mL of ether. The ether solution was dried over magnesium sulfate and evaporated to give 796 mg (100% by weight) of orange-colored solid residue which was chromatographed on silica gel, using 98:2 chloroform:cyclohexane. Separation was clean, giving fractions containing, in order of elution, 703 mg of mainly **7**, 5.15 mg of a mixture of **7** and **3**, 70.7 mg (0.302 mmol, 8.9%) of reasonably pure **2**, and 1.7 mg of unknown amine-like product(s). **7** and the mixture of **3** and **7** were further purified and separted on a column of alumina, using 8:3 benzene: petroleum ether as eluent to remove 699 mg (88.7%) of **7** and methanol to remove 9.7 mg (1.22%) of **3**. The final results are listed in run 2, Table I.

The solution which had been kept for 48 h in the refrigerator was treated similarly. Workup gave finally 133.9 mg (0.572 mmol, 95.3%) of **2**, 2.5 mg (1.9%) of **3**, and 2.0 mg (1.4%) of **7**.

Rearrangements to other conversions were carried out similarly for all KIE runs.

The **2** obtained from silica gel chromatography was dissolved in 5 mL of benzene to which 5 mL of trifluoroacetic anhydride was added. After being left to stand overnight the mixture was evaporated to dryness. The bis(trifluoroacetyl) derivative of **2** thus obtained was purified by sublimation, twice for mass spectrometric analyses (^{15}N and ^{13}C) and three times for scintillation counting (^{14}C). Each sample of the bis(trifluoroacetyl) derivative had mp 183-184 or 184-185 °C.

KIE Measurements. (A) Whole-molecular-ion mass ratios in the bis(trifluoroacetyl) derivative of **2** were determined with a Hewlett-Packard Model 5995 mass spectrometer, using the selected-ion-monitoring (SIM) mode. All samples were introduced into the mass spectrometer via the solid sample inlet, using the direct insertion probe. Samples were heated as required to maintain a constant source pressure of 8×10^{-7} torr. Data collection for nitrogen KIE was achieved by monitoring the abundances of ions of *m/e* 426 and 428 at 70 eV. The average dwell time was 50 ms/ion. Three runs of approx 5000 scans each were made for each sample. The data were normalized for 100% *m/e* 426 and then corrected for the abundances of ions 426 and 428 in the unenriched derivative of **2**, measured similarly. In this way the enrichment of ion *m/e* 428 was determined in samples at each conversion. Calculations of KIE were made as described earlier.[1]

(B) Mass ratios $^{29}N_2/^{28}N_2$ and $^{45}CO_2/^{44}CO_2$ were measured in the laboratories of Krueger Geochron with use of a VG Micromass model 903 triple collector isotope-ratio mass spectrometer. In this method a sample was mixed with preburned CuO, sealed in an evacuated tube, and heated at 550 °C for 8 h to convert the sample into a mixture of nitrogen, carbon dioxide, and water. The gases were separated cryogenically for mass ratio analyses. The method has been described by Sofer.[19]

(C) The ^{14}C content of samples was measured by scintillation counting with use of a Beckman Model LS 7000 counter with its appropriate programs. Approximately 3 ± 0.001 mg of sample was weighed on a Cahn balance and dissolved in 10.0 mL of cocktail (Packard SC INT-O No. 6013183). Three samples were weighed for each conversion, and each sample was counted 18 times. The average count per sample was in the range of 38500-39100, and the standard deviation in counting ranged from 0.05 to 0.55%. KIE were calculated with the use of eq 3 and 4; the iteration procedure for eq 4 has been described earlier.[1]

(19) Sofer, Z. *Anal. Chem.* **1980**, *52*, 1389.

Synthesis and Diatropicity of a Phenanthrene-Annelated *trans*-Dimethyldihydropyrene: A Novel Molecule To Indicate the High π-Bond Order of the 9,10 Bond of Phenanthrene

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Abstract: The *trans*-phenanthrodimethyldihydropyrene **6** has been synthesized from phenanthraquinone and 2,6-dichlorotoluene in 0.3-0.5% overall yield by using Stevens or Wittig rearrangements and a Hofmann elimination sequence on the thiacyclophane **8B** followed by valence tautomerization of the resulting cyclophanediene **9**. This novel aromatic molecule **6** is used as a model to study the effect of phenanthroannelation on the diatropicity of an annulene. The internal methyl protons of **6** appear at δ -3.32, indicating a strong diamagnetic ring current. As predicted, the high π-bond order of the 9,10 bond of phenanthrene has resulted in much less bond localization in the 14π macrocyclic ring compared to the related benzannelated system **7**. An unexpectedly low 1.0:6.1 ratio of **6**:**9** was obtained in the synthesis, which represents the first example of the dimethyldihydropyrene ⇄ [2.2]metacyclophanediene system to have the latter as a major tautomer. This is believed to be due to adverse steric strains caused by the interaction between the H(1)-H(16) and H(8)-H(9) protons when **6** achieves planarity. Reduction in diatropicity of **6** compared with the parent **3** is discussed in terms of effects of annelation, deviation from planarity, and conjugation.

The works by Sondheimer,[1] Nakagawa,[2] Vogel,[3] Boekelheide[4] and Mitchell[5] on different families of nonbenzenoid [4*n* + 2]-annulenes have collectively led to the better understanding of various aspects of aromaticity. One of the more interesting areas is the effect of annelation, in particular benzannelation,[5,6] on the diatropicity of the annulenes. The effect could be clearly observed from ^1H NMR studies of changes in chemical shifts of the "internal" protons or substituents of the annulenes. For example, benzannelated [14]annulenes **2**[7] and **4**[5a,8] have internal protons and methyl protons significantly shifted compared with their respective parent [14]annulene systems **1**[9] and **3**.[10] Although

(1) See, for example: (a) Sondheimer, F. *Pure Appl. Chem.* **1963**, *7*, 363. (b) Sondheimer, F.; Calder, I. C.; diMaio, G.; Mayer, J.; Sargent, M. V.; Wolovsky, R. *Spec. Publ.-Chem. Soc.* **1967**, *21*, 75. (c) Sondheimer, F. *Proc. R. Soc. London, A* **1967**, *297*, 173. (d) Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81. (e) Sondheimer, F. *Chimia* **1974**, *28*, 163.

(2) For a review, see: Nakagawa, M. *Pure Appl. Chem.* **1975**, *44*, 885.

(3) For reviews, see: (a) Vogel, E. *Spec. Publ. Chem. Soc.* **1967**, *21*, 113. (b) Vogel, E. *Chimia* **1968**, *22*, 21. (c) Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237. (d) Vogel, E. *Ibid.* **1971**, *28*, 355. (e) Vogel, E. *Chimia* **1979**, *33*, 57.

