **7** or **6** is from **1** or **5**, respectively. Indeed there was some uncertainty in our view as to whether **2** could be synthesized from **8**!

We also though that **2** might be suitable to test for classical aromatic reactions such as electrophilic substitution, since no such reactions had been reported for a benzannulene. Further, the symmetry of **2** should make assignment of the position of substitution easier than for **1**. The objective of this paper is thus the description of the synthesis and properties of **2**.

Results and Discussion

Synthesis. Our approach to the synthesis of **8** (and hence **2**) was first to prepare the thiacyclophane **9**. This was obtained as white crystals, mp 201–202 °C, in 48% yield by reaction of the bisbromide[10] **10** with sodium sulfide under high dilution conditions.



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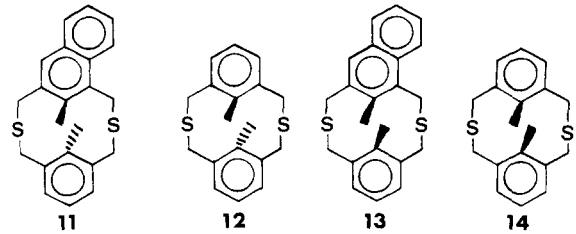
The stereochemistry of **9** was assigned as the anticonformer from its ^{1}H NMR spectrum in which the internal methyl protons appear shielded by the opposite ring at δ 0.94. These can be compared with the corresponding methyl protons of **11** and **12** which appear



11 12 13 14

at δ 0.92 and 1.42 for **11**[1] and δ 1.30 for **12**,[11] whereas those of

(1) Benzannelated Annulenes. 7. For part 6 see: R. H. Mitchell, R. J. Carruthers, L. Mazuch, and T. W. Dingle, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) *Chemical Abstracts* would probably call this *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*e*]pyrene.

(3) For a preliminary account see: R. H. Mitchell and J. S. H. Yan, *Can. J. Chem.*, **55**, 3347 (1977).

(4) H. Vogler and G. Ege, *Tetrahedron*, **32**, 1789 (1976).

(5) D. Cremer and H. Günther, *Justus Liebigs Ann. Chem.* **763**, 87 (1972).

(6) H. A. Staab, U. E. Meissner, W. Weinacht, and A. Gensler, *Chem. Ber.*, **112**, 3895 (1979).

(7) H. R. Blattmann and W. Schmidt, *Tetrahedron*, **26**, 5885 (1970); W. Schmidt, *Helv.-Chim. Acta*, **54**, 862 (1971); H. R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965).

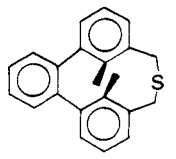
(8) Nakagawa (A. Yasuhara, T. Satake, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, 895 (1975)) estimates this to be 21 kcal/mol for naphthalene and 36 kcal/mol for benzene.

(9) For a preliminary report, see: R. H. Mitchell and J. S. H. Yan, *Tetrahedron Lett.*, 1289 (1979).

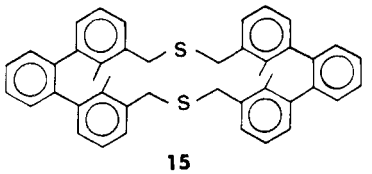
(10) R. H. Mitchell and J. S. H. Yan, *Can. J. Chem.*, **58**, 2584 (1980).

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

the corresponding syn-conformers **13** and **14** appear in the normal toluene region at δ 2.62 and 2.45 for **13** and δ 2.54 for **14**. Our preliminary report[3] also indicated that this reaction gave some of the syn conformer of **9**. This assignment is now known to be incorrect and was based on the ^{1}H NMR signal of the internal methyl protons which appeared at ca. δ 2.1, comparable with those of **13** and **14** above. We subsequently discovered after successfully



syn-**9**



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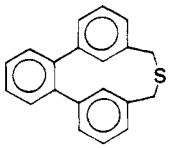

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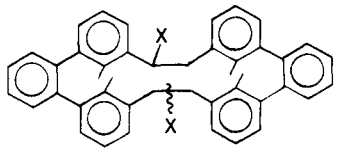


16 : X = SMe

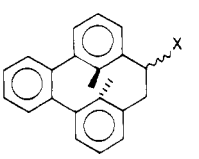
17 : X = H

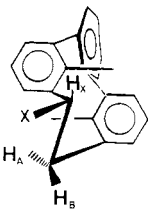
converting *anti*-**9** into *anti*-**2** that *syn*-**9** could not be converted to *syn*-**2**, but rather gave high molecular weight products. We thus redetermined the mass spectrum of *syn*-**9** on an MS50 and now found a small peak at *m/e* 632 corresponding to the molecular weight of the dimer **15**. The base peak, however, corresponded to symmetrical cleavage, *m/e* 316, also the molecular weight of **9**. The structure of **15** was then confirmed by Wittig rearrangement of **15**, using LDA and then CH_3I, into **16** followed by reduction with W-7 Raney Nickel to the first [2.2]terphenylophane **17**, mp 245–246 °C, $M^{+\cdot}$ at *m/e* 568 (100%). In the ^{1}H NMR spectrum of **17**, the internal methyl protons were a broad singlet at δ 1.90. Both the aromatic and methylene protons of **17** were complex multiplets and thus **17** probably exists in a (as yet undetermined) folded conformer.[12]

The parent thiacyclophane **18**, which has internal hydrogen substitutents has very recently been reported by Vögtle[13] and unlike **9** is conformationally mobile. Thus in our hands, none of the syn-conformer **9** could be isolated. This contrasts with the parent system, where a 7:1 ratio of anti:syn products, **12** and **14**, is obtained,[11] and to the benzo[*a*] series **11** and **13**, where an 11:1 ratio of anti:syn was observed.[1] It would seem that contraction of one of the three-membered bridges of **12** to the two-membered bridge of **9** makes formation of syn-**9** energetically unprofitable, and hence entirely *anti*-**9** is formed. Molecular models of *syn*-**9** indicate severe steric crowding of the methyl groups.

Conversion of **9** and **2** could be affected in several ways: We first attempted a Wittig rearrangement of **9**, using LDA followed by methyl iodide. Ring contraction occurred in 80% yield to give **19** as a mixture of isomers, from which a single isomer **19A** could be obtained by crystallization. The –SMe signal of this isomer was at δ 2.28, indicating[1] it to be a pseudoequatorial substituent, in agreement with the fact that both internal arylmethyl groups occurred at δ 0.80, whereas one would have been deshielded from the other if the –SMe were pseudoaxial. Remethylation of **19** with $(CH_3O)_2CHBF_4$[14] proceeded in 80% yield to **20**, which with potassium *tert*-butoxide in THF at reflux for 30 min gave 75% of the desired **2**.

The alternative benzyne-induced Stevens rearrangement[15] of **9** was also investigated; reaction of **9** with benzyne generated[16] in situ from anthranilic acid and isoamyl nitrite gave an 86% yield





19 : X = SMe

20 : X = $\overset{+}{S}Me_2\ \bar{B}F_4$

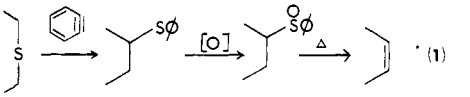
21 : X = SØ

22 : $SO_2Ø$

23 : SO_2Me

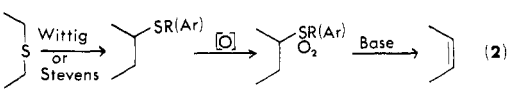
19A
21A
22A
23A

of **21**, which again crystallized as a single isomer, **21A**, mp 161–163 °C, analogous to **19A** on the basis of its ^{1}H NMR spectra. Although Boekelheide[15] carried out a sulfoxide elimination to introduce a double bond (eq 1), such eliminations require



(1)

rather high temperatures, and hence we investigated an alternative: whereas sulfonate (e.g., tosylate) eliminations under basic conditions are well known, the analogous eliminations of sulfinate are much rarer;[17] however there seemed to us no reason why eq 2 should not be possible.



(2)

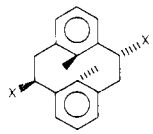
Indeed phenyl sulfide **21** was readily oxidized in 80% yield to the sulfone **22**, mp 238–239 °C, using hydrogen peroxide in acetic acid. Treatment of **22** with potassium *tert*-butoxide in tetrahydrofuran at reflux then gave an 84% yield of the desired **2**. Analogously methyl sulfide **19** gave 93% of the sulfone **23**, mp 227–229 °C, and then 47% of **2** after treatment with base as above. This elimination of aryl (or alkyl) sulfinate is thus an alternative to the better known sulfonium salt or sulfoxide eliminations, and may be useful when they give poor yields;[18] however, the reaction did not work when other solvents or bases were tried.

