Use of Bridge Annelation To Retain the Syn Stereochemistry of [*m*.*n*]Metacyclophane Derivatives: A Route to an Elusive *syn*-[2.2]Metacyclophanediene

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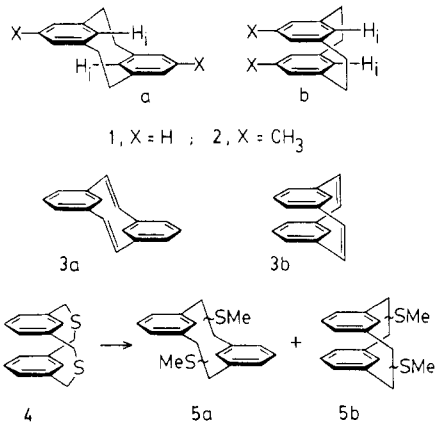
Free-radical bromination of 9,10-di-*m*-tolylphenanthrene (**6**) afforded the anti and syn conformers of the bis(bromomethyl) derivative **7** with the barrier of interconversion estimated at 90 kJ mol^{-1}. Sodium sulfide coupling of **7** surprisingly yielded only the *syn*-thiacyclophanene **8b**. The anti isomer **8a** is believed to be less favorable due to steric interaction between the protons at C1 and C8 and those at C7′ and C13′. The bridge annelation has induced a sufficiently high energy barrier to restrict the isomerization of the syn isomer to the anti conformation either by rotation of the aryl rings or direct flipping of the cyclophane. The syn stereochemistry was clearly retained in the respective products from Wittig rearrangement of syn-isomer **8b** and Raney nickel desulfurization of syn-isomer **12**—the first examples of such reactions not to result in the anti isomer as a major product. A comparison of the chemical shifts of H_i protons in the syn-isomers **4**, **1b**, **8b**, and **14b** clearly illustrates the anisotropic effect of the annelated bridge. A Hofmann elimination of the sulfonium salt derived from syn-isomer **12** afforded only the known phenanthropyrene **18**. It is believed that the *syn*-cyclophanediene **24** formed was not sufficiently stable and tautomerized to the *cis*-dihydropyrene **25**, which oxidized readily to the polycyclic aromatic hydrocarbon **18**.

Introduction

The parent [2.2]metacyclophane was first reported as early as in 1899 by Pellegrin.[1] It has subsequently been shown to exist in the anti-stepped conformation **1a** in both solution (^{1}H NMR analysis)[2] and the solid state (X-ray crystallographic studies).[3] The synthesis[4] of the corresponding parent *syn*-[2.2]metacyclophane (**1b**) was however realized only 85 years later. Using (arene)chromium carbonyl complexation to control the stereochemistry, Mitchell et al. successfully characterized syn-isomer **1b** at low temperature.[4] However, syn-isomer **1b** isomerized readily to anti-isomer **1a** above 0 °C. More recently, Itô et al. reported[5] the characterization and isolation of syn-isomer **2b** without complexation. Although syn-isomer **2b** was prepared via reduction of a thiacyclophane at low temperature, it was found to be stable at room temperature and would only sublime at ca. 75 °C and isomerize to the known anti-isomer **2a**.[6] ^{1}H NMR distinction of the anti and syn isomers of **1** and **2** was very apparent. The internal aryl protons H_i of anti-isomers **1a** and **2a** appeared shielded at δ 4.25 and 4.10 respectively due to the fixation of their steric positions above the opposite benzene rings; those of syn-isomers **1b** and **2b** appeared near the normal benzene region at δ 6.58 (−40 °C) and 6.83 (−60 °C) respectively.