(4) For a review, see: Boekelheide, V. *Pure Appl. Chem.* **1975**, *44*, 751.

(5) See, for example: (a) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2544. (b) Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *Ibid.* **1982**, *104*, 2551. (c) Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *Ibid.* **1982**, *104*, 2560.

(6) (a) Mitchell, R. H. *Isr. J. Chem.* **1980**, *20*, 594. (b) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y.-H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571.

(7) (a) Meissner, U. E.; Gensler, A.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 365. (b) Staab, H. A.; Meissner, U. E.; Weinach, W.; Gensler, A. *Chem. Ber.* **1979**, *112*, 3895.

(8) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L. *J. Am. Chem. Soc.* **1978**, *100*, 1007.

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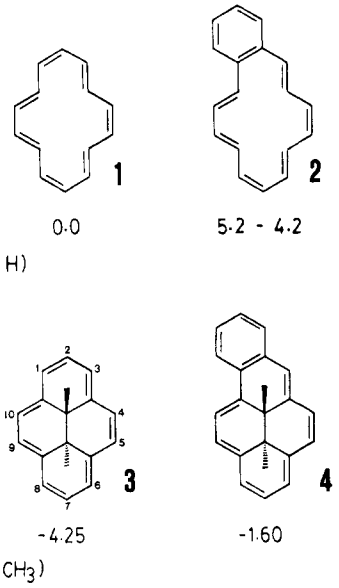
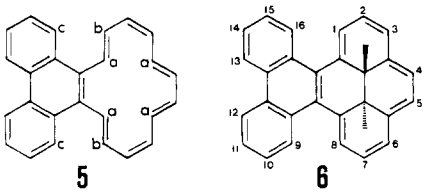


the degree of the effect varies, annelation commonly results in a decrease in diatropicity of the macrocyclic ring. This is believed to be due to bond localization caused by annelation. In this respect, phenanthro[4*n* + 2]annulenes in which the 9,10 bond of phenanthrene is involved in annelation should behave rather differently from benzannelated systems. As the 9,10 bond of phenanthrene is well-known to have a high π-bond order, such annelation would be expected to result in a much smaller effect on the diatropicity of the annulene with the 9,10 bond participating more freely in the macrocyclic ring current.

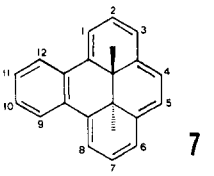
The synthesis of the phenanthro[14]annulene **5** was reported by Staab.[7b] ^{1}H NMR studies[7b] have, however, indicated that **5** is nondiatropic (internal protons appear at δ 5.9–7.2, –20 °C) compared with its parent system **1** (internal protons appear at δ



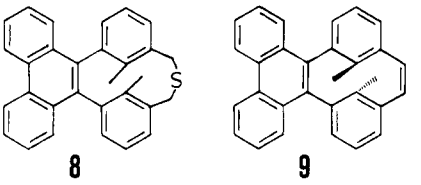
0.0, –60 °C).[9] The nondiatropic nature of **5** is believed to be due to the failure of the macrocyclic ring to achieve planarity. Besides the interaction among the internal H_a protons, large steric interaction is also expected from the close proximity of the outer H_b protons on the macrocyclic ring to the H_c protons on the phenanthrene moiety if the whole molecule is to assume a planar geometry. Dimethyldihydropyrene (**3**),[10] with a rigid near-planar structure,[11] has been used successfully as a more ideal model aromatic system for the studies of the effects of annelation.[5,6,12] Thus the derivative **6** should serve as a better model when compared with **5** to indicate the effect of phenanthroannelation. As the synthesis of the benzannelated system **7** has also been reported,[5b] a comparison of the diatropicities of **3**, **6**, and **7** would clearly indicate the extent of π-bond localization in **6**.

Results and Discussion

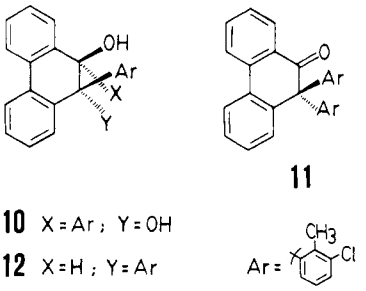
Synthesis. The parent *trans*-dimethyldihydropyrene (**3**)[13] and several of its derivatives[5,12] have been successfully obtained from



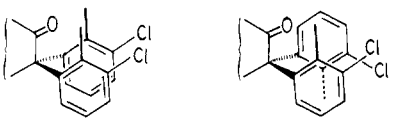
the valence tautomerization of the corresponding [2.2]metacyclophanedienes. Thiacyclophanes, on the other hand, are common precursors to cyclophanedienes via ring-contraction reactions.[14] Our approach to the synthesis of **6** was first to prepare the thiacyclophane **8**, which was expected to afford the cyclophanediene **9** (and hence **6**) subsequently.



The 9,10-diarylphenanthrene **13** was prepared in several steps similar to those reported for the synthesis of 9,10-diphenylphenanthrene derivatives.[15] Thus treatment of phenanthraquinone with the mono-Grignard reagent prepared from 2,6-dichlorotoluene yielded the 1,2-diol **10** after hydrolysis. The addition of the

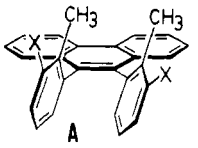


Grignard is expected to be stepwise and anti due to steric factors to give the *trans*-diol **10** without the formation of the diastereomeric *cis*-diol (similar results were observed in other related systems[15]). This was well supported by a sharp melting point (234–236 °C) and the ^{1}H NMR spectrum of **10**, which showed only one type of methyl proton at δ 2.06 as a sharp singlet. The pinacol rearrangement of **10** in refluxing acetic acid with sulfuric acid as a catalyst was slow. However, the ketone **11** was obtained readily in an 85–90% yield by using trifluoroacetic acid at room temperature (30–45 min). The ^{1}H NMR spectrum of **11** showed two singlets for the methyl protons at δ 2.09 and 1.76 ($\approx$1:1) respectively. The large difference in chemical shifts ($\Delta\nu$ = 30 Hz) suggests a mixture of the syn and anti isomers **11A** and **11B**

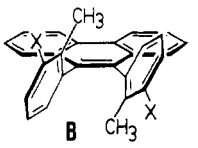


with the methyl groups of the latter shielded by the opposite benzene rings and appearing at δ 1.76. Reduction of **11** with $LiAlH_4$ afforded the alcohol **12**, which upon treatment with 0.3% acetic acid solution of iodine led to the desired dichloride **13**. The UV spectrum of **13** with a λ_{max} at 258 nm (ϵ 52000) is very similar to that of 9,10-diphenylphenanthrene,[15a] and thus the two aryl rings are expected to be noncoplanar with the phenanthrene nucleus. The ^{1}H NMR spectrum of **13** showing two methyl signals

