4586 J. Org. Chem. 1989, 54, 4586-4590

syn-8,16-Dimethylphenanthro[9,10:1′,2′][2.2]metacyclophane-1,9-diene: The First Derivative of 8,16-Dimethyl[2.2]metacyclophanediene Failing To Undergo Spontaneous Valence Isomerization to the Dihydropyrene System

Yee-Hing Lai* and Pu Chen

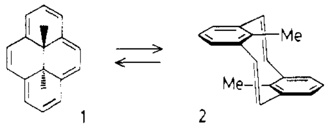
Department of Chemistry, National University of Singapore, Kent Ridge, Republic of Singapore 0511

Received February 14, 1989

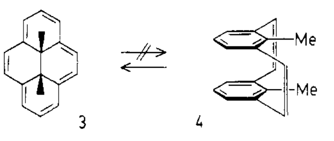
Relative stabilities of the anti and syn conformations of 9,10-di-*o*-tolylphenanthrene (**11**) were estimated by molecular mechanics calculations, the results of which helped to assign the isolated minor isomer of **13** as the syn conformer. The stereochemistry was confirmed experimentally by the successful conversion of *syn*-**13** to the corresponding *syn*-thiacyclophanene **8a**. Variable-temperature ^{1}H NMR studies indicated a rigid conformation for **8a**, namely IIa, with no evidence for the conversion IIa → IIb up to 150 °C. A possible conformational process was, however, the tilting of the meta-bridged rings. Ring contraction of **8a** also retained the syn stereochemistry and afforded only the syn isomer **19** with a pseudoaxial methylthio group. Hofmann elimination of the corresponding sulfonium salt **21** unexpectedly resulted in the isolation of the first *syn*-8,16-dimethyl[2.2]metacyclophanediene derivative **22**, which failed to undergo valence isomerization to the dihydropyrene system thermally or photochemically under normal conditions. The significant cofacial interactions of the syn transannular rings in **22** could be illustrated readily by ^{1}H NMR (shielded methyl protons and aryl protons of meta-bridged rings) and UV (bathochromically shifted β and p bands of meta-bridged rings) spectroscopic studies.

Introduction

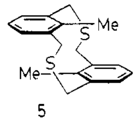
Although *trans*-10b,10c-dimethyldihydropyrene (**1**) and its many derivatives have been used extensively as probes to study the effect of benzannelation on the diatropicity of the 14π-macroring,[1] another interesting behavior of **1** is its reversible photochemical valence isomerization into the *trans*-8,16-dimethyl[2.2]metacyclophanediene (**2**).[2,3] The dihydropyrene **1** is the thermodynamically more stable valence isomer, but irradiation of **1** with visible light converts it to **2**. Synthetically[4] **2** is the precursor to **1** and the thermal conversion, **2** → **1**, represents one of those unusual concerted, symmetry-forbidden reactions.[3] The chemistry of the corresponding *cis*-10b,10c-dimethyldihydropyrene (**3**)[4,5] is relatively less well explored. An interesting observation however was the lack of evidence for **3** to undergo a similar reverse photochemical conversion to afford **4**. This could be attributed to the unfavorable π-π interaction of the near parallel benzene rings in the latter. *cis*-10b,10c-Dimethyldihydropyrene **3** (or *syn*-cyclophanediene **4**) is also synthetically less accessible than its trans isomer **1** (or *anti*-cyclophanediene **2**). A common route to **2** (and thus **1**) and **4** (and thus **3**) involves the preparation of dithiacyclophanes **5** and **6**, respectively, in one single cyclization reaction, the latter being obtained as the minor isomer (**5**:**6** = 7:1).[4]



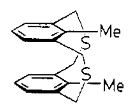
1 2



3 4

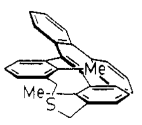


5

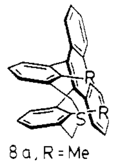


6

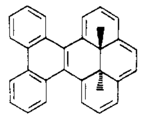
In the synthesis of the phenanthroannelated derivatives **7** and **8a**,[6] these were obtained in a 2:1 ratio—the highest syn:anti ratio reported among the series of related thia- or dithiacyclophanes. The corresponding thiacyclophanene **8b**[7] was also reported to retain the syn stereochemistry in subsequent ring contraction reactions. It would seem that **8a** may be synthetically more accessible than other related *syn*-cyclophanes and thus should readily lead to the *cis*-phenanthrodimethyldihydropyrene **10**. This would allow the study of the effect of phenanthroannelation on a *cis*-dihydropyrene system. Complete separation of the isomers **7** and **8a** however proved to be of great difficulty,[6] although a sample of pure **7**, which was successfully converted to the *trans*-phenanthrodimethyldihydropyrene **9**, could be isolated. Attention was then drawn to the precursors of **7** and **8a**, a series of 9,10-diarylphenanthrenes, **12**–**16**. These have been shown to exist in anti and syn isomers, and conformational studies on **11**,[8,9] **12**,[9] and **17**[10] have shown that the interconversion energy barriers are exceptionally high. Successful isolation of the syn isomer of any of **12**–**16** would then mean a possible route to *syn*-thiacyclophanene **8a**, and thus the *cis*-dimethyldihydropyrene **10**.