The preparation of *anti*-[2.2]metacyclophanediene (**3a**) has also been reported.[7,8] *syn*-[2.2]Metacyclophanediene (**3b**), however, has remained unknown, and its synthesis would certainly pose a great challenge. Only one derivative of **3b** has been reported.[9] The common synthetic routes[10]



to [2.2]-cyclophanedienes would involve the transformation of the sulfide linkage(s) in a thia- or dithiacyclophane into a carbon–carbon double bond. From the ready isomerization of syn-isomers **1b** and **2b** to the respective anti-isomers **1a** and **2a**, it is clear that the syn conformation is much less stable probably due to electronic repulsion of the closely stacked parallel benzene rings. Thus the ring contraction reactions of a thia- or dithiacyclophane, which are believed to involve ring-opened radical intermediates undergoing easy conformational flip, would result in the formation of predominantly the anti conformer.[8] This was clearly illustrated in the Stevens rearrangement[7,8] of dithiacyclophane **4** which is known[11] to exist in the syn conformation. Ring contraction afforded only anti-isomer **5a**.[4] Thus retention of the syn stereochemistry could only be realized if there is a way to increase the energy barrier to ring flipping. Conformational studies[12] of 9,10-di-*m*-tolylphenanthrene (**6**) revealed that the free energy at coalescence for the interconversion **6a** ⇌ **6b** was about 85 kJ mol^{-1}, with a coalescence temperature at 98 °C. This seems to be a sufficiently high energy barrier to restrict free rotation of the aryl rings at room temperature. An indication is that if the corresponding *syn*-thiacyclophanene **8b** derived from syn-isomer **6b** could be isolated,

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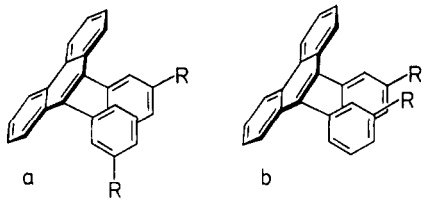
it could in principle retain its syn stereochemistry under similar conditions[10] of the ring-contraction reactions.

Results and Discussion

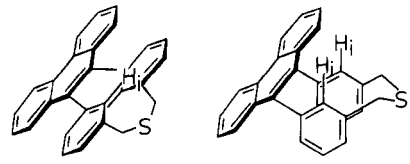
Conformational Studies of 7. The methyl protons of anti-isomer **6a** and syn-isomer **6b** seemed to be in a very similar environment resulting in almost identical chemical shifts observed in most solvents.[12] Introduction of electronegative atoms at the methyl carbons, however, would be expected to induce significantly different dipole–dipole interactions in the anti and syn conformers. Treatment of **6** with *N*-bromosuccinimide under free radical bromination conditions afforded an 85% yield of the bis(bromomethyl) derivative **7**. As expected, the methylene



6, R = CH_3 ; 7, R = CH_2Br

protons now appeared as two partially overlapped broad singlets at δ 4.39 and 4.43 (ratio 1:1.4) in the ^1H NMR spectrum (90 MHz) of **7**, supporting the presence of the anti and syn conformers. The ^1H NMR spectrum of the mixture determined at 250 MHz, however, showed a sharp singlet at δ 4.423 and a doublet centered at δ 4.387. We believe that the latter are the inner lines of an AB quartet with the outer lines unresolved or too low in intensity for the measurement of the coupling constant. Although there is restricted rotation of the aryl rings in anti-isomer **7a**, the methylene protons on one ring are in fact enantiotopic to the respective methylene protons on the other ring. On the contrary, the structure of syn-isomer **7b** has a plane of symmetry (meso) but the methylene protons are diastereotopic. The diastereotopic methylene protons of syn-isomer **7b** are thus expected to be better resolved and appeared as the AB quartet, while those of anti-isomer **7a** remained isochronous and appeared as a singlet. Despite considerable efforts, both TLC and column chromatography failed to separate any isomer free from another. Variable-temperature ^1H NMR (90 MHz) studies, however, have clearly shown that the two peaks at δ 4.39 and 4.43 collapsed to a single peak at their average position at higher temperatures. The coalescence-temperature method[13] to estimate $\Delta G^{\ddagger}_c$ (the transition-state free energy at coalescence) gave a barrier to rotation in **7** (syn ⇌ anti) of ca. 90 kJ mol^{-1} (T_c = 393 K; $\Delta\nu$ = 3.6 Hz), 5 kJ mol^{-1} higher than that observed for the parent **6**.[12] A survey of spatial requirements of organic substituents[14] reveals that the above results are consistent with the change in $\Delta G^{\ddagger}$ for other reported conformationally mobile systems[15] involving a substitution of bromine for hydrogen.