(9) (a) Gaoni, Y.; Melera, A.; Sondheimer, F.; Wolovsky, R. *Proc. Chem. Soc., London* **1964**, 397. (b) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. (c) Gilles, J. M.; Oth, J. F. M.; Sondheimer, F.; Woo, E. P. *J. Chem. Soc. B* **1971**, 2177.
(10) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695.
(11) Hanson, A. W. *Acta Crystallogr.* **1965**, *18*, 599.
(12) Mitchell, R. H.; Slowey, P. D.; Kamada, T.; Williams, R. V.; Garratt, P. *J. Am. Chem. Soc.* **1984**, *106*, 2431.
(13) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.
(14) For a review, see: Mitchell, R. H. *Heterocycles* **1978**, *11*, 563.
(15) (a) Fuson, R. C.; Tomboulian, P. *J. Am. Chem. Soc.* **1957**, *79*, 956. (b) Moriconi, E. J.; Wallenberger, F. T.; Kuhn, Y. P.; O'Connor, W. F. *J. Org. Chem.* **1957**, *22*, 1651.



A



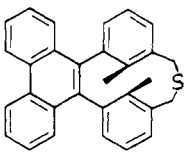
B

	X
13	Cl
14	CN
15	CH_2NH_2
16	CH_2OH
17	CH_2Br

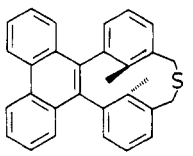
at δ 1.97 and 2.08 ($\approx$1:8.5) further suggests the presence of the two isomers **13A** and **13B** due to restricted rotation of the aryl rings.[16] Similar results were observed for all 9,10-diarylphenanthrenes **14–17**. No attempt was made at any stage to separate the isomers, but satisfactory C,H elemental microanalyses and/or GC–MS analyses in each case ruled out the possibility of the presence of two different compounds.

Conversion of **13** to the dinitrile **14** (IR 2240 cm^{-1}) was readily achieved in 92% yield by the von Braun reaction using CuCN in refluxing *N*-methyl-2-pyrrolidinone. Reduction of **14** with $LiAlH_4$ afforded the diamine **15** (quantitative), mp >300 °C dec (IR 3500 cm^{-1}). The ^1H NMR and IR spectral data of the reaction product obtained from diazotization of the diamine **15** in aqueous acetic acid—a method for conversion of a benzylamine to benzyl alcohol[17]—indicated esterification at the benzylic position(s); direct NaOH hydrolysis of the mixture, however, gave the desired diol **16** in an 81% overall yield. Treatment of the diol **16** with PBr_3 then led to the bis(bromomethyl) compound **17** (84%).

Sodium sulfide coupling[14] of the dibromide **17** under high dilution conditions afforded a low but reproducible yield ($\approx$20%) of a mixture of the two thiacyclophanes **8A** and **8B** in a 1:2 ratio.



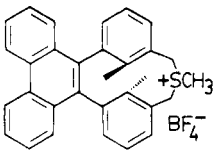
syn **8A**



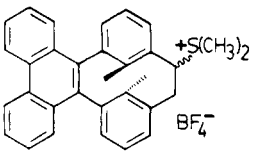
anti **8B**

Although the anti conformer is always obtained as the major isomer for thiacyclophanes leading to **3** (syn:anti ratio = 1:7)[13] and its derivatives,[5] the ratio of syn:anti product for **8A**:**8B** is the highest so far reported. All attempts (fractional crystallization and repeated chromatography) to separate the two isomers have, however, thus far been unsuccessful. Several chromatographs on silica gel have only afforded a pure sample of *anti*-**8B**, mp 275–277 °C, but *syn*-**8A** could not be obtained free from its anti isomer. However, ^1H NMR distinction of **8A** and **8B** was very apparent; the internal methyl protons of *anti*-**8B** appeared shielded by the opposite benzene rings at δ 1.10, and those of *syn*-**8A** appeared normal in the toluene region at δ 2.10. These assignments are comparable to those reported for similar isomeric thiacyclophanes.[5] GC–MS studies showed that **8A** and **8B** could be well separated, and the respective mass spectra of the two isomers gave a strong molecular ion ($M^{+\cdot}$ at m/z 416) as the base peak with similar fragmentation patterns.

Ring contraction of the thiacyclophane **8B** could be effected in two ways. The sulfonium salt **18** was obtained in 86% yield by treating **8B** with $(CH_3O)_2CHBF_4$.[18] A Stevens rearrangement[19] of **18** using potassium *tert*-butoxide gave a rather low yield (34%) of a mixture of the isomers **19A** and **19B**. The alternative



18



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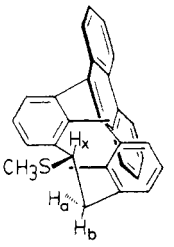
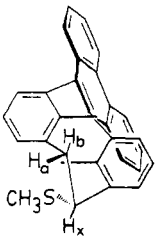


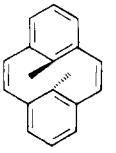
19A



19B

Wittig rearrangement[20] of **8B** with *n*-butyllithium in THF followed by methyl iodide quench gave mixed isomers **19A** and **19B** in 41% yield. No inversion to the syn geometry was expected in any of these rearrangements due to both the high barrier of rotation[16] and the high degree of steric repulsion between the two aromatic rings in the syn isomers.[19] Recrystallization of the mixture, however, yielded a single isomer **19A** ($\sim$80%) with the SCH_3 group at the pseudoequatorial position. The signals for Ar CH_3 (δ 0.79, s), SCH_3 (δ 2.19, s), H_aH_b (δ 2.60, t; δ 3.27, dd), and H_x (δ 3.88, dd) are in close agreement with those of the corresponding cyclophane obtained in the synthesis of **7**.[5b] A pseudoaxial SCH_3 group in **19B** would be expected to deshield one of the arylmethyl groups. Remethylation of **19** with $(CH_3O)_2CHBF_4$ proceeded in 60% yield to **20**, which with potassium *tert*-butoxide in THF in reflux for 45 min afforded deep orange crystals (53%). The ^1H NMR spectrum of the product mixture, mp 154–164 °C, however, showed two singlets for the methyl protons in a 1.0:6.1 ratio at δ −3.32 and +1.48 respectively expected to be a mixture of the dimethyldihydropyrene **6** and its valence tautomer metacyclophanediene **9**. Despite considerable efforts, we were unable to separate **6** or **9** from each other using crystallization and chromatography. However, a satisfactory elemental microanalysis for the general formula $C_{30}H_{22}$ was obtained for a purified sample of the mixture.