The structure of the sulfones **22** and **23** were readily evident from their mass spectra which had molecular ions at *m/e* 424 and 362, respectively, with base peaks corresponding to loss of $-SO_2Ph(Me)$, and their IR spectra which showed strong $-SO_2-$ bands at ca. 1300 and 1150 cm^{-1}. As can be seen from Table I, conversion to the sulfone shields the H_x proton and deshields the H_A and H_B protons, consistent with indications from molecular models which suggest that H_x falls in the shielding cone[19] of the $-SO_2-$ group whereas H_A and H_B fall in the deshielding region.

Properties of the Benzodihydropyrene 2. The benzannulene **2** was obtained from the above elimination reactions as deep purple-red crystals, mp 136–138 °C. After being exposed to light for some time, crystals of **2** become pale on the surface, indicating some conversion to the cyclophanediene form **8** (see below). The structure of **2** was supported by its mass spectrum, $M^{+\cdot}$ at *m/e* 282, with very strong peaks corresponding to loss of one and two methyls and formation of benzo[*e*]pyrene. In its ^{1}H NMR spectrum, the internal methyl protons appear highly shielded at δ –1.85, very similar to those of the benzo[*a*] derivative **1**, which are at δ –1.60. Clearly the gross reduction of ring current for **1** or **2** is about the same (50%) and is not affected much by the position of benzannelation. The actual difference between **1** and **2**, however, is 0.25 ppm which is probably too large[1] to be caused

(12) For a recently discovered related example see: R. H. Mitchell and Y. H. Lai, *Tetrahedron Lett.*, **21**, 2633 (1980).
(13) E. Hammerschmidt and F. Vögtle, *Chem. Ber.*, **113**, 1125 (1980).
(14) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).
(15) T. Otsubo and V. Boekelheide, *Tetrahedron Lett.*, 3881 (1975); *J. Org. Chem.*, **42**, 1085 (1977).
(16) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).
(17) See, for example: P. D. Magnus, *Tetrahedron*, **33**, 2019 (1977).
(18) R. H. Mitchell, *Heterocycles*, **11**, 563 (1978).
(19) D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", 2nd ed., McGraw-Hill Ltd., London, 1973, p 81.

Table I. ^{1}H NMR Spectra (δ) of the Bridge and Methyl Protons of Several Thio-Substituted Cyclophanes

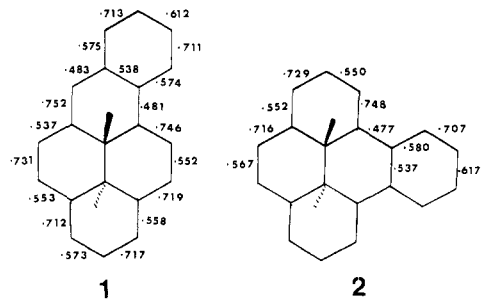
compd	X	H_X	H_A	H_B	$-CH_3$	-SMe ($-SO_2$-Me)
21A	-SPh	4.23	3.25	2.60	0.72, 0.67	
22A	$-SO_2Ph$	3.92	3.70	2.95	0.67, 0.47	
19A	-SMe	3.88	3.28	2.60	0.80	2.28
23A	$-SO_2Me$	3.85	3.72	2.88	0.72, 0.70	3.02
	-SMe	4.02	3.21	2.62	0.64	2.13

(ref 11)

Table II. Calculated Bond Orders[a] ($P_{\mu,\nu}$), Alternance Parameter (Q), and Coupling Constants ($^3J_{\mu,\nu}$) for **3** (and hence **2**) and Experimental Values for **2**

μ,ν	$P_{\mu,\nu}$	Q	$^3J_{\mu,\nu}$ (calcd), Hz	$^3J_{\mu,\nu}$ (calcd) [corrected for steric effect], Hz	$^3J_{\mu,\nu}$ (exptl), Hz
12,11	0.707	1.146	7.95	8.25	8.26
11,10	0.617		7.09	7.09	6.93
3,2	0.729	1.325	8.16	8.24	8.97
2,1	0.550		6.44	6.74	6.84

[a] See the previous paper,[1] ref 40, for a detailed description.



1 2

Figure 1. Calculated[20] π-SCF bond orders for benzannulenes **1** and **2**.

by a deshielding effect of the benzo ring. Figure 1 shows the calculated[20] π-SCF bond orders for both **1** and **2**, and it can be seen that there are small differences in bond order between the two systems; however, the average deviation from the Hückel value for a 14-annulene of 0.642 is 0.099 for **1** and 0.101 for **2**. If the gross difference in shielding between the parent **5** and the benzannulenes **1** or **2** (which is about 2.5 ppm) is primarily caused by this increased bond localization[21] in the benzannulenes **1** and **2** (represented by the deviation of bond order of ca. 0.100), then the difference in average deviation between **1** and **2** (0.002) is much too small to produce a chemical shift difference between them of 0.25 ppm. Given that the most severe deviations from Hückel bond order occur around the points of ring fusion, and that these points occur at different positions on the noncircular current loop, it is possible that the actual difference in chemical shift between **1** and **2** is mainly caused by this anisotropy.[22]

Figure 2 presents the 250-MHz ^{1}H NMR spectrum of the aryl protons of **2**, together with the 90-MHz actual and simulated spectra for H-9 and -12. The assignments were made as follows.

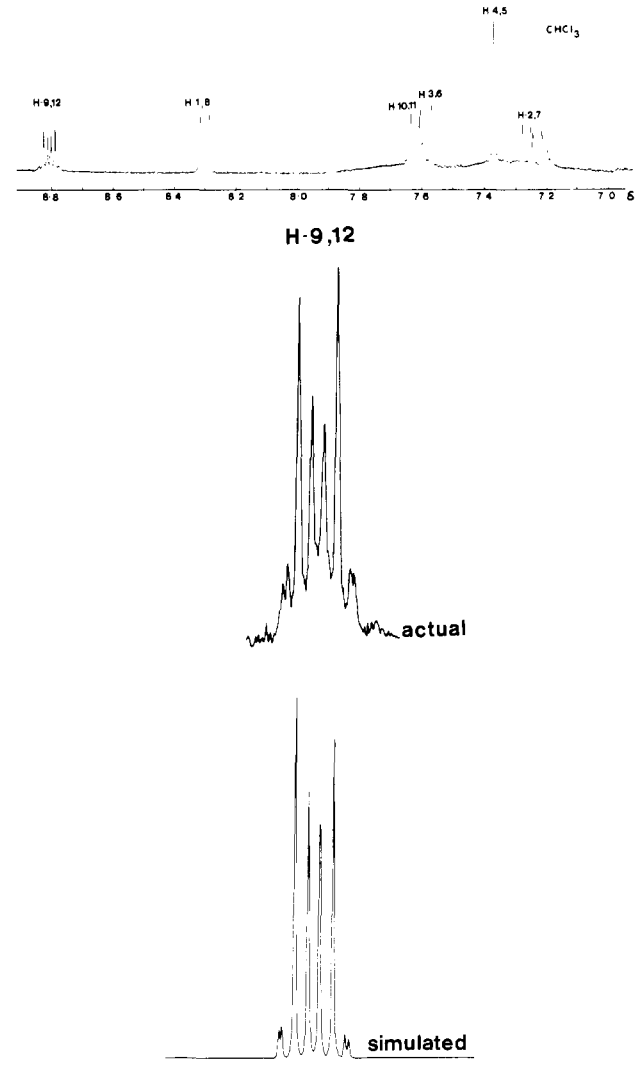


Figure 2. The 250-MHz (Brucker WM250) ^{1}H NMR spectrum of **2** (aryl protons only) and the 90-MHz (Perkin-Elmer R32) ^{1}H NMR spectrum of H-9, -12 of **2** with a simulated spectrum (lower) using $J_{9,10} = J_{11,12} = 8.26$ Hz; $J_{10,11} = 6.93$ Hz; $J_{9,11} = J_{10,12} = 1.37$ Hz; and $J_{9,12} = 0.49$ Hz, with $\Delta\nu = 112$ Hz.