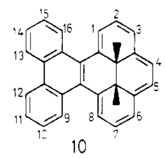


7



8a, R = Me
b, R = H


9



10

Results and Discussion

***syn*-9,10-Bis(3-cyano-2-methylphenyl)phenanthrene (13).** The existence of anti and syn isomers in the

---

[1] (a) Mitchell, R. H. Dihydropyrenes. Bridged [14]Annulenes Par Excellence: A Comparison with Other Bridged Annulenes; *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press, Inc.: New York, 1989; Vol. 1, pp 135–199. (b) Mitchell, R. H. *Isr. J. Chem.* **1980**, *20*, 594. (c) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y.-H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571.

[2] (a) Blattmann, H. R.; Meuche, D.; Heilbronner, E.; Molyneux, R. J.; Boekelheide, V. *J. Am. Chem. Soc.* **1965**, *87*, 130. (b) Blattmann, H. R.; Schmidt, W. *Tetrahedron* **1970**, *26*, 5885.

[3] Schmidt, W. *Helv. Chim. Acta* **1971**, *54*, 862; *Tetrahedron Lett.* **1972**, *13*, 581.

[4] Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.

[5] Mitchell, R. H.; Boekelheide, V. *J. Chem. Soc., Chem. Commun.* **1970**, 1555.

[6] Lai, Y.-H. *J. Am. Chem. Soc.* **1985**, *107*, 6678.

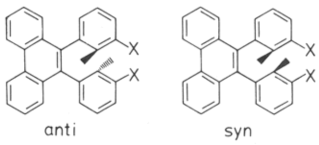
[7] Lai, Y.-H.; Lee, S.-M. *J. Org. Chem.* **1988**, *53*, 4472.

[8] Lai, Y.-H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1667.

[9] Marriott, P. J.; Lai, Y.-H. *J. Chromatogr.* **1988**, *447*, 29.

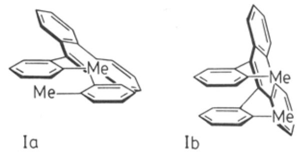
[10] Lai, Y.-H.; Marriott, P. J.; Tan, B.-C. *Aust. J. Chem.* **1985**, *38*, 307.

0022-3263/89/1954-4586$01.50/0



	X
11	H
12	Cl
13	CN
14	CH_2NH_2
15	CH_2OH
16	CH_2Br
17	CH_3
18	CHO

series of 9,10-diarylphenanthrenes **11**–**17** was clearly evident when their ^{1}H NMR spectra ($CDCl_3$) at room temperature always showed two separate singlets ($\Delta\delta = 7.2$–9.9 Hz) for the methyl protons. Preliminary assignment[8,9] was based on related cyclophane chemistry which would suggest that the anti-stepped conformation Ia has the methyl groups located partially over the benzene rings and thus slightly shielded to higher field. The isomer with the more shielded methyl signal was however the minor isomer in all cases. In fact, in the case of the dichloro derivative **12**,[6] the methyl signals at δ 1.97 and 2.08 were observed to be in a ratio of ca. 1.0:8.5. This would contradict the fact that with the unfavorable π–π interaction resulting from two near-parallel benzene rings, *syn*-Ib should be the expected minor isomer instead. In order to acquire an estimate of the relative stability of Ia and Ib, MMP2 calculations[11] were carried out on the parent 9,10-diarylphenanthrene, **11**. Results from the calculations indeed indicate that the anti isomer is about 2.6 kJ mol^{-1} more stable than the syn isomer but the conformations Ia and Ib are probably incorrect. Structures of minimized geometries derived from the MMP2 calculations are shown in Figure 1. Both "benzene" rings in the anti isomer are perpendicular to the "phenanthrene" moiety; whereas the two "benzene" rings in the syn isomer are tilted at angles of ca. 77° and 64°, respectively. Molecular models showed that the methyl groups in such an anti conformation are far from the shielding zones of the respective opposite benzene rings; on the other hand the tilting of the benzene rings in the syn conformation in fact put the methyl protons in positions more likely to experience a small shielding effect. The methyl signals of both *anti*-**11** and *syn*-**11** (δ 2.04, 1.94),[8] however, seemed to be at a higher field than that of toluene (δ 2.35).[12] This we believe is probably due to the shielding effect of the phenanthrene moiety similar to that observed in other biaryl systems.[13] Thus the preliminary assignment[8,9] of the isomers of **11**–**17** is probably incorrect, and efforts were then directed to isolating the minor (syn) isomer of any of **12**–**16**.