Valence Tautomerization. Besides its exceptionally high diatropicity observed from ^1H NMR studies, another interesting aspect of dimethyldihydropyrene **3** is its reversible photochemical valence tautomerization into the [2.2]metacyclophanediene **21**.[21]



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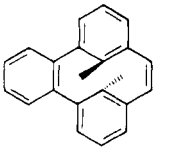


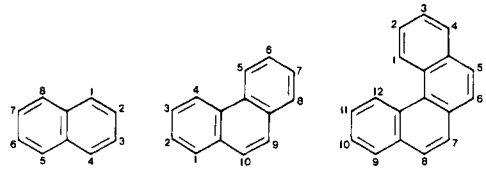
22

For **3** and its other known derivatives the tautomerization[5,21] always has the former as the thermodynamically more stable tautomer, presumably due to steric strains caused by the internal methyl groups in the anti stepped stereochemistry of the cyclophanediene. In addition, the Hofmann elimination[14] has always afforded directly the aromatic dimethyldihydropyrene system with little or no detectable amount of the corresponding cyclophanediene photoisomer. The observed 1.0:6.1 ratio of **6** and **9** from the

(16) Conformational studies of the parent 9,10-di-*o*-tolylphenanthrene and 9,10-di-*m*-tolylphenanthrene are currently being investigated. No free rotation of the aryl rings in the former was observed at room temperature.
(17) Funke, A.; Rougeaux, O. *Bull. Soc. Chim. Fr.* **1945**, *12*, 1050.
(18) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.
(19) Mitchell, R. H.; Boekelheide, V. *Tetrahedron Lett.* **1970**, 1197.
(20) Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 219.
(21) (a) Blattmann, H. R.; Schmidt, W. *Tetrahedron* **1970**, *26*, 5885. (b) Blattman, H. R.; Meuche, D.; Heilbronner, E.; Molyneux, R. J.; Boekelheide, V. *J. Am. Chem. Soc.* **1965**, *87*, 130. (c) Schmidt, W. *Helv. Chim. Acta* **1971**, *54*, 862.

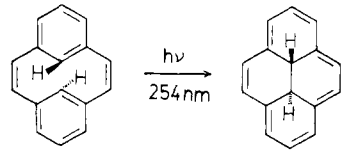
Hofmann elimination of **20** was rather remarkable and represents the first example of the dimethyldihydropyrene–cyclophanediene family to have the latter as a major tautomer. In fact irradiation of a solution of the deep orange mixture with visible light readily converts **6** fully to the colorless **9** to allow the recording of a clean ^{1}H NMR spectrum of **9**. Rapid concentration under reduced pressure yielded **9** as very pale yellowish crystals, mp 194–197 °C,[22] which turned pale orange on the surface after some time due to formation of **6**. ^{1}H NMR studies, however, indicated no measurable degree of tautomerization of **9** to **6** at 30 °C after <24 h. The internal methyl protons and vinyl protons of **9** appeared at δ 1.48 and 6.49, respectively, comparable with those observed for cyclophanediene **22** (δ 1.41, 6.63).[5b] The UV spectrum of **9** showed a λ_{max} at 252 nm (ϵ 71 800) similar to those observed for diarylphenanthrenes **13**–**17**.

The exceptionally slow thermal conversion **9** → **6** was next studied by the ^{1}H NMR method[5b] at a concentration of 30 mg mL^{-1}. A solution of **9** in CCl_4 or hexachlorobutadiene was kept in a constant temperature bath, and the conversion **9** → **6** was followed by obtaining the ratio of the methyl peaks at δ −3.32 and +1.48 in the ^{1}H NMR spectrum at suitable time intervals. Rate constants of 2.56×10^{-6}, 6.40×10^{-6}, and 2.83×10^{-5} s^{-1} were obtained at 60, 68, and 80.5 °C, respectively, indicating a much slower rate for **9** → **6** compared with **21** → **3**[21] and **22** → **7**.[5b] The adverse steric interactions between H1–H16 and H8–H9 in the near-planar structure of **6** should account for the less favorable tautomerization in the former system. The rate constants from the variable-temperature results gave an estimate of ca. 115 kJ mol^{-1} as the energy of activation for **9** → **6** compared with values of 97 kJ mol^{-1} (UV method)[21] and 105 kJ mol^{-1} (NMR method)[5b] for **21** → **3** and **22** → **7**, respectively. The order of energy of activation observed, i.e., **21** → **3** < **22** → **7** < **9** → **6**, is consistent with the increasing steric strains between H1–H10 and H8–H9 in **3**, H1–H12 and H8–H9 in **7**, and H1–H16 and H8–H9 in **6**, similar to those known for H1–H8 in naphthalene **23**, H4–H5 in phenanthrene **24**, and H1–H12 in benzo[*c*]phenanthrene **25**.



23 **24** **25**

Although dimethylcyclophanediene **21** and its derivatives undergo rapid valence tautomerization to the corresponding dimethyldihydropyrenes, the cyclophanediene **26**[13,23] and its derivatives[5a,c] could be readily isolated. The valence tautomerization of **26** → **27** (and derivatives), however, could be achieved by



26 **27**

irradiation with light at 254 nm.[13,23] When a sample of a mixture of **9** and **6** was similarly irradiated, a dark reddish purple solution was obtained. The tautomerization followed by ^{1}H NMR indicated gradual conversion of **9** → **6**, but prolonged irradiation seemed to cause decomposition after a ~50:50 mixture of **9** and **6** was obtained. Comparison of the ^{1}H NMR spectrum of the mixture and that of **9** indicated extensive overlaps in the aromatic region that disallowed any clear assignments for the aromatic protons of **6**.

(22) The crystals turned orange on slow heating; however, the pale yellowish crystals of **9** melted spontaneously when introduced at 195 °C.
(23) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3510.

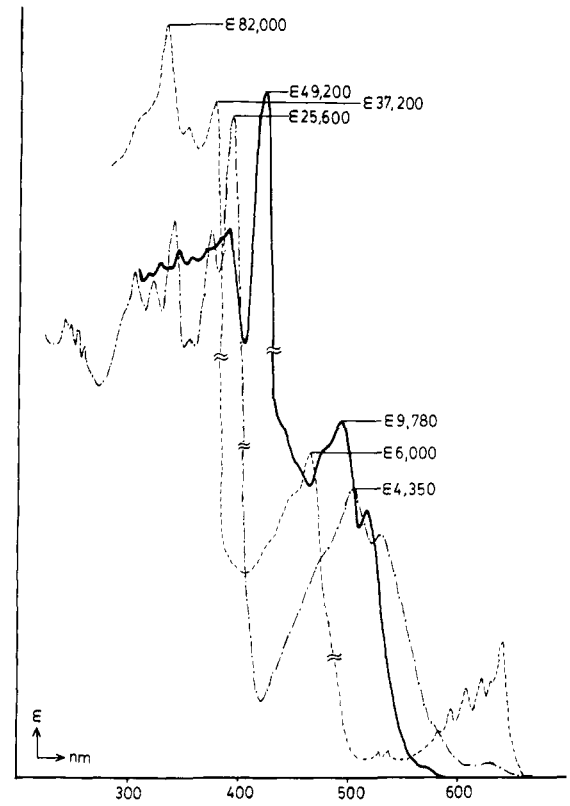


Figure 1. UV–vis Spectra of **3** (- - -), **6** (—), and **7** (–·–).