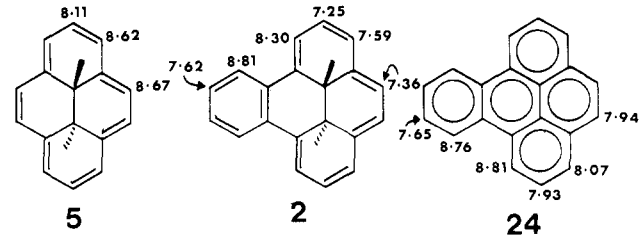


Figure 3. ^{1}H chemical shift (δ) values for benzannulene **2**, benzo[*e*]pyrene (**24**),[25] and parent **5**.[26]

As with hydrocarbon **1**, the bay protons of **2**, H-9,12 and H-1,8, appear at lowest field, δ 8.81 and 8.30, respectively. H-9,12 appear as part of an AA′XX′ multiplet, and this is shown in detail in Figure 2, since the coupling constants can easily be obtained by analysis[24] and simulation (discussed later). On the other hand, H-1,8 appear as a doublet, $J = 6.84$ Hz, coupled to H-2,7, with the meta coupling to H-3,6 too small to be observed. H-4,5 appear as the only singlet at δ 7.36, and H-10,11 as the other part of the AA′XX′ multiplet at δ 7.62, leaving only H-3,6 which like H-1,8 appear as a doublet, $J = 8.97$ Hz, at δ 7.59 and H-2,7 which

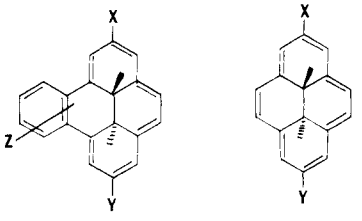
(20) See ref 1 for a detailed explanation of the calculations.
(21) Evidence for this hypotheses is presented in the final accompanying paper.
(22) The calculation of proton shieldings in conjugated hydrocarbons is rather complex[23] but certainly depends upon the position of the proton, relative to the current loop.
(23) H. Vogler, *J. Am. Chem. Soc.*, **100**, 7464 (1978).
(24) H. Günther, *Angew. Chem., Int. Ed. Engl.*, **11**, 861 (1972).

appear as a double doublet at δ 7.25. These assignments are consistent with those known[25] for benzo[*e*]pyrene (**24**), and as in the case of **1** when it was compared to benzo[*a*]pyrene in the previous paper,[1] the protons on the [14]annulene rings in both cases are ca. 0.5 ppm less deshielded than the corresponding protons on the pyrene rings. The [14]annulene protons of **2** are also ca. 0.9 ppm less deshielded than those of the parent **5**, consistent with a smaller ring current in the macroring of **2** than in **5**.

Table II gives the calculated and observed coupling constants for **2**. The corrected $^3J_{\mu,\nu}$ values were obtained by adding phenanthrene type (0.30 Hz) and naphthalene type (0.08 Hz) corrections as explained previously.[1] The results were amazingly good except for the $J_{3,2}$ value which appears to be 0.73 Hz larger than calculated. This may be because of the limited number of data points available in collecting the spectra (250 MHz). The results support the hypothesis[5] that cofusion of two aromatic rings results in considerable bond localization in each. On examination of the actual coupling constants it can be observed, in agreement with the *Q* values calculated, that the benzene ring localizes the 14π ring more than the 14π ring localizes the benzene ring. This result will be of considerable importance for the dibenzannulenes to be discussed in the following paper.

Electrophilic Substitution of 2. The ^{1}H NMR results obtained above for **2** indicated that while it was less diatropic than the parent **5**, the macroring of **2** still retained some diatropicity. While diatropicity does not necessarily imply[27] aromaticity, we thought it worthwhile to investigate whether this benzannulene was capable of undergoing the classic reaction of aromatic hydrocarbons, electrophilic substitution—particularly since no such reaction had ever been reported for a benzannulene, and indeed are sparse even for the parent annulenes.[28,29]

We first attempted nitration of **2** with cupric nitrate in acetic anhydride, the conditions used successfully for the parent[29] **5** and also previously for azulene.[30] The reaction was first carried out at 0 °C when the major product, isolated in 35% yield, was the **2**-nitro derivative **25**, dark blue crystals and mp 163–164 °C. Its structure was assigned on the basis of its $M^{+\cdot}$ at *m/e* 327, which showed **25** to be a mononitro compound (confirmed by analysis), with cleavage peaks corresponding to loss sequentially of the internal methyl's and the nitro group. In the IR spectrum the



2: X=Y=Z=H
25: X=NO_2; Y=Z=H
26: X=Y=NO_2; Z=H
28: X=Y=Z=NO_2
29: X=$COCH_3$; Y=Z=H

5: X=Y=H
27: X=NO_2; Y=H

Table III. Hückel Localization Energies for **2**

position	localization energy (units of β)	predicted order of reactivity
1	2.321	5
2	2.128	1
3	2.243	3
4	2.203	2
11	2.381	6
12	2.251	4

–NO_2 bands could be seen at 1485 and 1285 cm^{-1}. The assignment of the position of substitution was more difficult, since **25** is not symmetrical, and hence the ^{1}H NMR spectrum is complex. However, the doublet due to H-1, -8 at δ 8.30 of **2** integrated for only one proton in **25** at δ 8.43 (H-8) with a new strongly deshielded broad singlet appearing at δ 9.15 (H-1), with H-12 and -9 now no longer being identical and appearing as a multiplet at δ 9.1–8.7. Further support for this assignment was obtained by carrying out the nitration at 20 °C which gave 20% of the dinitro compound **26**, also dark blue, but which decomposed on melting at 197 °C. Its mass spectrum was obtained under chemical ionization conditions and gave MH^+ at *m/e* 373. The IR spectrum gave the –NO_2 bands at 1500, 1320, and 1300 cm^{-1}, and then only three bands below 1000 cm^{-1}, indicating the molecule to be symmetric (by comparison **25** gave nine major bands in this region). This is confirmed by the ^{1}H NMR and ^{13}C NMR spectra which indicate the molecule has symmetry; the later has only five peaks corresponding to aromatic carbon atoms bearing a hydrogen. The 2,7 assignment for **26** is made on the basis of its ^{1}H NMR spectrum which shows H-1, -8 strongly deshielded as a doublet at δ 9.09 (J = 1.5 Hz) coupled to H-3, -6, which now are also deshielded as a doublet at δ 8.71. Further the AA′ part of the AA′XX′ of H-*9*, -*12* -10, -11 can still be seen centered at δ 8.95 consistent with substitution occuring in the 14π ring. The large 2 H singlet for H-4, -5 is still seen, and occurs at δ 7.92. The internal methyl protons appeared at δ –1.60 for **26** and unresolved at δ –1.85 for **25**. This was at first sight surprising, but those for **27** are also unresolved at δ –4.03 (in **5** they appear at δ –4.25).[29] Further, the chemical shift of the methyl group in the nitrotoluenes is almost the same as for toluene itself.[31] The effects on the ^{13}C NMR peaks are larger: the internal methyl carbon for **26** appears at δ 18.4 (for **2** at δ 16.8) and the internal bridge carbon at δ 36.6 (for **2** at δ 35.2). Also two of the five external carbon (bearing hydrogen) resonances were deshielded by ca. 4 ppm in **26** relative to **2**. Taken collectively, we believe this evidence is not consistent with any other substitution pattern.

When excess cupric nitrate (4–5 equiv) was used at room temperature, the major product was a trinitro derivative **28**, isolated in 18% yield as dark green crystals, decomposing at 198 °C. The mass spectrum, (CI) with MH^+ at *m/e* 418 indicated introduction of three nitro groups, and in the ^{1}H NMR spectrum the external protons appeared even more deshielded than for **26**, as a multiplet at δ 9.7–7.8 with the internal methyl protons as singlets at δ –1.50 and –1.55. We were not able to ascertain which ring the third nitro group entered. The UV spectra for the nitro derivatives of **2** showed the expected strong bathochromic shifts from the parent for its 502 and 390 nm bands, e.g., for **26** these were at 631 and 419 nm, respectively.