Syn Conformation of 8b.[16] The thiacyclophanene **8** was prepared from the intramolecular coupling of **7** with sodium sulfide using the high-dilution method.[17] A mixture of anti-isomer **8a** and syn-isomer **8b** was expected. Column chromatography, however, resulted in the isolation of only one component, mp 256–258 °C, with a molecular ion at m/z 408 (base peak) expected of **8**. The *anti*-thiacyclophanene **9a** showed a clearly shielded singlet at δ 6.08 for the internal H_i protons;[18] the anti-isomer **8a** would thus be expected to show a similar result. The corresponding H_i protons of the isomer of **8** isolated, however, appeared as a broad singlet at δ 7.36 and thus suggested the syn conformation **8b**. In addition, the other aromatic protons on the benzene rings appeared shifted upfield to δ 6.6–7.1, a common consequence of stacking two parallel aromatic rings.[8,19]



8a 8b

The isolation of only the syn-isomer **8b** was rather unexpected. In fact, this represents the first example of such cyclization to yield mainly a syn conformer of a thia[3.2]metacyclophane derivative. In addition, a related coupling reaction reported[20] earlier in fact yielded a mixture of anti-isomer **10a** and syn-isomer **10b** in a 2:1 ratio. Molecular models indicate that the ene bridge in anti-isomer **8a** has a tendency to encourage the two stepped benzene rings to "slide" outward (the spatial requirement of the internal H_i protons is small) and achieve near planarity with the phenanthrene moiety. This would result in severe steric interaction between the protons at C1 and C8 (on phenanthrene) and those at C7′ and C13′ (on benzene rings), thus making the anti conformation less favorable. The greater steric demand of the methyl groups in anti-isomer **10a**, however, does not allow significant "sliding" of the benzene rings.[21] The anti-isomer **10a** would then be locked in a considerably more stepped conformation and significantly reduce the unfavorable steric interaction observed in anti-isomer **8a**. This difference in the geometry of the molecules, we believe, accounts for the fact that anti-isomer **10a** was isolated as the major isomer[20] whereas there was no evidence for the presence of anti-isomer **8a** in the coupling reaction of **7**.

Wittig Rearrangement of 8b. With the desired *syn*-thiacyclophanene **8b** in hand, a ring contraction reaction was attempted via a Wittig rearrangement.[22] Under such reaction conditions, *syn*-dithiacyclophane **4** or **11** is known to yield a mixture of ring-contracted [2.2]metacyclophanes with the anti isomer as the major product (anti:syn ratio >99:1[4] and 98:2[22] respectively). It is, however, not clear whether this was a result of a driect conformational flip of the *syn*-cyclophane or a bond-breaking and bond-forming process which allowed the rotation of the aryl rings.

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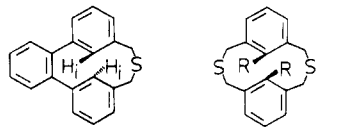
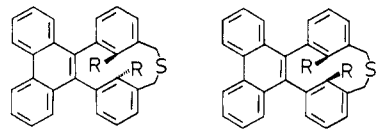
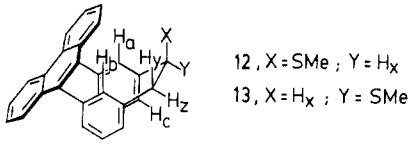