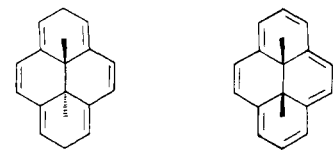
Table I. Comparison of the Diatropicities in Several Dimethyldihydropyrenes

compd	δ_{CH_3}	$\Delta\delta_{CH_3}$[a]	% ring current
3	−4.25	5.25	100
6	−3.32	4.32	82
7	−1.85	2.85	54
29	−2.06	3.06	58
30	−4.00, −4.03	5.00, 5.03	95–96
31	−3.81, −3.89	4.81, 4.89	92–93

[a] $\Delta\delta_{CH_3}$ is the shielding (in ppm) of the internal methyl protons relative to those in the nonaromatic model **28**.

Conjugation and Diatropicity. The UV spectrum of **6** (obtained from a 1.0:6.1 mixture of **6** and **9**) is shown in Figure 1 and compared with those of the parent dimethyldihydropyrene **3** and the benzannelated derivative **7** (reconstructed from literature data).[24,25] The major bands of **6** at 493 and 422 nm are bathochromically shifted from those of the parent **3** at 463 and 377 nm, respectively, consistent with the longer conjugated aromatic system in the former. The effect of the conjugation band can also be clearly observed on the ϵ values, which are considerably enhanced compared with those of **3** and **7**.

The chemical shifts of the internal methyl protons of **3** and its derivatives have been shown to be sensitive probes for the extent of delocalization (diatropicity) of the macroring.[5,6] A direct comparison of the observed ^{1}H NMR data for **3**, **6** and **7** (Table I) clearly indicates, as predicted, a much lower bond localization effect due to phenanthroannelation compared with benzannelation. Qualitatively, the comparison to the nonaromatic system **28** with

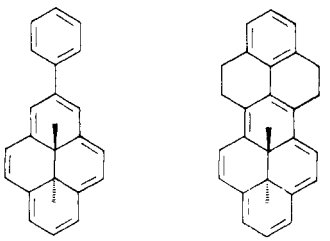


28 **29**

(24) Mitchell, R. H.; Boekelheide, V. *J. Chem. Soc. D* **1970**, 1555.
(25) Yan, J. S. H. M. Sc. Thesis, University of Victoria, 1978.

methyl protons in a similar environment (internal methyl protons at δ 1.0)[10] and the assumption that shielding is proportional to ring current[26] show that **6** sustains about 82% of the ring current of **3** compared with 55% for **7**.[10] Although the lower diatropicity of **6** compared with **3** could be due to the effect of annelation, we believe that another significant factor would be the puckering of the 14π macrocyclic ring in **6** due to steric strains between H1–H16 and H8–H9, as mentioned earlier, when **6** assumes planarity. Deviation of the π-system from planarity, for example the saucer-shaped *cis*-dimethyldihydropyrene **29**[24] (internal methyl protons at δ −2.06), has been shown to exhibit a smaller ring-current effect.

A third factor to be considered for the reduced diatropicity in **6** could be the effect of conjugation. Conjugation between two rings would, in principle, be expected to reduce the delocalization within any of the rings. Studies[27] on the diatropicities of **30** compared with that of **3** revealed a very small reduction (ca. 5%;



30 **31**

Table I) in the magnetic ring current in the macroring even though the conjugation effect is significant from comparison of the UV spectra of **3** and **30**. We believe that the small effect in diatropicity is due to the inability of the two rings in **30** to achieve complete planarity. This is well supported by a comparison (Table I) of the diatropicities of **3**, **31**[28] (**3** in full conjugation with one benzene ring), and **6** (**3** in full conjugation with two benzene rings assuming that the 9,10 bond of the phenanthrene moiety participates to a large extent in the ring current of the macroring). A decrease of about 10% in the ring current is observed going from **3** to **31** and **31** to **6**, which is consistent with reduction in delocalization in the macroring due to increasing conjugation. These results should clearly serve as preliminary evidence for the importance of the effect of conjugation on the diatropicity of an annulene, which is an interesting aspect of annulene chemistry, yet to receive as extensive a consideration as the effect of annelation.

Conclusion

The ^{1}H NMR studies on the diatropicity of the phenanthro-dimethyldihydropyrene **6** have provided experimental evidence for the prediction that the effects of benzannelation on the magnetic ring current of an annulene are reduced as the aromatic character of the annelated benzene ring is reduced. The possible isolation of the dimethylcyclophanediene **9** is also remarkable, and it has been found that the valence tautomerization of this cyclophanediene to the corresponding dihydropyrene system involves the highest activation energy so far known for any derivative of dimethyldihydropyrene **3**. We have also shown that the effect of conjugation, in addition to effects of annelation and deviation from planarity, could be responsible for the reduction in diatropicity of an annulene.

Experimental Section

All melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin-Elmer R32 (90 MHz) spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane, which was used as internal standard. IR spectra were recorded on a Pye-Unicam SP1000 or a Perkin-Elmer 1310 infrared spectrometer. UV spectra were recorded on a Hitachi 124 or Perkin-Elmer 551 spectrometer. The UV–vis spectrum of **6** was obtained by subtraction of the spectrum of **9** from that of the mixture **6** and **9**. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV using electron impact. Relative intensities are given in parentheses. Only the molecular ion containing ^{35}Cl or ^{79}Br is given for compounds containing these halogens. Correct isotope patterns were obtained in all cases. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. All evaporations were carried out under reduced pressure on a rotary evaporator at about 40 °C, and all organic layers were washed with water (unless otherwise stated) and dried with anhydrous magnesium or sodium sulfate.