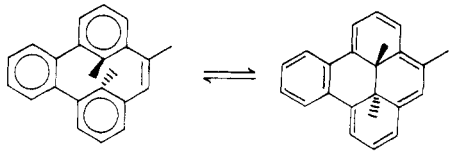
Friedel-Crafts acetylation of **2** also proceeded readily under mild conditions: acetic anhydride at 20 °C with a few drops of boron trifluoride etherate as catalyst gave the acetyl derivative **29** in 76% yield as dark purple crystals, mp 140–142 °C. The $M^{+\cdot}$ occurred at *m/e* 324 with peaks corresponding to facile loss of the methyls and –$COCH_3$. The IR spectrum gave a carbonyl stretch at 1660 cm^{-1}, and the ^{1}H NMR spectrum showed the –$COCH_3$ protons at δ 2.80 and internal methyl protons at δ –1.67. The assignment as the 2 derivative cannot be made with certainty, however, as with **25** H-8 still appears as a doublet at δ 8.25, but with a singlet (probably H-1) superimposed at δ 8.30. H-9, -12 also still appear at δ 9.1–8.6, but no longer are symmetrical, consistent with that assignment.

(25) M. Barfield, D. M. Grant, and D. Ikenberry, *J. Am. Chem. Soc.*, **97**, 6956 (1975).
(26) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).
(27) For an interesting discussion see: J. F. Labarre and F. Crasnier, *Top. Curr. Chem.*, **24**, 33 (1971).
(28) See, for example: Y. Gaoni and F. Sondheimer, *J. Am. Chem. Soc.*, **86**, 521 (1964); E. Vogel and W. A. Boll, *Angew. Chem., Int. Ed. Engl.*, **3**, 642 (1964); E. Vogel, W. A. Boll, and M. Biskup, *Tetrahedron Lett.*, 1569 (1966); I. C. Calder, P. J. Garrett, H. C. Longuet-Higgins, and F. Sondheimer, *J. Chem. Soc. C*, 1041 (1967).
(29) J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 1704 (1967).
(30) A. G. Anderson, Jr., J. A. Nelson, and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).
(31) C. J. Pouchert and J. R. Campbell, "The Aldrich Library of NMR Spectra", Vol. IV, Aldrich Chemical Co., 1974, p 1B; *ibid.*, Vol. V, pp 144C, 148D, and 151D.

Interestingly, localization energies calculated by the Hückel method also predict position 2 as the site for electrophilic substitution. These results are given in Table III. The benzannelating ring produces a noticeable perturbation in **2**, in that this method could not predict the results for the parent dimethyl dihydropyrene **5**, which also substitutes at position 2.

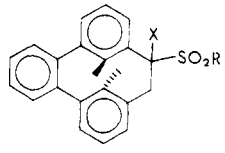
Clearly, however, these experiments have shown that a benzannulene such as **5** is stable enough to and is capable of undergoing electrophilic aromatic substitution and that this occurs in the macroring.

Synthesis of a 4-Methyl Derivative of 2. For our photoisomerization studies (to be described below) of **2** ⇌ **8**, we decided it would be desirable to have at least one compound where the substituent was on the cylcophane bridge. We thus decided to synthesize **30** and hence **31**.



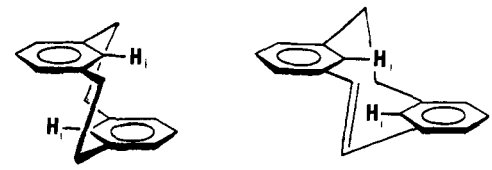
30 **31**

Direct introduction of a substituent at the 4 position in **31** or the parent **5** is not useful, since electrophilic substitution occurs mostly at positions 2 and 7. Boekelheide and Sturm,[32] however, have reported a synthesis for 4-methyl-**5**, but it is rather long and involved. It occurred to us, however, that substituents on the cyclophane bridge might possibly be introduced earlier in the synthesis making use of the thio-substituted cyclophane **22** or **23**.



22: X = H; R = Me
23: X = H; R = Ø
32: X = Me; R = Me
33: X = Me; R = Ø
34: X = H; R = Et
35: X = H; R = i-Pr

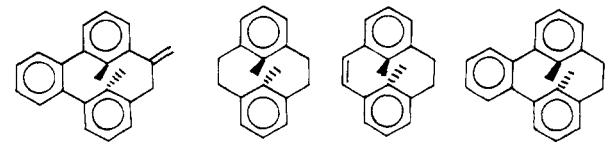
It is well known[33] that the strongly electron withdrawing sulfone group can stabilize an adjacent anion, and hence we projected that reaction of **22** or **23** with strong base and then methyl iodide would yield **32** or **33**. Somewhat to our surprise, however, reaction of **22** with lithium diisopropylamide (LDA) in THF at −78 °C followed by methyl iodide yielded first the ethylsulfone **34** and with excess LDA the isopropylsulfone **35** in 69% and 65% yields, respectively. The structure of **34**, mp 198–200 °C, was readily assigned on the basis of the ^{1}H NMR spectrum which showed a $-SO_2CH_2CH_3$ quartet at δ 3.21 and $-SO_2CH_2CH_3$ triplet at δ 1.34, and the $M^{+\cdot}$ at m/e 376 with base peak at m/e 283 (loss of $-SO_2Et$). For **35**, mp 242–244 °C, $M^{+\cdot}$ was at m/e 390 with base peak again at m/e 283 (loss of $-SO_2$-*i*-Pr). The phenylsulfone **23**, however, did give the desired **33** in 89% yield, mp 218 °C dec; $M^{+\cdot}$ at m/e 438 with base peak at m/e 297 (loss of $-SO_2Ph$). In its ^{1}H NMR spectrum, the bridge methyl appeared at δ 1.70, and the methylene bridge protons at δ 3.67 (deshielded by $-SO_2Ph$) and δ 2.62 as doublets, J = 15 Hz. This sulfone was then heated under reflux with potassium *tert*-butoxide in THF and gave 77% yield of the purple dihydropyrene **31**: mp 158–159 °C; $M^{+\cdot}$ at m/e 296 with facile loss of one and then two $-CH_3$ groups. The ^{1}H NMR spectrum was similar to that of **2** with the external methyl appearing at δ 2.61, considerably less deshielded than that of 4-methyl-**5** (δ 3.26)[32] which is consistent with the reduced ring current in **31** (or **2**). The internal methyl protons of **31** appeared at δ −1.90 and 1.95, very similar to those of **2**. The UV spectrum showed the expected bathochromic shift for methyl substitution.[34] The success of this synthesis indicates that it may be possible to introduce other substituents on the bridge.



42 **41**

Figure 4. A representation of the difference between molecular models of **42** and **41**.

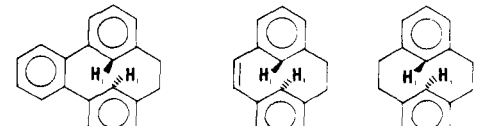
A Novel *exo*-Methylenecyclophane. As a minor product from the above sulfone elimination there was obtained a product of identical molecular weight, $M^{+\cdot}$ at m/e 296. This product could only be obtained pure by chromatographic separation from **31** in the dark, such that none of **30** (the photoisomer) of **31**) was present. The minor product was then obtained in 9% yield as colorless crystals, mp 143–145 °C. Its structure was assigned as the *exo*-methylenecyclophane **36** on the basis of its ^{1}H NMR spectrum which showed the internal methyl groups at δ 0.76 and 0.67, consistent with those for the related **37** (δ 0.56)[35] and **38** (δ 0.79),[36] and vinylic protons as broad singlets at δ 5.28 and 4.96. The methylene bridge protons appeared as a superimposed AB pattern at δ 3.46 (J = 14 Hz). To our knowledge, this is the first cyclophane prepared with an *exo*-methylene group on the bridge, and is an interesting product, in that it indicates that there cannot be a very great difference in stabilities between the two isomeric alkenes **30** and **36**, which would not be true if **30** were planar and unstrained. For comparison purposes we prepared the cyclophane **39** by reaction of **19** and **21** with W-7 Raney Nickel.[37] **39** was



36 **37** **38** **39**

δ CH_3: 0.76, 0.67 | 0.56 | 0.79 | 0.67

then obtained in 85–95% yield as colorless crystals: mp 156–157 °C; $M^{+\cdot}$ at m/e 284. In its ^{1}H NMR spectrum, the internal methyl protons were at δ 0.67 and the bridge protons at δ 3.15–2.40. Clearly, the *exo*-methylene group of **36** deshields the adjacent methylene bridge protons as expected, but produces only a very small effect on the internal methyl groups, as indeed does the benzoannelating ring of **39** itself. Vögtle and Hammerschmidt[13] have very recently reported the compound with internal hydrogen atoms **40** and compared it to the previously known[38] **41** and **42**. In these examples the benzannealing ring of **40** or the double bond of **41** have quite marked *apparent* deshielding effects on the internal hydrogens of **42**, but not on the internal methyl protons of **37**. It seems to us *un*likely that this effect is



40 **41** **42**

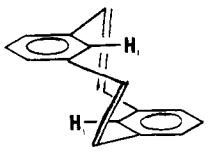
δ_H 5.44 | 5.62 | 4.25

(32) V. Boekelheide and E. Sturm, *J. Am. Chem. Soc.*, **91**, 902 (1969).
(33) E. M. Kaiser and C. R. Hauser, *Tetrahedron Lett.*, 3341 (1967); L. Field, *Synthesis*, 122 (1972); N. Bosworth and P. Magnus, *J. Chem. Soc., Perkin Trans 1*, 2319 (1973).
(34) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).
(35) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).
(36) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 3675 (1970).
(37) E. C. Horning, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 176.
(38) H. Blaschke and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 2747 (1967); D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *J. Am. Chem. Soc.* **82**, 6302 (1960).