Ia   Ib

In a series of TLC studies on silica gel using various solvent systems, the largest difference in R_f values were consistently observed for the anti and syn isomers of **13**. The polar cyano groups in **13** are believed to induce the most significantly different dipole–dipole interactions in the anti and syn conformations, thus the largest difference in adsorption properties on silica gel. The anti:syn ratio of **12** was observed to be ca. 8.5:1.0[6] with an activation energy of probably > 115 kJ mol^{-1} for the conversion *anti*-**12** → *syn*-**12**.[9] However, in the conversion of **12** to **13** by the von Braun reaction, the reaction mixture was heated in refluxing *N*-methylpyrrolidinone (bp 202–204 °C) for ca. 28 h, resulting in an equilibration of the anti and syn isomers of **13** to a ratio of ca. 2.6:1.0. This was not unexpected as the free energy difference determined at 196 °C between *anti*-**11** and *syn*-**11** was reported[8] to be only 2.6 kJ mol^{-1}. Thus chromatography of the product mixture of **13** on silica gel using dichloromethane/hexane (1:2) as eluant successfully resulted in the separation of *anti*-**13** (36%) and *syn*-**13** (14%). Mass spectra of both isomers gave cleanly the molecular ion as the base peak. The methyl protons of *anti*-**13** (IR 2240 cm^{-1}) and *syn*-**13** (IR 2220 cm^{-1}) were clearly observed at δ 2.25 and 2.14 in their respective ^{1}H NMR spectra.

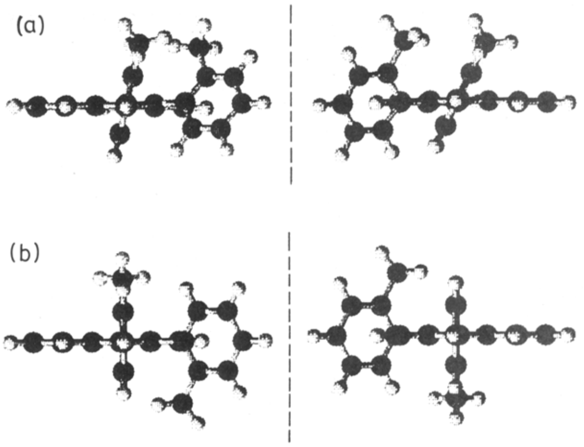


Figure 1. Conformations of (a) *syn*-**11** and (b) *anti*-**11** with minimized geometries derived from MMP2 calculations.

***syn*-Thiacyclophanene (8a).** The syn stereochemistry of the minor isomer of **13** could only be eventually confirmed experimentally via successful conversion to the *syn*-thiacyclophanene **8a**. As the energy barriers for aryl rotation in the 9,10-diarylphenanthrene systems are high, the following reactions, all of which were carried out at room temperature, are expected to retain the original conformation in *syn*-**13**. Thus treatment of *syn*-**13** with diisobutylaluminum hydride resulted in only one isomer of **18**, mp 252–254 °C. Only one sharp singlet (δ 2.27) was observed for the methyl protons; the formyl (IR 1660 cm^{-1}) protons also appeared as a singlet at δ 10.25. Reduction of *syn*-**18** with sodium borohydride gave a quantitative yield of *syn*-**15**. Reaction of *syn*-**15** with phosphorus tribromide then afforded *syn*-**16**. The respective methyl signals observed for *syn*-**15** (δ 1.90) and *syn*-**16** (δ 2.01) are indeed at higher fields than those of the corresponding anti isomers (δ 2.02, 2.08).[6] These are consistent with earlier discussion on the slight shielding effect on the methyl groups by opposite benzene rings in the syn conformation (Figure 1).

An intramolecular cyclization of *syn*-**16** with sodium sulfide was carried out under high dilution conditions.[14] As expected, only one isomer of the thiacyclophanene was isolated, mp 274–275 °C, which gave a molecular ion at m/z 416 as the base peak in its mass spectrum. The observed melting point was similar to that reported for the

---

[11] Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399.

[12] *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich: Milwaukee, WI, 1983; Vol. 1, p 733B.

[13] See, for example: (a) Mitchell, R. H.; Yan, J. S.-H. *Can. J. Chem.* **1980**, *58*, 2584. (b) Clough, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1018.

[14] Rossa, L.; Vogtle, F. *Top. Curr. Chem.* **1983**, *113*, 1.

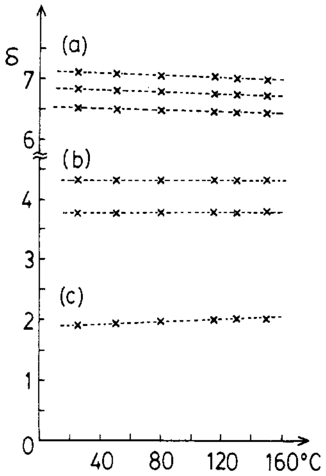
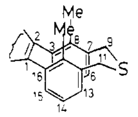
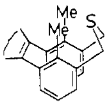


Figure 2. A plot of chemical shift of (a) aryl protons of the meta-bridged rings; (b) bridging methylene protons and (c) methyl protons of **8a** vs temperature.