9,10-Bis(3-chloro-2-methylphenyl)-9,10-dihydroxy-9,10-dihydrophenanthrene (10). The Grignard reagent was first prepared by reacting 2,6-dichlorotoluene (17.71 g, 110.0 mmol) with magnesium (2.67 g, 110.0 mmol) in dry THF (100 mL) with 1,2-dibromoethane as an initiator. The reaction mixture was heated under reflux under a stream of argon until a homogeneous solution was obtained. The Grignard reagent was cooled, and 9,10-phenanthraquinone (10.4 g, 50 mmol) was then added in batches. The reaction mixture was heated under reflux for 22 h, cooled in an ice–water bath, and hydrolyzed with H_2O/H_2SO_4 (1:4). The mixture was extracted with dichloromethane, washed with water and aqueous $NaHCO_3$ solution, dried, and evaporated to give a pale yellow solid. Recrystallization from chloroform yielded colorless crystals of **10**: 7.10 g (31%), mp 234–236 °C; ^{1}H NMR δ 8.12 (broad d, 2 H, J = 8.0 Hz, Ar H4, H5), 6.72–7.62 (m, 12 H, Ar H), 2.06 (s, 6 H, CH_3), 1.85 (s, 2 H, OH, exchanged with D_2O); IR (KBr) 3450 (OH), 2910, 1570, 1490, 1450, 1430, 1380, 1300, 1250, 1220, 1000, 900, 845, 790, 770, 745, 730, 710 cm^{-1}; MS M$^{+\cdot}$ m/z 460 (4), 445 (13), 308 (12), 307 (63), 306 (36), 253 (10), 252 (12), 153 (100), 152 (11). Anal. Calcd for $C_{28}H_{22}O_2Cl_2$: C, 72.89; H, 4.81. Found: C, 72.88; H, 4.96.

9,9-Bis(3-chloro-2-methylphenyl)-10-oxo-9,10-dihydrophenanthrene (11). A sample of **10** (2.29 g, 5.0 mmol) was dissolved in CF_3COOH (8 mL), and the solution was stirred at room temperature for 45 min. Saturated aqueous $NaHCO_3$ solution was added gradually until no effervescence was observed. The mixture was extracted with dichloromethane, washed, and evaporated. Recrystallization of the crude product from chloroform gave colorless crystals of **11**: 1.91 g (86%), mp 264–269 °C; ^{1}H NMR δ 6.40–8.02 (m, 14 H, Ar H), 2.09 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3); IR (KBr) 1700 (C=O), 1605, 1570, 1450, 1435, 1390, 1290, 1265, 1030, 1010, 860, 785, 765, 750, 720 cm^{-1}; MS M$^{+\cdot}$ m/z 442 (10), 426 (19), 425 (12), 424 (33), 389 (14), 299 (10), 253 (13), 163 (12), 151 (22). Anal. Calcd for $C_{28}H_{20}Cl_2O$: C, 75.85; H, 4.55. Found: C, 75.94, H, 4.61.

9,9-Bis(3-chloro-2-methylphenyl)-10-hydroxy-9,10-dihydrophenanthrene (12). A solution of **11** (7.54 g, 17.0 mmol) in dry THF was added to a suspension of $LiAlH_4$ (1.89 g, 49.8 mmol) in dry THF (150 mL). The mixture was heated under reflux in a stream of argon for 1.5 h. The reaction mixture was then decomposed by ethyl acetate, followed by addition of dilute HCl. The hydrolyzed mixture was extracted with dichloromethane, washed, dried, and evaporated to yield the alcohol **12**, 7.58 g (quantitative). A sample was recrystallized from ethanol/cyclohexane to give colorless crystals; no shapr mp could be obtained, but a range of 84–183 °C was observed: ^{1}H NMR δ 8.66 (broad d, 2 H, J = 8.0 Hz, Ar H4, H5), 6.42–7.90 (m, 12 H, Ar H), 5.58 (broad d, 1 H, J = 9.0 Hz, CH), 2.21 (broad d, 1 H, J = 9.0 Hz, OH, exchanged with D_2O), 1.97 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3); IR (KBr) 3250 (OH), 2920, 1590, 1570, 1450, 1440, 1390, 1205, 1010, 790, 745, 730, 700 cm^{-1}; MS M$^{+\cdot}$ m/z 444 (3), 429 (13), 428 (35), 427 (17), 426 (68), 266 (12), 265 (21), 181 (100), 168 (15). M_r calcd for $C_{28}H_{22}Cl_2O$, 444.1048; found (MS), 444.1049.

9,10-Bis(3-chloro-2-methylphenyl)phenanthrene (13). The alcohol **12** (8.92 g, 20.0 mmol) was dissolved in a 0.3% acetic acid solution of iodine (300 mL) and heated under reflux for 1.5 h. The reaction mixture was cooled and then decomposed by an ethanolic solution of sodium bisulphite. The crystalline precipitate was collected by filtration to give **13**, 8.56 g (quantitative). A sample was recrystallized from cyclohexane to yield colorless crystals of **13**: mp 259–261 °C; ^{1}H NMR δ 8.82 (broad d, 2 H, J = 9.0 Hz, Ar H4, H5), 6.85–7.78 (m, 12 H, Ar H), 1.97, 2.08 (s, total 6 H, ratio 1:8.5, CH_3); IR (KBr) 1565, 1440, 1380, 1320, 1135, 1025, 795, 780, 760, 730 cm^{-1}; UV (CH_2Cl_2) λ_{max} 258 nm, ϵ 52 000; MS M$^{+\cdot}$ m/z 426 (100), 376 (15), 339 (10), 299 (14), 266 (16), 265 (29), 168 (23). Anal. Calcd for $C_{28}H_{20}Cl_2$: C, 78.69; H, 4.72. Found: C, 78.69, H, 4.67.

9,10-Bis(3-cyano-2-methylphenyl)phenanthrene (14). Copper(I) cyanide (9.40 g, 105.0 mmol) was added to a solution of **13** (4.48 g, 10.5 mmol) in *N*-methyl-2-pyrrolidinone (75 mL). The reaction mixture was heated under reflux for 30 h, cooled to ca. 100 °C, and poured into concentrated NH_3/ice (1:1, 300 mL). After mixing thoroughly for 15 min, the mixture was filtered. The residue was successively extracted

(26) Mitchell, R. H.; Yan, J. S. H. *Can. J. Chem.* **19778** *55*, 3347.
(27) Mitchell, R. H.; Chaudhary, M.; Dingle, T. W.; Williams, R. V. *J. Am. Chem. Soc.* **1984**, *106*, 7776.
(28) Mitchell, R. H.; Mahadevan, R. *Tetrahedron Lett.* **1981**, *22*, 5131.

with dichloromethane and filtered. The organic fractions were combined, and evaporated to give a brown residue. The crude product was preadsorbed onto silica gel and chromatographed with hexane/dichloromethane (3:7) as eluent. The fractions found to contain the products were combined and evaporated to give **14**, 3.95 g (92%). A sample recrystallized from chloroform afforded colorless crystals of **14**: mp 248–253 °C; ^{1}H NMR δ 8.85 (broad d, 2 H, J = 8.5 Hz, Ar H4, H5), 7.11–7.87 (m, 12 H, Ar H), 2.15, 2.25 (s, total 6 H, ratio 1:3.6, CH_3); IR (KBr) 2920, 2240 (C≡N), 1450, 1390, 870, 770, 750, 725 cm^{-1}; MS M$^{+\cdot}$ m/z 408 (100), 290 (16), 204 (10). Anal. Calcd for $C_{30}H_{20}N_2$: C, 88.21; H, 4.93; N, 6.86. Found: C, 88.04; H, 5.12; N, 6.92.