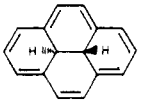
controlled by the anisotropy of the bridge, but likely from a change of geometry of the molecule: molecular models indicate that **42** should be considerably more stepped than **40** or **41**, with the net effect that H_i in **42** are pushed further over the opposite benzene ring in **42** than in **40** or **41** and hence are more shielded (see Figure 4). Models of **37**, **38**, **36**, and **39**, however, indicate the internal methyl groups are all similarly located with respect to the opposite benzene ring, probably because of the greater steric demand of a methyl group than a hydrogen atom, and hence appear at similar chemical shift.

The Photochemistry of Benzannulene 2 and Its Derivatives. One of the most interesting aspects of diemthyldihydropyrene **5** is its reversible photochemical valence tautomerization into the [2.2]metacyclophane-1,9-diene **6**. This is a specialized example of the more general *cis*-stilbene to 4a,4b-dihydrophenanthrene isomerization studied by Fischer[39] and others.[40] The tautomerization between **5** and **6** has been well studied by Blattmann and Schmidt[7] and has been observed in ca. 30 derivatives of **6**, with in each case the dihydropyrene being the thermodynamically more stable (for **5** and **6** by ca. 11 kJ/mol). The isomerization is fast because E_{ACT} (ca. 97 kJ/mol) is relatively low, probably because little change in geometry is required, unlike the *cis*-stilbene ⇌ dihydrophenanthrene case where rotation of the phenyl rings is involved. That the rate of tautomerization is sensitive to geometry is evident in the case of [2.2]metacyclophane-1,9-diene (**43**) itself, which can be isolated and obtained cyrstalline, though it is not reformed from dihydropyrene **44**, whereas **6** only exists in solution and rapidly reforms **5**.[11]

This is presumably because the samller size of the internal hydrogens of **43** make it less strained than **5** which has internal methyls. It does not explain why **43** → **44** is not reversible. Given the final balance of this tautomerization and the fact that, as discussed in the introduction, the benzo[*a*]annulene **7** was not in equilibrium with its tautomer **1**, there was considerable interest to investigate **2** ⇌ **8**.



43

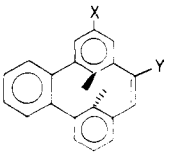


44

We found that the cyclophanediene tautomer **8** and its derivatives were considerably more stable than any previously obtained. In fact, their lifetime was sufficiently great that we preferred to use ^{1}H NMR methods to study the tautomerization since the internal methyl protons of **2** and **8** and their derivatives are well separated and sharp markers. The dihydropyrene was dissolved in C_6D_6 and irradiated with visible light to convert it fully to the colorless cyclophanediene form, and the thermal return to dihydropyrene was followed by recording the integration of the internal $-CH_3$ signals of both forms at suitable intervals. The rate constants obtained for **8** and its derivatives are given in Table IV.

The order of rate constants obtained is nitro-diene **45** > acetyl-diene **46** > parent-diene **8** > methyl-diene **30**, which is consistent with the UV derived results of Blattmann and Schmidt[7] for the analogous **6** → **5** systems. He reports for **6** → **5** a rate constant at 30 °C of 10×10^{-4} min^{-1}, which is greater than for **8**, consistent with our observations. These results are not directly comparable, however, because of the vastly different concentration involved. At UV concentration, the rate for **8** → **2** was inconveniently slow. An estimate of the energy of activation for **8** → **2** at a concentration of 20 mg/mL in C_6D_6 was obtained from the variable temperature results as ca. 105 kJ/mol. For **6** → **5** a value of 97 kJ/mol was found (UV method).[7]

Table IV. Rate Constants of Valence Tautomerization for **8** → **2** and Several Derivatives ($k \times 10^4$ min^{-1})



8: X=Y=H
45: X=NO_2; Y=H
46: X=$COCH_3$; Y=H
30: X=H; Y=CH_3

tautomerization	$k_{22\,°C}$	$k_{32\,°C}$	$k_{42\,°C}$
8 → **2**	0.78	4.4	11
45 → **25**		600	
46 → **29**		135	
30 → **31**		4.3	

As a result of the considerably greater stability of the cyclophanediene tautomers in this series, their ^{1}H NMR spectra were, for the first time, easy to obtain cleanly. The internal methyl protons of **30** appear at δ 1.41, considerably deshielded from those of **39** (δ 0.67), but comparable to those of the parent **6** (δ 1.52).[36] We have suggested previously[11] that the marked deshielding of the internal protons of the diene **43** (δ 7.90) relative to the monoene **41** (δ 5.62) is much too large to be caused by the anisotropy of the double bond, but probably arises from the known[41] flattening of the molecule which moves H_i out of the shielding into the deshielding region[42] of the opposite benzene ring. A similar affect for **30** seems likely, but is not so marked since the more sterically demanding[43] methyl groups allow less flattening.

Conclusions

The successful synthesis of the symmetrical benzannulene **2** has allowed us to analyse its ^{1}H NMR spectrum in sufficient detail to indicate that each annelating ring localizes the other but that the benzannelating ring has the largest effect, and this verifies Günther's calculations.[5] We have shown that the position of benzannelation has only a minor perturbation on the gross ring current of the macroring but a large effect on the photoisomerization to the cyclophanediene form and in the examples reported here stabilizes this tautomer. We have also shown that the benzannulene **2** is stable enough to undergo electrophilic aromatic substitution reactions.

Experimental Section

***anti*-9,21-Dimethylbenzo(10,11-*a*)-2-thia[2.3]metacyclophane (9) and Dimer 15.** A solution of the bisbromide **10**[10] (6.0 g, 13.5 mmol) in dry benzene (250 mL) was added through one dropping funnel at the same rate as a solution prepared by dissolving powdered $Na_2S{\cdot}9H_2O$ (3.57 g, 14.9 mmol) in N_2 purged H_2O (80 mL) and then adding N_2 purged 100% ethanol (170 mL) in a second addition funnel to vigorously stirred 95% ethanol (700 mL) under N_2 over 70 h. The mixture was stirred for a 12 h more and then evaporated. The residue was extracted with dichloromethane and water and the organic layer was washed, dried, and evaporated. The residue was preadsorbed and chromatographed on silica gel with pentane–dichloromethane (7:3) as eluant to yield first the anti-dimer **9**, 2.03 g (48%), as white crystals from cyclohexane: mp 201–202 °C; ^{1}H NMR (60 MHz) δ 7.75–7.0 (m, 10, ArH), 3.67 (ABq, J = 13 Hz, $\delta\nu$ = 7 Hz, 4, $-CH_2S-$), and 0.94 (s, 6, $-CH_3$); ^{13}C NMR δ 141.8, 139.5, 138.9, 134.5 (Ar–quaternary C) 130.6, 129.7, 129.0, 128.0, 126.0 (aryl CH), 30.7 ($-CH_2S-$), and 17.4 ($-CH_3$; $M^{+\cdot}$ *m/e* 316 (100), 284 (43),

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(44) For general experimental notes see the preceding paper in this issue.

283 (100), 282 (43), 269 (70), and 267 (50), and many lower *m/e* peaks. Anal. ($C_{22}H_{20}S$) C, H.