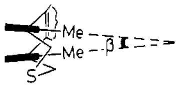
anti-thiacyclophanene, **7** (mp 275–277 °C).[6] The methyl protons of the isolated product, however, appeared as a sharp singlet at δ 2.11 in its ^1H NMR spectrum, thus confirming that it is in fact the syn isomer **8a** (*anti*-**7**: methyl protons at δ 1.10).[6] The aryl protons of the meta-bridged rings of **8a**, which were shifted upfield (relative to the phenanthrene protons) due to the stacking of two near-parallel benzene rings,[15,16] were unexpectedly well resolved (90 MHz) compared with those observed for **6** (singlet at δ 6.59).[15] We believe that this is due to a rigid conformation, namely IIa. The H5/H14 protons of **8a** appeared clearly as a triplet at δ 6.80. With the bridging sulfur atom in close proximity to the H6/H13 protons in IIa, a significant anisotropic effect shifts these protons to appear as a broad doublet at δ 7.09. The shorter ene bridge should bring C3/C16 closest together. The H4/H15 protons would then experience stronger induced ring current effect of the respective opposite transannular rings (compared with H5/H14) and appeared as a broad doublet further upfield at δ 6.50. A similar effect was also clearly observed for the methyl protons (δ 2.11) of **8a** when compared with those (δ 2.51)[15] of **6**.



IIa



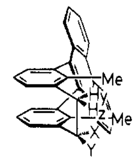
IIb



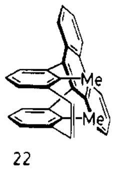
III

The conformation IIb is believed to be unfavorable due to large nonbonded interactions between the sulfur atom and the methyl groups. An attempt to investigate the possible interconversion IIa ⇄ IIb was carried out with a variable-temperature ^1H NMR experiment using nitrobenzene-d_5 as the solvent (Figure 2). In IIb, the H6/H13 protons would be relieved from the anisotropic effect of the sulfur atom, but the methyl protons would experience it instead. Thus we would expect significant changes on the chemical shifts of these protons if conversion IIa → IIb was possible within the temperature range studied. The experimental results (Figure 2), however, showed otherwise. Small appreciable shifts (Δδ = 5–12 Hz) were observed for the methyl protons and those of the meta-bridged rings. The chemical shifts of the bridging methylene protons (an AB quartet), however, remained practically unchanged. The above results do not seem to support the interconversion IIa ⇄ IIb. The small observed shifts however could be due to a tilting process (varying β values in III) of the benzene rings. Similar conformational behavior has been observed in related dithiametacyclophanes.[17]

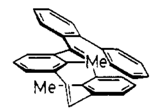
***syn*-Cyclophanediene (22).** Ring contraction of *syn*-dithiacyclophane (**6**) via a Wittig rearrangement[18] is known to result in isomerization to several *anti*-[2.2]metacyclophanes (anti:syn ratio = 98:2). The successful conversion of *syn*-**13** to **8a**, however, suggests that the high isomerization barrier in such systems should retain the syn stereochemistry in **8a** in a similar rearrangement, although two isomeric *syn*-[2.2]metacyclophanenes, namely **19** and **20**, could be formed. Unexpectedly, treatment of **8a** with *n*-butyllithium gave, after quenching with iodomethane, only one isolated isomer in a 68% yield. The arylmethyl protons were observed as two singlets at δ 1.98 and 2.07 in a 1:1 ratio, clearly indicating a syn isomer (arylmethyl protons of the corresponding anti isomer of **20** appeared shielded at δ 0.79).[6] The aryl protons of the meta-bridged rings were no longer resolved (see later discussion on **22**) but appeared shielded as a multiplet at δ 6.4–6.6, consistent with two syn benzene rings. The above observation is clearly in agreement with the isomer **19**, having one of the arylmethyl groups shielded by the adjacent methylthio group. The three bridging protons H_x, H_y, and H_z correspond to a typical AMX system with the tertiary H_x proton appearing as a double doublet centered at δ 5.04. The H_z proton was observed as another double doublet at δ 2.39 expected of secondary benzylic protons, whereas H_y (also a double doublet), being held eclipsed to the adjacent methylthio group, was shielded downfield to δ 3.96.



	X	Y
19	SMe	H_x
20	H_x	SMe
21	$^+SMe_2$	H_x



22



23

The cyclophanene **19** could be methylated readily with dimethoxycarbonium fluoroborate[19] to yield the sulfonium salt **21**. The Hofmann elimination of the salt **21** when treated with potassium *tert*-butoxide in refluxing THF resulted surprisingly in the isolation of the *syn*-cyclophanediene **22**, mp 204–206 °C. Under similar conditions, the cyclophanedienes **2**[4] and **4**[4] and all of their other annelated derivatives so far reported[1,20] are known to undergo facile thermal valence isomerization, leading to the isolation of only the corresponding dimethyldihydropyrenes. The only exception was the trans-phenanthro derivative **9**[6] found to exist in a 1:6 ratio with its corresponding *anti*-cyclophanediene **23** after isolation. The *anti*-cyclophanediene **2** has recently been isolated,[1] which was only quite stable in the absence of light or below 0 °C. In addition, no example of the series of *cis*-dimethyldihydropyrenes has been known to undergo the reverse

---

[15] Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.

[16] (a) Mitchell, R. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 530. (b) Cram, D. J.; Dalton, C. K.; Knox, G. R. *J. Am. Chem. Soc.* **1963**, *85*, 1088.