9 11, R = CH_3

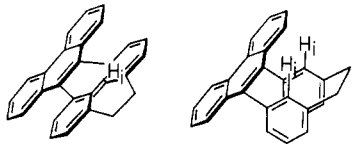


10a (R = CH_3) 10b

Wittig rearrangement of syn-isomer **8b** surprisingly afforded only one isomer. The absence of an upfield-shifted proton signal characteristic of the anti isomers clearly indicated that the syn stereochemistry was retained. On the other hand, the expected aryl protons of the two syn benzene rings were again observed as a slightly shielded multiplet at δ 6.6–6.8. The internal protons of the isolated isomer in fact appeared as two broad singlets in a 1:1 ratio at δ 7.19 and 7.48 respectively. The above data are clearly consistent with the syn-isomer **12**, with the internal H_a proton showing a marked downfield shift as would be expected for deshielding by the neighboring pseudoaxial sulfur atom. The sulfur atom in the other isomer **13** would be expected to deshield the H_c proton instead. The H_x, H_y, and H_z protons in **12** were observed as three well-separated double doublets centered at δ 4.07 (J_{xy} = 8.8 Hz; J_{xz} = 6.6 Hz), 3.68 (J_{yx} = 8.8 Hz; J_{yz} = 13.2 Hz), and 2.89 (J_{zx} = 6.6 Hz; J_{zy} = 13.2 Hz) respectively. The downfield shift of the H_y proton compared with the chemical shift of the H_z proton would also be due to the deshielding effect of the adjacent cis sulfur atom.



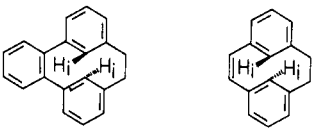
12, X = SMe ; Y = H_X
13, X = H_X ; Y = SMe



14a 14b

The above results prompted an attempt to convert syn-isomer **12** to the *syn*-cyclophanene **14b** by desulfurization with Raney nickel. Treatment of syn-isomer **12** with W-7 Raney nickel in refluxing ethanol seemed to afford a mixture of two isomers which were apparent on TLC studies, but with one component barely visible. The ^1H NMR spectrum (90 MHz) showed two broad singlets at δ 5.40 and 7.09 respectively in a ratio of 5:95, suggesting the presence of anti-isomer **14a** and syn-isomer **14b** with the latter as the major isomer. The above NMR data are in fact comparable to the respective chemical shifts observed for the internal protons H_i (δ 5.44)[18] of anti-isomer **15** and H_b (δ 7.19) in syn-isomer **12**, thus supporting our assignment. This would again represent the first example of such a desulfurization reaction to yield mainly the syn isomer of a [2.2]metacyclophane derivative. Recrystallization from a cyclohexane/ethanol mixture afforded a pure sample of syn-isomer **14b**, but the expected anti-isomer **14a** could not be isolated free from the syn isomer either by recrystallization or column chromatography. The other aryl protons of the two syn benzene rings in **14b** appeared clearly in the expected shielded region at δ 6.6–6.9.

The two reactions described for syn-isomer **8b** and syn-isomer **12** have clearly indicated that the syn stereochemistry of an [*m.n*]metacyclophanene could be successfully retained. In addition, syn-isomer **14b** is thermally very stable. A NMR study of syn-isomer **14b** showed no significant change in the spectrum when the sample was heated to 150 °C. This would rule out the possibility of a direct conformational flip from syn-isomer **14b** to anti-isomer **14a** under the reaction conditions. On the contrary, the presence of anti-isomer **14a** observed in the product mixture would further support the formation of ring-opened intermediates in the Raney nickel desulfurization of thiacyclophanes. The bridge annelation with a phenanthrene moiety, however, has clearly resulted in a sufficiently high energy barrier to significantly reduce conformational rotation of the aryl rings which would lead to the formation of the anti isomer.