9,10-Bis(3-(aminomethyl)-2-methylphenyl)phenanthrene (15). A solution of **14** (1.63 g, 4.0 mmol) in dry THF (50 mL) was added dropwise to a suspension of $LiAlH_4$ (0.30 g, 8.0 mmol) in dry THF (10 mL). The mixture was heated under reflux for 1 h and cooled, and sufficient water was added to decompose the excess hydride, followed by 20% potassium sodium tartrate solution (200 mL). The mixture was extracted with dichloromethane, dried, and evaporated to give a white solid. Recrystallization from chloroform afforded fine crystals of **15**: 2.15 g (quantitative), mp >300 °C dec.; ^{1}H NMR δ 8.80 (broad d, 2 H, J = 8.0 Hz, Ar H4, H5), 6.98–7.73 (m, 12 H, Ar H), 3.81 (s, 4 H, CH_2N), 1.90, 2.00 (s, total 6 H, ratio 1:2.6, CH_3), 1.47 (s, 4 H, NH_2); IR (KBr), 3500 (NH), 2920, 1580, 1450, 1380, 795, 770, 750, 730 cm^{-1}; MS M$^{+\cdot}$ m/z 416 (15), 400 (32), 399 (100), 398 (63), 385 (25), 384 (90). M_r calcd for $C_{30}H_{28}N_2$, 416.2252; found (MS), 416.2275.

9,10-Bis(3-(hydroxymethyl)-2-methylphenyl)phenanthrene (16). A sample of **15** (1.01 g, 2.4 mmol) dissolved in a minimum amount of glacial acetic acid/water (5.5:1) was stirred in an ice–water bath maintained at ca. 10 °C. Sodium nitrite (0.5 g) dissolved in a minimum amount of water was gradually added. The mixture was allowed to warm to room temperature and stirred for an additional 20 min. It was then cooled in water and aqueous $NaHCO_3$ solution was added to neutralize the excess acid. The resulting alkaline mixture was extracted with dichloromethane, washed, dried, and evaporated. ^{1}H NMR and IR spectra of the product mixture clearly indicated esterification of the benzylic positions. The crude product was then dissolved in methanol and NaOH solution (0.59 g in 10 mL of water) was added. The reaction mixture was heated under reflux for 2 h, cooled, and diluted with water. The mixture was extracted with dichloromethane, washed, dried, and evaporated. Recrystallization from benzene gave colorless crystals of **16**: 1.58 g (81%), mp 235–249 °C; ^{1}H NMR δ 8.80 (broad d, 2 H, J = 9.0 Hz, Ar H4, H5), 6.97–7.78 (m, 12 H, Ar H), 4.62, 4.66 (s, total 4 H, ratio 1:2.5, CH_2O), 1.94, 2.02 (s, total 6 H, ratio 1:2.6, CH_3), 1.65 (broad s, 2 H, OH, exchanged with D_2O); IR (KBr) 3400 (OH), 2920, 1450, 1380, 1000, 795, 770, 750, 730 cm^{-1}; MS M$^{+\cdot}$ m/s 418 (100), 416 (27), 355 (11), 279 (28), 278 (11). M_r calcd for $C_{30}H_{26}O_2$, 418.1933; found (MS), 418.1930.

9,10-Bis(3-(bromomethyl)-2-methylphenyl)phenanthrene (17). Phosphorus tribromide (3 mL, 32.0 mmol) was added to a vigorously stirred solution of the diol **16** (0.85 g, 2.0 mmol) in benzene (15 mL) followed by a few drops of pyridine at room temperature. After stirring for 15 h, the reaction mixture was decomposed by water and extracted with dichloromethane. The organic layer was washed with water and aqueous $NaHCO_3$ solution, dried, and evaporated. The crude product was filtered through silica gel with hexane/dichloromethane (7:3) as eluant to give colorless crystals of **17**: 0.92 g (84%), mp 165–190 °C; ^{1}H NMR δ 8.80 (broad d, 2 H, J = 9.0 Hz, Ar H4, H5), 6.90–7.75 (m, 12 H, Ar H), 4.45, 4.49 (s, total 4 H, ratio 1:5, CH_2Br), 2.00, 2.08 (s, total 6 H, ratio 1:5, CH_3); IR (KBr) 2920, 1735, 1460, 1385, 1265, 800, 770, 750, 730 cm^{-1}; MS M$^{+\cdot}$ m/z 542 (32), 463 (59), 369 (12), 265 (18), 191 (26), 177 (27), 176 (20). Anal. Calcd for $C_{30}H_{24}Br_2$: C, 66.20; H, 4.44. Found C, 66.43; H, 4.70.

9,29-Dimethylphenanthro[10,11-*l*]-2-thia[2.3]metacyclophan-10-ene (8A, 8B).[29] A solution of the dibromide **17** (1.24g, 2.3 mmol) in benzene (40 mL) was added through a syringe simultaneously with a solution prepared by dissolving powdered $Na_2S{\cdot}9H_2O$ (0.58 g, 2.3 mmol) in water (40 mL) in another syringe to vigorously stirred 95% ethanol (600 mL) under argon over 6 h. The mixture was further stirred for 12 h and evaporated. The residue was extracted with dichloromethane, and the organic layer was dried and evaporated. The residue was preadsorbed onto silica gel, and several chromatographs with hexane/dichloromethane (7:3) eluted first the anti isomer **8B**, 83 mg (~9%), mp 275–277 °C; ^{1}H NMR δ 8.76 (broad d, 2 H, J = 9.0 Hz, Ar H4, H5), 8.22 (d, 2 H, J = 9.0 Hz, Ar H), 6.95–7.82 (m, 10 H, Ar H), 3.92, 3.72 (AB, 4 H, J_{AB} = J_{BA} = 13 Hz, CH_2S), 1.10 (s, 6 H, CH_3); IR (KBr), 2920, 1745, 1450, 1415, 1380, 1265, 795, 760, 730 cm^{-1}; MS M$^{+\cdot}$ m/z 416 (100), 384 (11), 383 (36), 382 (12), 369 (17), 367 (16), 353 (12), 279 (23), 278 (15). M_r calcd for $C_{30}H_{24}S$, 416.1599; found (MS), 416.1598. Eluted next was a mixture of **8A** and **8B**, 196 mg, (~14%).