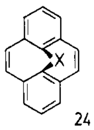
[17] Mitchell, R. H.; Vinod, T. K.; Bodwell, G. J.; Weerawarna, K. S.; Anker, W.; Williams, R. V.; Bushnell, G. W. *Pure Appl. Chem.* **1986**, *58*, 15.

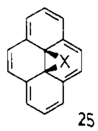
[18] Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 219.

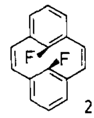
[19] Borch, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5303; *J. Org. Chem.* **1969**, *34*, 627.

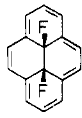
[20] Mitchell, R. H.; Mahadevan, R. *Tetrahedron Lett.* **1981**, *22*, 5131.

photochemical conversion to the *syn*-cyclophanediene. The related *syn*-cyclophanedienes **24a**,[21] **24b**,[22] and **24c**[23] have also been reported. No conversion to the dihydropyrenes **25a–c** were observed under normal conditions, although these were postulated as intermediates in the pyrolytic or photolytic rearrangements[21–23] of **24a–c**.

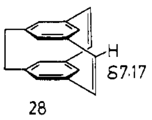

24


25

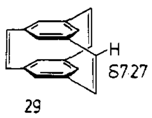

26


27

a, X = CH$_2$; b, X = O ; c, X = NH



28



29

Molecular models and results from molecular mechanics calculations[1] suggest that **3** should have a saucer like shape, with the internal methyl groups projecting "away from each other" from the convex side of the saucer. Thus in **25a–c** where the internal C–X bonds have to bend "toward each other" would certainly induce large unfavorable angle strains in these systems. *syn*-Difluoro[2.2]metacyclophanediene (**26**) is the only other example known which undergoes valence isomerization readily to dihydropyrene **27**.[17] Thus *syn*-**22** represents both the first isolated *syn*-8,16-dimethyl[2.2]metacyclophanediene and the first example of an 8,16-dimethyl[2.2]metacyclophanediene (anti or syn) which failed to undergo spontaneous thermal valence isomerization to the dimethyldihydropyrene system.

The *syn*-cyclophanediene **22** was found to be thermally stable up to 150 °C in a variable-temperature ^{1}H NMR study and showed no evidence for the conversion **22** → **10**. In addition, irradiation of **22** with UV light (254 nm) for 3–4 h also resulted only in the recovery of the cyclophanediene. The driving force for the valence isomerization of **3**[4] and its derivatives[20] to the dihydropyrenes is believed to be the relief of electronic repulsion between the syn aryl rings and the concurrent formation of a 14π aromatic system. In **10**, although the dihydropyrene moiety is also expected to have a saucerlike shape, severe steric interactions between the H1 and H16 (H8 and H9) protons seem to be the main factor discouraging the valence isomerization of **22** to afford **10**. The fact that **23** was found[6] to exist in equilibrium with **9** (which also experienced similar steric strains as described for **10**) serves as yet another example to illustrate the more diatropic (stable) nature of the *trans*-dihydropyrene system having a near-planar periphery.

In the ^{1}H NMR spectrum of **22**, the vinyl protons were observed at δ 7.35—a value significantly shifted from that (δ 6.49) of the α-hydrogens of *cis*-stilbene[24] but similar to chemical shifts observed for vinyl protons in rigid models of *syn*-[2.2]metacyclophanedienes, namely **28** and **29**.[25] A more significant cofacial shielding effect, a result of the more closely stacked benzene rings, is experienced by both the methyl protons and the aryl protons of the meta-bridged rings in **22** compared with those in **8a**, which has a longer C–S–C bridge on one side. The methyl signal of the former is shielded further to δ 2.02, the first reported reference for a *syn*-8,16-dimethyl[2.2]metacyclophanediene, although the shielding effect may be expected to be more significant than what the chemical shift indicates due to a possible opposing deshielding effect from steric distortion of the two methyl groups held in close proximity. The aryl protons of the meta-bridged rings in **22** are now similarly affected (almost identical bridges leading to near-parallel rings) and thus unresolved. As expected, their chemical shifts (a multiplet at δ 6.4–6.6) are, however, similar to that of H4/H15 (δ 6.50) adjacent to the shorter ene bridge in **8a** (IIa). As UV absorption spectroscopy has been employed to illustrate the face-to-face interaction between two benzene rings in cyclophanes,[26] the spectra of *syn*-**22** and *anti*-**23** were recorded for comparison (Figure 3). The entire spectrum of **23** (λ_{max} at 251 nm) and that of **22** in the region of 230–350 nm (λ_{max} at 259 nm) closely resemble the spectra of 9,10-diphenylphenanthrene (λ_{max} at 257 nm)[27] and phenanthrene itself (λ_{max} at 252 nm).[28] The β band[29] (<190 nm) of the "normal" benzene rings in **23** was probably not observed with the p band[29] obscured by other transitions of the phenanthrene moiety in the region of 200–215 nm. A unique feature in the spectrum of **22**, however, is the absorptions at 206 and 223 nm, which could be assigned to the respective β and p bands of the benzene rings in **22**. This observation is clearly consistent with the expected strong bathochromic shift of these bands when the benzene rings are closely stacked in a *syn*-cyclophane.[26]