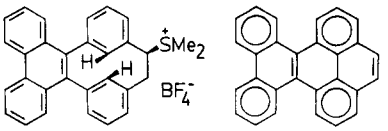
15 16

Anisotropic Effect in 8b and 14b. In the series of anti isomers, the marked downfield shift of the internal H_i protons in passing from **1a** (δ 4.25) to **15** (δ 5.44) and **16** (δ 5.62) was initially attributed to the deshielding effects of the benzene ring and the double bond respectively.[18] A comparison with results from the related series of dimethyl derivatives, the internal methyl protons of which appeared at very similar chemical shifts, however, suggests that the true effect observed for **1a**, **15**, and **16** is in fact due to a change in molecular geometry resulting from the "sliding" of the stepped benzene rings.[21] Such a change is not expected in the series of syn-isomers **4**, **1b**, **8b**, and **14b**. A marked deshielding effect on the internal H_i protons is, however, also observed when **8b** (δ 7.35) and **14b** (δ 7.09) are compared with **4** (δ 6.82) and **1b** (δ 6.58) respectively. Molecular models indicate that the internal H_i protons in **8b** and **14b** are located in the vicinity of the central ring of the phenanthrene moiety in the syn conformation. The anisotropic effect of the annelated bridge should in this case be responsible for the downfield shift of the internal H_i protons concerned. The H_i protons of **8b** and **14b** are in fact deshielded similarly about 0.5 ppm from those of **4** and **1b** respectively. The difference in chemical shifts of the H_i protons of **1a** and **15** (or **16**), however, is larger than 1 ppm, a value too large to be expected of a similar anisotropic effect. Our results would thus further help to confirm that a change in molecular geometry is the major effect responsible for the chemical shift difference observed for **1a** and **15** (or **16**).

Another examination shows a slight upfield shift for the internal H_i protons when **4** (δ 6.82) and **8b** (δ 7.35) are compared with **1b** (δ 6.58) and **14b** (δ 7.09) respectively. Desulfurization of a $-CH_2SCH_2-$ function to a saturated $-CH_2CH_2-$ unit would undoubtedly result in a shorter bridge of the *syn*-cyclophane. The aromatic protons of the two parallel benzene rings brought closer by the shorter bridge(s) in **1b** and **14b** would then be expected to appear shifted further upfield compared with those of **4** and **8b**.

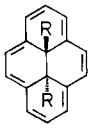
Hofmann Elimination of 17. Remethylation of **12** with dimethoxycarbonium fluoroborate readily gave an 87% yield of the sulfonium salt **17**. Hofmann elimination of **17** was then carried out with potassium *tert*-butoxide in refluxing THF. Only one product could be isolated after

chromatography over silica gel. The ^1H NMR spectrum indicated the presence of only aromatic protons, which suggested the structure of the known polycyclic aromatic hydrocarbon **18**.[23] This was further confirmed by a molecular ion at m/z 352 in its mass spectrum. The UV spectrum recorded was also identical with that reported.[23]

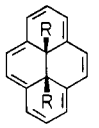


17

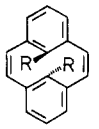
18



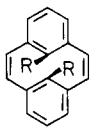
19, R = H
20, R = CH_3



21, R = CH_3

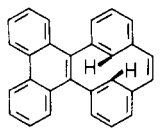


22 (R = CH_3)



23

In the syntheses of dihydropyrenes **19**,[7,8] **20**,[8] and **21**,[8,24] a similar Hofmann elimination was employed to afford initially the respective cyclophanedienes **3a**, **22**, and **23** respectively. **3a** could be isolated cleanly and yielded **19**, only upon irradiation with light (254 nm). Both **20** and **21** were, however, directly isolated free from the tautomeric **22** and **23** respectively after chromatography. Although the reverse conversion of **20** to **22** could be achieved thermally or photochemically, similar treatment of **21** failed to afford **23** but led to ready decomposition. The above results indicate that a *syn*-cyclophanediene would presumably be much less stable than an *anti*-cyclophanediene. We believe that the Hofmann elimination of **17** initially yielded the *syn*-cyclophanediene **24**, which was not sufficiently stable to be isolated but tautomerized readily to the *cis*-dihydropyrene **25**. The latter would be expected to undergo oxidation readily to afford the polycyclic aromatic compound **18**, consistent with the fact that *trans*-dihydropyrene **19** undergoes rapid conversion to pyrene.[7,8]



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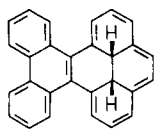
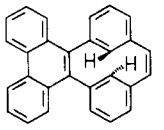
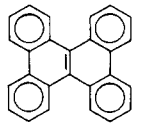