Eluted next was the dimer, 9,21,30,42-tetramethyl-2,23-dithia-[3.0.0.3.0.0]meta-ortho-meta-meta-ortho-metacyclophane (**15**), 1.75 g (20%), as white crystals from benzene: mp 251–253 °C; ^{1}H NMR (90 MHz) δ 7.5–6.7 (m, ArH), 3.25 (s, $-CH_2S$), and 2.1–1.4 (several unequal s, $-CH_2S-$ and $-CH_3$). The overall integration of aryl H to other H was about 1:1, but the compound was only poorly soluble and hence it was difficult to obtain a satisfactory spectrum; $M^{+\cdot}$ *m/e* 632. Anal. ($C_{44}H_{40}S_2$) C, H.

Wittig Rearrangement of Thiacyclophane 9. A solution of lithium diisopropylamide (prepared from *n*-BuLi (3.3 mmol in hexane 1.7 mL) and diisopropylamine (0.66 mL, 3.3 mmol)) in dry THF (25 mL) was added dropwise over 10 min to a solution of the thiacyclophane **9** (0.52 g, 1.65 mmol) under N_2 in dry THF (25 mL). After a further 10 min, methyl iodide ($\sim$ 0.3 mL, 5 mmol) was added such that the dark color was discharged. Water and dichloromethane were then added, and the organic layer was washed, dried, and evaporated. The residue was chromatographed over silica gel, using pentane–dichloromethane (85:15) as eluant, to yield mixed isomers of cyclophane **19**, 45 mg (80%). A portion was recrystallized from cyclohexane to yield colorless crystals of the single isomer **19A**: mp 165–166 °C; ^{1}H NMR (60 MHz) δ 8.0–7.1 (m, 10, ArH) 3.88 (dd, J_{XB} = 11 Hz, J_{XA} = 3 Hz, 1, $-SCH_x-$) 3.28 (dd, J_{AB} = 11 Hz, J_{AX} = 3 Hz, 1, $-CH_AH_B-$), 2.60 (t, J_{BA} = J_{BX} = 11 Hz), 1, $-CH_AH_B-$), 2.28 (s, 3, $-SCH_3$), and 0.80 (s, 6, Ar–CH_3); $M^{+\cdot}$ *m/e* 330 (41), 315 (4), 285 (17), 267 (100), and 252 (76). Anal. ($C_{23}H_{22}S$) C, H.

Hofmann Elimination of Sulfonium Salt 20 to *trans*-12c,12d-Dimethyl-12c,12d-dihydrobenzo[*e*]pyrene(2). (a) Salt 20. Mixed isomers of **19** (183 mg, 0.55 mmol) in dichloromethane (5 mL) were added to a stirred suspension of $(CH_3O)_2CHBF_4$[14] (0.25 g, 1.5 molar equiv) in dichloromethane (5 mL) at −30 °C under N_2 and this was then stirred without further cooling for 3 h. Ethyl acetate ($\sim$5 mL) was then added and after thee solution was stirred for about 12 h the white precipitate was collected and dried to give 220 mg (80%) of **20**, 287 °C dec.

(b) Elimination. Potassium *tert*-butoxide (78 mg, 0.69 mmol) was added to a suspension of the salt from (a) above (200 mg, 0.46 mmol) in dry THF (10 mL) at ca. 20 °C under N_2. The reaction mixture was then heated under reflux for 30 min. After the solution was cooled aqueous 1 M HCl and dichloromethane were added and the organic layer was washed, dried, and evaporated. The residue was chromatographed over silica gel, using pentane as eluant, to give the benzannulene **2**, 98 mg (75%), as dark reddish crystals from hexane: mp 136–138 °C; ^{1}H NMR (250 MHz, see text) (60 MHz) δ 8.70 (m, 2, H-9, 12), 8.18 (d, J = 7 Hz, 2, H-1, -8), 7.62–6.94 (m, 8, ArH), and −1.85 (s, 6, $-CH_3$); ^{13}C NMR δ 138.1, 134.7, 128.9 (Ar–quaternary C), 125.7 (double), 124.5, 122.7, 122.1, 117.0 (aryl CH), 35.2 (internal bridge C), and 16.8 (internal $-CH_3$); UV (cyclohexane) λ_{max} (log ϵ_{max}) 634 nm (2.27), 531 (3.57), 502 (3.64), 390 (4.41), 372 (4.22), 354 (3.91), 338 (4.24), 322 (4.11), 304 (4.14), 259 (3.89), 253 (3.96), 247 (3.98), and 242 (3.99); $M^{+\cdot}$ *m/e* 282 (52), 267 (96), and 252 (100). Anal. ($C_{22}H_{18}$)C, H.

Benzyne-Induced Stevens Rearrangement of Thiacyclophane 9. A solution of anthranilic acid (68 mg, 0.50 mmol) in 1,2-dichloroethane (20 mL) was added dropwise over 1.5 h under N_2 to a refluxing solution of thiacyclophane **9** (126 mg, 0.40 mmol) and isoamyl nitrite (210 mg, 2.16 mmol) in 1,2-dichloroethane (20 mL). After the reaction mixture had refluxed for an additional 15 min it was evaporated and the residue was taken up in benzene–pentane (1:1) and chromatographed over silica gel to give the product **21**, 138 mg (86%), which on recrystallization from cyclohexane gave white crystals: mp 161–163 °C (**21A**); ^{1}H NMR (60 MHz) δ 8.0–6.9 (m, 10, ArH), 4.23 (dd, J_{XB} = 11 Hz, J_{XA} = 3 Hz, 1, Ar CH_xS–), 3.25 (dd, J_{AB} = 11 Hz, J_{AX} = 3 Hz, 1, Ar–CH_AH_B–), 2.60 (t, J_{BA} = J_{BX} = 11 Hz, 1, Ar–CH_AH_B–), 0.72 and 0.67 (s, 3 each, Ar–CH_3); $M^{+\cdot}$ *m/e* 392 (23), 283 (100), 268 (45), 267 (90), 253 (69), and 252 (96). Anal. ($C_{28}H_{24}S$) C, H.

Phenyl Sulfone 22. H_2O_2 (30%, 38 mL) was added to a solution of the phenylsulfide **21** (1.5 g, 3.8 mmol) in acetic acid (75 mL) and benzene (150 mL). The reaction mixture was then refluxed for 5 h, cooled, and evaporated. The residue was filtered through a short column of silica gel in dichloromethane and gave the sulfone **22**, 1.3 g (80%), as white cyrstals from benzene: mp 238–239 °C; ^{1}H NMR (60 MHz) δ 8.2–6.9 (m, 10, ArH), 3.92 (dd, J_{XB} = 12 Hz, J_{XA} = 3 Hz, 1, $-CH_xSO_2Ph$), 3.70 (dd, J_{AB} = 12 Hz, J_{AX} = 3 Hz, 1, Ar–CH_AH_B–) , 2.95 (t, J_{BX} = J_{BA} = 12 Hz, 1, Ar–CH_AH_B–), 0.67 and 0.47 (s, 3 each, Ar–CH_3); IR (KBr) 1320, 1295, 1155, and 1145 cm^{-1} ($-SO_2-$); $M^{+\cdot}$ *m/e* 424 (18), 360 (8), and 283 (100). Anal. ($C_{28}H_{24}O_2S$) C, H.

Elimination of Phenylsulfinic Acid from 22 under Basic Conditions. Benzannulene 2. Potassium *tert*-butoxide (26 mg, 0.24 mmol) was added to a refluxing solution of the sulfone **22** (20 mg, 0.047 mmol) in THF (5 mL) under N_2. After 1 h, the reaction was cooled and CH_2Cl_2, H_2O, and aqueous HCl were added. The organic layer was washed, dried, and evaporated. Chromatography of the residue on silica gel, using pentane as eluant, yielded benzannulene **2**, 11.1 mg (84%), identical (^{1}H NMR, UV, TLC) with the previous sample.