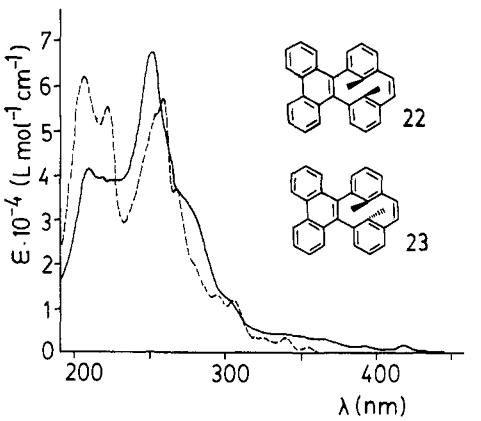


Figure 3. UV absorption spectra of **22** (---) and **23** (—) taken in cyclohexane.

Experimental Section

All melting points were determined by using a Sybron-Thermolyne MP-12615 melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined in CDCl$_3$ on a JEOL FX90Q (90 MHz) Fourier Transform spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer. UV/visible spectra were determined in cyclohexane on a Shimadzu UV240 Graphicord spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV using electron impact methods. Relative

---

(21) (a) Wirz, J.; Persy, G.; Rommel, E.; Murata, I.; Nakasuji, K. *Helv. Chim. Acta* **1984**, *67*, 305. (b) Nakasuji, K.; Katada, M.; Murata, I. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 946. (c) Murata, I.; Nakasuji, K. *Isr. J. Chem.* **1980**, *20*, 244.

(22) Hess, B. A., Jr.; Bailey, A. S.; Bartusek, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1969**, *91*, 1665.

(23) Hess, B. A., Jr.; Boekelheide, V. *J. Am. Chem. Soc.* **1969**, *91*, 1672.

(24) Curtin, D. Y.; Gruen, H.; Shoulders, B. A. *Chem. Ind.* **1958**, 1205.

(25) Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3201.

(26) See, for example: (a) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691. (b) Otsubo, T.; Kitasawa, M.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1515.

(27) Fuson, R. C.; Tomboulian, P. *J. Am. Chem. Soc.* **1957**, *79*, 956.

(28) *Spectral Atlas of Polycyclic Aromatic Compounds*; Karcher, W., Fordham, R. J., Dubois, J. J., Glaude, P. G. J. M., Ligthart, J. A. M., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1985; p 52.

(29) For nomenclature of bands, see: (a) Clar, E. *Polycyclic Hydrocarbons*; Academic: London, 1964; Vol. I. (b) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.

intensities are given in parentheses. Only the molecular ion containing ^{79}Br is given for compound **16**; correct isotope pattern was obtained. 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 ca. 40 °C, and all organic layers were washed with water, unless otherwise stated, and dried with anhydrous magnesium sulfate.

***anti*- and *syn*-9,10-Bis(3-cyano-2-methylphenyl)phenanthrene (13).** Copper(I) cyanide (4.60 g, 51 mmol) was added to a solution of **12**[6] (2.54 g, 6 mmol) in *N*-methyl-2-pyrrolidinone (100 mL). The reaction mixture was heated at reflux for 8 h. Another portion of copper(I) cyanide (4.60 g, 51 mmol) was added to the reaction mixture, which was further refluxed for 20 h. The reaction mixture was cooled and poured into ammonia/ice water (1:1; 300 mL). After thorough mixing the mixture was filtered. The residue was successively extracted with dichloromethane. The organic fractions were combined, washed, and evaporated to give a brown residue. The crude product was preadsorbed onto silica gel and chromatographed with hexane/dichloromethane (2:1) as eluent.

Eluting first was *anti*-**13**: 0.87 g (36%); mp 250–253 °C; ^{1}H NMR δ 8.85 (br d, 2 H, J = 8.5 Hz, Ar H4, H5), 7.1–7.9 (m, 12 H, Ar H), 2.25 (s, 6 H, CH_3); IR (KBr) 2240 ($C{\equiv}N$), 1450, 1390, 870, 770, 750, 725 cm^{-1}; MS ($M^{\bullet+}$) 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.

Eluting next was *syn*-**13**: 0.35 g (14%); mp >280 °C subl; ^{1}H NMR δ 8.84 (br d, 2 H, J = 8.3 Hz, Ar H4, H5), 7.1–7.6 (m, 12 H, Ar H), 2.14 (s, 6 H, CH_3); IR (KBr) 2220 ($C{\equiv}N$), 1480, 1360, 1230, 1140, 800, 755, 720 cm^{-1}; MS ($M^{\bullet+}$) m/z 408 (100), 391 (24), 289 (18), 204 (10). Anal. Calcd for $C_{30}H_{20}N_2$: C, 88.21; H, 4.93; N, 6.86. Found: C, 88.29; H, 4.71; N, 7.17.