Stevens Rearrangement of Thiacyclophane 8B. (a) Salt 18. A solution of the thiacyclophane **8B** (126 mg, 0.3 mmol) in dichloromethane (5 mL) was added to a suspension of $(CH_3O)_2CHBF_4$[18] (96 mg, 0.6 mmol) in dichloromethane (5 mL) under N_2 at −30 °C. The mixture was then stirred without further cooling for 2 h, ethyl acetate (5 mL) was added, and the mixture was stirred an additional 2 h. The crystals of sulfonium salt **18** were collected and dried to give 130 mg (86%), mp >300 °C dec.

(b) Rearrangement. Potassium *tert*-butoxide (34 mg, 0.3 mmol) was added to a stirred suspension of the salt **18** (130 mg, 0.26 mmol) in dry THF (20 mL) under N_2 and the mixture was stirred for 1 h at room temperature. Dilute aqueous HCl and dichloromethane were then added, and the organic layer was washed, dried, and evaporated to give a mixture of **19A** and **19B**, 38 mg (34%). Recrystallization from cyclohexane gave crystals of **19A**: 30 mg (~27%), mp 202–204 °C; ^{1}H NMR δ 8.74 (broad d, 2 H, J = 9.0 Hz, Ar H4, H5), 8.36 (dd, 2 H, J = 8.0, 2.0 Hz, Ar H), 6.90–7.90 (m, 10 H, Ar H), 3.88 (dd, 1 H, J_{XB} = 12 Hz, J_{XA} = 3 Hz, SCH_x), 3.27 (dd, 1 H, J_{AB} = 12 Hz, J_{AX} = 3 Hz, CH_aH_b), 2.60 (t, 1 H, J_{BA} = J_{BX} = 12 Hz, CH_aH_b), 2.19 (s, 3 H, SCH_3), 0.79 (s, 6 H, Ar CH_3); MS M$^{+\cdot}$ m/z 430 (100), 415 (66), 407 (16), 366 (15), 354 (13), 152 (27), 350 (13), 309 (20), 265 (17). M_r calcd for $C_{31}H_{26}S$, 430.1755; found (MS), 430.1742.

Wittig Resrrangement of Thiacyclophane 8B. A solution of *n*-butyllithium (0.45 mmol in hexane) was added dropwise to a solution of the thiacyclophane **8B** (126 mg, 0.3 mmol) under N_2 in dry THF (15 mL) at 0 °C. After a further 10 min, methyl iodide (0.45 mmol from a 2 M solution in dry THF) was added and the brown color was discharged. Water and dichloromethane were then added, and the organic layer was washed, dried, and evaporated. The residue was chromatographed on silica gel, using hexane-dichloromethane (2:1) as eluant, to yield mixed isomers **19A** and **19B**, 53 mg (41%). Recrystallization from cyclohexane gave **19A**, 40 mg (~31%), identical with the previously obtained sample (mp, ^{1}H NMR, MS).

Hoffman Elimination of Sulfonium Salt 20 to *anti*-8,28-Dimethylphenanthro[9,10-*l*][2,2]metacyclophan-1-ene (9) and *trans*-16d,16e-Dimethyl-16d,16e-dihydrophenanthro[9,10-*e*]pyrene (6). (a) Salt 20. Mixed isomers of **19** (160 mg, 0.37 mmol) in dichloromethane (5 mL) were added to a stirred suspension of $(CH_3O)_2CHBF_4$ (96 mg, 0.6 mmol) in dichloromethane (5 mL) at −30 °C under N_2 and this was then stirred without further cooling for 2 h. Ethyl acetate (5 mL) was then added, and after the mixture was stirred for about 5 h the crystals were collected and dried to give 118 mg (60%) of **20**, mp >300 °C dec.

(b) Elimination. Potassium *tert*-butoxide (145 mg, 0.34 mmol) was added to a suspension of the salt **20** (118 mg, 0.22 mmol) in dry THF (10 mL) at room temperature under N_2. The reaction mixture was then heated under gentle reflux for 45 min. After the solution was cooled aqueous dilute HCl and dichloromethane were added, and the organic layer was washed, dried, and evaporated. The residue was chromatographed over silica gel, using hexane as eluant, to give a mixture of **6** and **9**: 45 mg (53%), mp 154–164 °C; ^{1}H NMR δ 6.7–9.2 (m, 14 H, Ar H), 6.49 (s, 2 H, CH=CH), 1.48, −3.32 (s, total 6 H, Ar CH_3); IR (KBr) 1600, 1482, 1440, 1428, 1370, 1258, 1090, 1020, 880, 794, 750, 728 cm^{-1}; MS M$^{+\cdot}$ m/z 382 (9), 367 (75), 366 (100), 352 (78), 351 (34), 349 (48). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.26; H, 5.64.

A solution of the mixture **6** and **9** in cyclohexane was irradiated by visible light from a slide projector for ca. 0.5 h when **6** was fully converted to the colorless cyclophanediene **9**; UV (cyclohexane) λ_{max} 252 nm (ϵ 71 800). Rapid concentration under reduced pressure gave very pale yellowish crystals of **9**: mp 194–197 °C; ^{1}H NMR δ 8.67 (dd, 2 H, J = 2, 8 Hz, Ar H), 8.35 (dd, 2 H, J = 2, 8 Hz, Ar H), 7.30–7.75 (m, 4 H, Ar H), 7.10 (t, 2 H, J = 8, 8 Hz, Ar H), 6.70–6.95 (m, 4 H, Ar H), 6.49 (s, 2 H, CH=CH), 1.48 (s, 6 H, CH_3).

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Registry No. 3, 956-84-3; **6**, 98421-71-7; **7**, 65649-31-2; **8A**, 98523-82-1; **8B**, 98421-65-9; **9**, 98421-72-8; **10**, 98421-59-1; **11**, 98421-60-4; **12**, 98421-61-5; **13**, 98421-62-6; **14**, 98464-66-5; **15**, 98464-67-6; **16**, 98421-63-7; **16** (diacetate), 98464-68-7; **17**, 98421-64-8; **18**, 98421-67-1; **19A**, 98421-68-2; **19B**, 98523-83-2; **20**, 98421-70-6; **29**, 52028-44-1; **30**, 92720-02-0; **31**, 81715-63-1; 2,6-dichlorotoluene, 118-69-4; 9,10-phenanthraquinone, 84-11-7.

(29) The locants [10,11-*l*] reverse the usual order in fusion names, the 10,11 referring to the cyclophane and the *l* referring to the phenanthrene.