Methyl Sulfone 23. This was obtained in 93% yield from H_2O_2 (10 mL) and Wittig-product **19** (400 mg) in acetic acid (20 mL)–benzene (40 mL) exactly as described for **22** above. Recrystallization from benzene gave white crystals of **23**: mp 227–229 °C; ^{1}H NMR (90 MHz) δ 8.1–7.0 (m, 10, ArH), 3.85 (dd, J_{XB} = 12 Hz, J_{XA} = 3 Hz, 1, $-CH_xSO_2$), 3.72 (dd, J_{AB} = 12 Hz, J_{AX} = 3 Hz, 1, Ar–CH_AH_B–), 3.02 (s, 3, $-SO_2CH_3$), 2.88 (t, J_{BA} = J_{BX} = 12 Hz, 1, Ar–$CHAH_B$–), and 0.72 and 0.70 (s, 3 each, $ArCH_3$); IR (KBr) 1315, 1295, and 1140 cm^{-1} ($-SO_2-$); $M^{+\cdot}$ *m/e* 362 (40), 283 (100), 268 (70), 267 (97), 253 (96), and 252 (98). Anal. ($C_{23}H_{22}O_2S$) high resolution mass spectrum.

Elimination of Methylsulfinic Acid from 23 under Basic Conditions. Benzannulene 2. This was carried out as described for **22** above. From **23** (50 mg) and *t*-BuOK (77 mg) there was obtained 19 mg (47%) of **2**, identical with previous samples.

***anti*-8,20-Dimethylbenzo(9,10-*a*)[2.2]metacyclophane (39).** A mixture of the Wittig product **19** (500 mg, 1.5 mmol) and W-7 Raney Nickel[37] (9 g, excess) in absolute ethanol (50 mL) was refluxed for 12 h. After the mixture was cooled, the catalyst was removed by filtration and the solvent evaporated to yield cyclophane **39**, 420 mg (85%), as colorless crystals from cyclohexane: mp 156–157 °C; ^{1}H NMR (90 MHz) δ 7.80–7.25 (m, 6, ArH), 7.03 (s, 4, ArH), 3.15–2.40 (m, 4, $-CH_2-$), and 0.67 (s, 6, $-CH_3$); UV (cyclohexane) λ_{max} (log ϵ_{max}) 285 nm (3.50), 250 (4.61), 233 (4.56), and 211 (4.66); $M^{+\cdot}$ *m/e* 284 (28), 269 (100), 254 (38), 253 (38), and 252 (37). Anal. ($C_{22}H_{20}$) C, H.

Raney Nickel reduction of phenylsulfide **21** in exactly the same manner produced a 96% yield of **39**, identical with that above.

Nitration of Benzannulene 2. (a) 2,7-Dinitro-*trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*e*]pyrene (26). Powdered $Cu(NO_3)_2{\cdot}3H_2O$ (0.2 g, 1.1 mmol) was added to a solution of benzannulene **2** (0.2 g, 0.71 mmol) in acetic anhydride (40 mL) at ca. 20 °C. After the mixture was stirred for 30 min, the color of the reaction changed from purple to green. After the solution was stirred for an additonal 2 h, ice and ether were added. When the hydrolysis of acetic anhydride was complete, the ether layer was separated, washed, dried, and evaporated. The residue was chromatographed over silica gel, using pentane–dichloromethane (8:2) as eluant, to yield **26** (probably with other isomers), 50 mg (20%), which gave pure **26** on recrystallization from benzene as dark blue crystals: mp 197 °C dec; ^{1}H NMR (90 MHz) δ 9.09 (d, J = 1.5 Hz, 2, H-1, -8), 9.2–8.6 (m, 2, H-9, -12), 8.71 (d, J = 1.5 Hz, 2, H-3, -6), 8.1–7.7 (m, 2, H-10, -11, 7.92 (s, 2, H-4, -5), and −1.60 (s, 6, $-CH_3$); ^{13}C NMR δ 131.3, 128.6, 125.5, 123.9, and 111.5 (aryl *C*H), 36.6 (internal bridge C), and 18.4 (internal $-CH_3$), note the quaternary aryl–C were probably the very small peaks observed at δ 149.4, 144.3, 140.6, and 138.1; IR (KBr) 1500, 1320, 1300, 1085, 885, 755, and 735 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ_{max}) 631 nm (3.64), 589 (3.70), 530 (sh, 3.53), 419 (4.00), 398 (3.85), 338 (3.31), 322 (4.09), 275 (sh, 3.67), 259 (3.74), 253 (3.75), 247 (3.77), 237 (3.80), and 213 (4.14); $MH^{+\cdot}$ (CI) *m/e* 373 (100), 358 (31), 327 (9), 312 (20), and 281 (12). Anal. ($C_{22}H_{10}N_2O_4$) high resolution mass spectrum.

(b) 2-Nitro-*trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*e*]pyrene (25). When the above reaction was carried out at 0 °C for 40 min and then worked up as above, ca. 35% of the mononitro compound **25** was obtained. Recrystallization from cyclohexane yielded dark blue crystals of **25**: mp 163–164 °C; ^{1}H NMR (60 MHz) δ 9.2–7.3 (m, 11, ArH) and −1.85 (s, 6, $-CH_3$); IR (KBr) 1485, 1325, 1285, 1065, 875, 860, 815, 800, 740, 730, 725, 720, and 715 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ_{max}) 592 nm (3.74), 550 (sh, 3.70), 386 (4.09), 342 (4.20), 324 (4.19), 307 (4.22), 258 (4.69), and 232 (4.87); $M^{+\cdot}$ *m/e* 327 (38), 312 (63), 297 (23), 266 (100), 250 (39), and 239 (23). Anal. ($C_{22}H_{11}NO_2$) C, H, N.

(c) A Trinitro Derivative of 2, 28. When a 4 M excess of $Cu(NO_3)_2{\cdot}3H_2O$ was used in reaction (a) above and the solution was worked up after 20 min, chromatography yielded 18% of a dark green trinitro derivative of **2** as dark green crystals from benzene: mp 198 °C dec; ^{1}H NMR (60 MHz) δ 9.7–7.85 (m, 9, ArH), −1.50 and −1.55 (s, 3 each, $-CH_3$); IR (KBr) 1530, 1510, 1315, 1100, 895, 870, 815, 780, 765, 755, 735, and 685 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ_{max}), 682 nm, (sh, 3.04), 612 (3.61), 580 (sh, 3.57), 424 (3.85), 325 (3.84), and 222 (3.78); $MH^{+\cdot}$ (CI) *m/e* 418 (100). Anal. ($C_{22}H_{15}N_3O_6$) high resoultion mass spectrum.

2-Acetyl-*trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*e*]pyrene (29). Acetic anhydride (4 mL) and $BF_3{\cdot}(C_2H_5)_2O$ (30 drops) were added to a solution of **2** (0.25 g, 0.87 mmol) in CH_2Cl_2 (50 mL) at ca. 20 °C. After 3 min, the reaction was poured into ether and saturated sodium carbonate solution. The organic layer was washed, dried, and evaporated. The residue was chromatographed over silica gel, using first pentane to elute any unchanged **2** and second pentane–ether (95:5) to give the acetyl

compound **29.** In order to obtain a 76% yield of **29**, unchanged **2** had to be recycled twice. Recrystallization of **29** from cyclohexane gave dark purple crystals: mp 140–142 °C; ^{1}H NMR (60 MHz) δ 9.2–7.1 (m, 11, ArH), 2.80 (s, 3, $-COCH_3$), and −1.67 (s, 6, Ar–CH_3); IR (KBr) 1660 cm^{-1} (C=O); UV (cyclohexane) λ_{max} (log ϵ_{max}) 538 nm (3.72), 397 (4.08), 379 (4.06), 337 (4.21), 318 (4.26), 305 (4.30), and 231 (4.87); $M^+\cdot$ *m/e* 324 (45) 309 (54) 294 (16) 279 (20) 267 (100), and 266 (52). Anal. ($C_{24}H_{20}O$) C, H.

Methylation of Methyl Sulfone **22** To Give Ethyl Sulfone **34** and Isopropyl Sulfone **35**. Lithium diisopropylamide (LDA) prepared from *i*-Pr_2NH (0.12 mL, 0.62 mmol) and *n*-BuLi (0.62 mmol) in dry THF (5 mL)) was added in one portion to a solution of methyl sulfone **22** (0.15 g, 0.41 mmol) in dry THF (20 mL) at −78 °C under N_2. After 30 min methyl iodide (excess) was added to the dark reaction mixture, which was then warmed to ca. 20 °C before addition of water and dichloromethane. The organic layer was washed, dried, and evaporated and the residue filtered through silica gel in dichloromethane to give ethyl sulfone **34**, 107 mg (69%), as white crystals from benzene: mp 198–200 °C; ^{1}H NMR (90 MHz) δ 8.2–7.0 (m, 10, ArH), 4.0–3.5 (m, 2, Ar–CH_2–CH–) 3.21 (q, J = 7 Hz, 2, $-SO_2-CH_2-CH_3$), 2.90 (t, J = 12 Hz, 1, ArC*H*(SO_2–)CH_2–, 1.34 (t, J = 7 Hz, 3, $-SO_2-CH_2-CH_3$), and 0.70 (s, 6, Ar–CH_3); $M^+\cdot$ *m/e* 376 (14), 283 (100), 268 (32), 267 (50), 25 (73), and 252 (81). Anal. ($C_{24}H_{24}O_2S$) high resolution mass spectrum.