***syn*-9,10-Bis(3-formyl-2-methylphenyl)phenanthrene (18).** A solution of diisobutylaluminum hydride (6.37 mmol in hexane) was added dropwise to a solution of *syn*-**13** (0.65 g, 1.59 mmol) in dry benzene (50 mL) at room temperature under nitrogen. The mixture was stirred for 5 h and then decomposed using methanol (15 mL), methanol/water (1:1; 15 mL), and concentrated HCl/water (1:2). The mixture was stirred until all solids dissolved and extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The crude product was filtered through silica gel with hexane/dichloromethane (1:1) as eluant to yield colorless crystals of *syn*-**18**: mp 252–254 °C; ^{1}H NMR δ 10.25 (s, 2 H, CHO), 8.85 (br d, 2 H, J = 8.1 Hz, Ar H4, H5), 7.2–7.8 (m, 12 H, Ar H), 2.27 (s, 6 H, CH_3); IR (KBr) 1660 ($C{=}O$), 1550, 1480, 1370, 1235, 1190, 1140, 910, 790, 760, 720, 670 cm^{-1}; MS ($M^{\bullet+}$) m/z 414 (42), 343 (12), 265 (13), 219 (15), 149 (70). Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.54; H, 5.32.

***syn*-9,10-Bis(3-(hydroxymethyl)-2-methylphenyl)phenanthrene (15).** A reaction mixture of *syn*-**18** (0.35 g, 0.86 mmol) and sodium borohydride (66 mg, 1.74 mmol) in THF (50 mL) was stirred at room temperature for 15 h. The mixture was then decomposed using 1 N HCl until the solution was acidic. The aqueous layer was then saturated with sodium chloride and extracted with dichloromethane. The organic layer was washed, dried, and evaporated. Recrystallization from benzene gave colorless crystals of *syn*-**15**: 0.35 g (99%); mp 278–280 °C; ^{1}H NMR δ 8.82 (br d, 2 H, J = 7.8 Hz, Ar H4, H5), 7.1–7.8 (m, 12 H, Ar H), 4.47 (d, 4 H, J = 2.1 Hz, CH_2), 2.59 (br d, 2 H, J = 2.1 Hz, OH), 1.90 (s, 6 H, CH_3); IR (KBr) 3360 (O–H), 1435, 1370, 1315, 1255, 1225, 1145, 1070, 1030, 1010, 900, 855, 785, 755, 720 cm^{-1}; MS ($M^{\bullet+}$) m/z 418 (59), 384 (24), 382 (28), 354 (42), 353 (37), 279 (59), 277 (27), 265 (32); M_r calcd for $C_{30}H_{26}O_2$ 418.1933, found (MS) 418.1928.

***syn*-9,10-Bis(3-(bromomethyl)-2-methylphenyl)phenanthrene (16).** Phosphorus tribromide (1.3 mL, 13.2 mmol) was added dropwise via a syringe to a solution of *syn*-**15** (0.34 g, 0.82 mmol) in benzene (20 mL). After being stirred for 14 h, the reaction mixture was cooled in an ice bath, decomposed with water, and extracted with dichloromethane. The organic layer was washed with water and aqueous sodium bicarbonate solution, dried, and evaporated. The crude product was filtered through silica gel with hexane/dichloromethane (2:1) as eluant to give colorless crystals of *syn*-**16**: 0.30 g (67%); mp 272–274 °C; ^{1}H NMR δ 8.83 (br d, 2 H, J = 6.8 Hz, Ar H4, H5), 7.0–7.6 (m, 12 H, Ar H), 4.47 (s, 4 H, CH_2), 2.01 (s, 6 H, CH_3); IR (KBr) 1430, 1370, 1250, 1200, 1065, 1015, 905, 865, 855, 785, 750, 715, 665 cm^{-1}; MS ($M^{\bullet+}$) m/z 542 (57), 500 (24), 498 (20), 463 (100), 419 (25), 408 (27), 386 (25), 384 (40), 369 (47), 368 (22), 353 (41), 339 (26), 279 (54), 265 (25). Anal. Calcd for $C_{30}H_{24}Br_2$: C, 66.20; H, 4.44. Found: C, 66.10; H, 4.36.

***syn*-8,17-Dimethylphenanthro[9,10:1′,2′]-10-thia[2.3]metacyclophan-1-ene (8a).** A solution of *syn*-**16** (0.25 g, 0.46 mmol) in benzene (200 mL) and a solution of 95% sodium sulfide nonahydrate (0.11 g, 0.46 mmol) in 95% ethanol/water (1:1; 200 mL) were prepared. These solutions, in separate rotaflow dropping funnels, were added at the same rate into vigorously stirred 95% ethanol (1 L) under nitrogen over a period of 6 h. The mixture was further stirred for 15 h and evaporated. The residue was extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The crude product was preadsorbed onto silica gel and chromatographed using hexane/dichloromethane (2:1) as eluant to yield colorless crystals of *syn*-**8a**: 54 mg (28%); mp 274–275 °C; ^{1}H NMR δ 8.87 (br d, 2 H, J = 8.2 Hz, Ar H4′, H5′), 7.6–7.9 (m, 6 H, phenanthrene Ar H), 7.09 (br d, 2 H, J = 7.4 Hz, Ar H6, H13), 6.80 (t, 2 H, J = 7.4 Hz, Ar H5, H14), 6.50 (br d, 2 H, J = 7.4 Hz, Ar H4, H15), 4.39, 3.79 (AB q, 4 H, J = 14.7 Hz, CH_2), 2.11 (s, 6 H, CH_3); IR (KBr) 1475, 1415, 1380, 1265, 795, 760, 730 cm^{-1}; MS ($M^{\bullet+}$) m/z 416 (100), 383 (42), 382 (17), 353 (18), 279 (27), 175 (21), 169 (14). Anal. Calcd for $C_{30}H_{24}S$: C, 86.50; H, 5.81. Found: C, 86.19; H, 6.33.

(±)-*syn*-8,16-Dimethyl-9-(methylthio)phenanthro[9,10:1′,2′][2.2]metacyclophan-1-ene (19). A solution of *n*-butyllithium (1 mL, 0.1 mmol in hexane) was added slowly to a solution of *syn*-**8a** (30 mg, 0.05 mmol) in dry THF (10 mL) at 0 °C under nitrogen. After the mixture was stirred for 20 min, excess methyl iodide was added to discharge the brown color. Water and dichloromethane were added, and the organic layer was separated, washed, dried, and evaporated. The crude product was filtered through silica gel with hexane/dichloromethane (2:1) as eluant to give colorless crystals of *syn*-**19**: 23 mg (68%); mp 232–235 °C; ^{1}H NMR δ 8.84 (br d, 2 H, J = 8.1 Hz, Ar H4′, H5′), 7.1–7.9 (m, 6 H, phenanthrene Ar H), 6.4–6.6 (m, 6 H, benzene Ar H), 5.04 (dd, 1 H, J_{xy} = 8.9 Hz, J_{xz} = 7.2 Hz, H_x), 3.96 (dd, 1 H, J_{yx} = 8.9 Hz, J_{yz} = 14.0 Hz, H_y), 2.39 (dd, 1 H, J_{zx} = 7.2 Hz, J_{zy} = 14.0 Hz, H_z), 2.25 (s, 3 H, SCH_3), 2.07 (s, 3 H, CH_3 at C8′), 1.98 (s, 3 H, CH_3 at C16′); IR (KBr) 1440, 1370, 1270, 1120, 1060, 1020, 755, 720 cm^{-1}; MS ($M^{\bullet+}$) m/z 430 (100), 415 (87), 382 (18), 354 (37), 353 (30), 352 (59), 309 (48); M_r calcd for $C_{31}H_{26}S$ 430.1755, found (MS) 430.1744.

***syn*-8,16-Dimethylphenanthro[9,10:1′,2′][2.2]metacyclophane-1,9-diene (22).** A solution of **19** (19 mg, 0.044 mmol) in dichloromethane (3 mL) was added to a stirred suspension of dimethoxycarbonium fluoroborate (20 mg, 0.12 mmol) in dichloromethane (3 mL) at −30 °C under nitrogen. The mixture was then stirred without cooling for 2 h. Ethyl acetate (4 mL) was then added, and the mixture was stirred for another 3 h. The crystals formed were filtered to yield the salt **21**: 13 mg (67%). The salt **21** was directly suspended in dry THF (10 mL), and potassium *tert*-butoxide (4.1 mg, 0.04 mmol) was added. The reaction mixture was heated at reflux for 45 min and cooled; 1 N hydrochloric acid was added, and the mixture was extracted with dichloromethane. The crude product was filtered through silica gel to yield colorless crystals of *syn*-**22**: 5 mg (45%); mp 204–206 °C; ^{1}H NMR δ 8.90, 8.81 (dd, 2 H, $J_{4',3'(5',6')}$ = 8.5 Hz, $J_{4',2'(5',7')}$ = 1.5 Hz, Ar H4′, H5′), 8.10, 8.03 (dd, 2 H, $J_{1,2(8,7)}$ = 6.8 Hz, $J_{1,3(8,6)}$ = 2.7 Hz, Ar H1, H8), 7.6–7.8 (m, 4 H, phenanthrene Ar H), 7.35 (s, 2 H, $CH{=}CH$), 6.4–6.6 (m, 6 H, benzene Ar H), 2.02 (s, 6 H, CH_3); IR (KBr) 1450, 1430, 1370, 1260, 1060, 1020, 850, 755, 720, 700 cm^{-1}; MS ($M^{\bullet+}$) m/z 382 (21), 368 (30), 367 (100), 352 (92), 350 (44), 177 (30), 175 (33), 149 (15); M_r calcd for $C_{30}H_{22}$ 382.1722, found (MS) 382.1727.

Acknowledgment. This work was supported by the National University of Singapore (RP860606). We thank the technical staff of the Department of Chemistry, National University of Singapore, for their assistance. The MMP2 calculations were performed with assistance from Dr. G. Yamamoto, Department of Chemistry, Faculty of Science, University of Tokyo.