When 5 mol equiv of LDA were used in the above reaction there was obtained the isopropyl sulfone **35**, 105 mg (65%), as white crystals from benzene: mp 242–244 °C; ^{1}H NMR (90 MHz) δ 8.1–7.0 (m, 10, ArH), 4.0–3.3 (m, 3, Ar–CH_2–CH–SO_2–C*H*<), 2.90 (t, J = 12 Hz, 1, Ar–C*H*–(SO_2–)–CH_2–), 1.47 and 1.23 (d, J = 7 Hz, 3 each, –CH–(CH_3)$_2$), and 0.70 (s, 6, Ar–CH_3); $M^+\cdot$ *m/e* 390 (15), 283 (100), 268 (35), 267 (40), 253 (67), and 252 (55). Anal. ($C_{25}H_{26}O_2S$) high resolution mass spectrum.

Methylation of Phenyl Sulfone 23 To Give 33. The procedure described above for **22** was followed with use of sulfone **23** (1.2 g, 3.1 mmol) and LDA (31 mmol) in THF (120 ml) , to give the product **33**, 1.1 g (89%), as white crystals from benzene: 218 °C dec; ^{1}H NMR (90 MHz) δ 8.1–7.0 (m, 15, ArH), 3.67 and 2.62 (d, J = 15 Hz, 1 each, $-CH_AH_B$–Ar), 1.70 (s, 3, $-C(CH_3)SO_2Ph$), 1.23 and 0.72 (s, 3 each Ar–CH_3); $M^+\cdot$ *m/e* 438 (<1), 297 (100), 282 (30), 281 (65), 268 (20), 267 (62), 266 (71), 253 (21), and 252 (39). Anal. ($C_{29}H_{26}O_2S$) C, H.

Elimination of Phenylsulfinic Acid from 33 To Give *trans*-4,12c,12d-Trimethyl-12c,12d-dehydrobenzo[*e*]pyrene (31) and *anti*-8,20-Dimethyl-1-*exo*-methylenebenzo(9,10-*a*)[2.2]metacyclophane (36). Potassium *tert*-butoxide (0.55 g, 4.9 mmol) was added to a refluxing solution of the sulfone **33** (200 mg, 0.49 mmol) in dry THF (10 mL) under N_2 and heated under reflux for 1 h. After the solution was cooled, dichloromethane and water were added and then the organic layer was washed, dried, and evaporated. The residue was preadsorbed onto alumina (activity III) and chromatographed on a foil wrapped column, using pentane as eluant, to give first cyclophane **36**, 11 mg (9%), and then pyrene **31**, 99 mg (77%).

A portion of the pyrene **31** was recrystallized from pentane as purple crystals: mp 158–159 °C; ^{1}H NMR (90 MHz) δ 9.0–8.7 (m, 2, H-9, -12), 8.35 and 8.30 (d, J = 7 Hz, 1 each, H-1, -8), 8.0–7.0 (m, 7, ArH), 2.61 (s, 3, 4-CH_3), −1.90 and −1.95 (s, 3 each, inner CH_3); UV (cyclohexane) λ_{max} (log ϵ_{max}) 640 nm (2.30), 532 (sh, 3.53), 507 (3.58), 393 (4.46), 374 (4.29), 357 (sh, 4.01), 340 (4.28), 325 (4.14), 307 (4.12), 243 (3.94), and 235 (3.97); $M^+\cdot$ *m/e* 296 (22), 281 (89), and 266 (100). Anal. ($C_{23}H_{20}$) C, H.

A portion of the *exo*-methylenecyclophane **36** was recrystallized from pentane as white crystals: mp 143–145 °C (some softening from 135 °C); ^{1}H NMR (90 MHz) δ 7.8–6.8 (m, 10, ArH), 5.28 and 4.96 (bs, 1 each, $=CH_2$), 3.46 (t (superimposed dd), J = 14 Hz, 2, Ar–CH_AH_B–), 0.76 and 0.67 (s, 3 each, $ArCH_3$); IR (KBr) 895 and 800 cm^{-1} ($=CH_2$); UV (cyclohexane) λ_{max} (log ϵ_{max}) 290 nm (sh, 4.83), 248 (4.86), and 245 (4.86); $M^+\cdot$ *m/e* 296 (19), 281 (97), and 266 (100). Anal. ($C_{23}H_{20}$) high resolution mass spectrum.

General Procecure for Photoisomerization of Dihydropyrenes 2, 29, 25, and 31 To Give *anti*-8,20-Dimethylbenzo(9,10-*a*)[2,2]metacyclophan-1-ene (8) and Its 5-Acetyl-46, 5-Nitro-45, and 1-Methyl-30 Derivatives. A solution of the dihydropyrene (20 mg) in C_6D_6 (1 mL) was irradiated in an NMR tube by visible light from a slide projector for ca. 0.5 h, when it was fully converted to the colorless open cyclophanene form. It was then immediately placed in the probe of the 90-MHz NMR spectrometer, which had been previously set at the desired temperature. The reversion to the closed dihydropyrene valence isomer was then followed by recording and integrating the internal methyl peaks for both valence isomers at suitable time intervals. Where necessry the samples were kept in a constant temperature bath out of the NMR probe.

Chemical shifts (90 MHz) thus obtained follow.

Parent **8**: δ 8.1–6.9 (m, 10, ArH), 6.63 (s, 2, H-1, -2), and 1.41 (s, 6, $ArCH_3$).

5-Acetyl derivative, **46**: δ 7.85–6.73 (m, 9, ArH), 6.49 (s, 2, H-1, -2), 2.52 (s, 3, $-COCH_3$), and 1.42 and 1.37 (s, 3 each, $ArCH_3$).

5-Nitro derivative, **45**: V 7.8–6.7 (m, 9, ArH), 6.48 and 6.46 (s, 1 each, H-1, -2), and 1.41 (s, 6, Ar CH_3).

1-Methyl derivative, **30**: δ 7.7–6.4 (m, 10, ArH), 6.22 (bs, 1, H-2), 2.21 (s, 3, 1-CH_3), and 1.29 and 1.25 (s, 3 each, $ArCH_3$).

^{13}C NMR of parent **8**: δ 143.1, 142.2, 140.3, 137.1 (quaternary Ar–C) 131.7, 131.0, 128.6, 128.2, 127.2 (aryl–*C*H), 125.4 (bridge alkene carbon), and 19.5 (internal methyl carbon).

8,20,28,40-Tetramethyl[2.0.0.2.0.0]meta-ortho-meta-meta-ortho-meta-cyclophane (17). A solution of LDA (see above, 3.2 mmol) in dry THF (20 mL) was added dropwise over 1 h under N_2 to a solution of the dimer **15** (500 mg, 0.79 mmol) in dry THF (50 mL). After 30 min methyl iodide (0.3 mL, 4.5 mmol) was added and then after another 30 min water and dichloromethane. The organic layer was washed, dried, and evaporated. The residue was heated under reflux with W-7 Raney Nickel[37] (10 g) in ethanol (50 mL) for 12 h. After the solution was cooled and the catalyst and solvent removed the residue was preabsorbed on silica gel and chromatographed, using pentane–dichloromethane (9:1) as eluant, to yield **17**, 170 mg (46%), as white crystals from cyclohexane: mp 245–246 °C; ^{1}H NMR (90 MHz) δ 7.6–6.6 (m, 20, ArH), 3.1–2.3 (m, 8, $ArCH_2$–), and 1.90 (bs, 12, Ar–CH_3); UV (cyclohexane) λ_{max} (log ϵ_{max}) 215 nm (5.06), with a tail to 350 nm; $M^+\cdot$ *m/e* 568 (100). Anal. ($C_{44}H_{40}$) C, H.

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