25

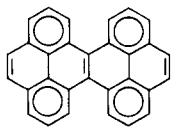
The formation of the *anti*-cyclophanediene **26** in the Hofmann elimination of **17** is considered unlikely. Whether such an elimination follows an E1- or E2-type mechanism would probably not involve ring-opened intermediates[25] and thus rule out the possibility of conformational rotation of the aryl rings. Although the barrier of conformational flipping in a cyclophanediene may differ from that of the corresponding cyclophane,[26] the high thermal stability of syn-isomer **14b** suggests that ring flipping in syn-isomer **24** to give anti-isomer **26** would be unlikely under the reaction conditions (refluxing THF, 45 min). In addition, molecular models indicate that anti-isomer **26** would involve more severe steric interaction similar to that described for anti-isomer **8a**.



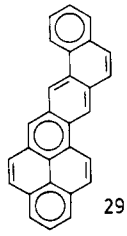
26



27



28



29

Comparison of the electronic spectra of **18** and the polycyclic aromatic hydrocarbons **27** and **28** has been extensively studied.[23,27] Bathochromic shifts were clearly observed for the β and p bands in passing from **27** to **18** and **28** resulting from a pure annelation effect.[28] We have noted, however, another interesting comparison between **18** and the only other known isomeric phenanthropyrene, **29**.[29] The stability of the isomers is expected to increase with the number of aromatic sextets and result in a shift of the β and p bands to the shorter wavelengths (hypsochromic shift).[28] The latter phenomenon is clearly apparent from the electronic spectra of **29** (3 aromatic sextets; λ_β = 337 nm; λ_p = 450 nm)[29] and **18** (4 aromatic sextets; λ_β = 314 nm; λ_p = 375 nm).

Conclusion

Although the isolation of the *syn*-cyclophanediene **24** was unsuccessful, our work represents the first possible route to retain the syn stereochemistry from a thiacyclophanene to a cyclophanediene. The bridge annelation has certainly induced sufficiently high energy barriers to conformational rotation of the aryl rings and direct ring flipping of the *syn*-cyclophane. We believe that this method of appropriate bridge annelation would be useful in future synthetic design of related *syn*-[2.2]metacyclophane derivatives. Our results have also shown that the internal protons or substituents in a *syn*-[*m.n*]metacyclophanene will clearly experience the anisotropic effect of the ene bridge.

Experimental Section

All melting points were determined by using a Sybron-thermolyne MP-12615 apparatus and are uncorrected. ^1H NMR spectra were determined in $CDCl_3$ on a Perkin-Elmer R32 (90 MHz), a JEOL FX90Q (90 MHz), or a Bruker WM-250 (250 MHz) spectrometer. Variable-temperature ^1H NMR studies were carried out on a Perkin-Elmer R32 (90 MHz) spectrometer. All chemical shifts are reported in parts per million downfield from tetramethylsilane used as internal standard. IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer. UV spectra were recorded on a Shimadzu UV160 spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70

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eV using electron impact. Relative intensities are given in parentheses. Only the molecular ion containing ^{79}Br is given for **7**. 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 sulfate.

9,10-Bis[3-(bromomethyl)phenyl]phenanthrene (7). A mixture of **6**[12] (303 mg, 0.85 mmol), *N*-bromosuccinimide (316 mg, 1.79 mmol), and a catalytic amount of benzoyl peroxide in CCl_4 (25 mL) was heated at refluxing temperature by using a light source for 30 min. The mixture was filtered, and the filtrate was washed, evaporated, and recrystallized from cyclohexane. Colorless crystals of **7** were obtained: 373 mg (85%); mp 203–212 °C; ^1H NMR δ 8.82 (br d, 2 H, J = 8.0 Hz, Ar H4, H5), 6.9–7.8 (m, 14 H, Ar H), 3.39, 49.43 (s, total 4 H, ratio 1:1.4, CH_2Br); IR (KBr) 1480, 1445, 1415, 1210, 1078, 1040, 905, 895, 756, 720, 702 cm^{-1}; MS ($M^{\bullet+}$), m/z 514 (47), 472 (19), 470 (13), 435 (45), 355 (48), 339 (43), 325 (28), 313 (20), 265 (44). Anal. Calcd for $C_{28}H_{20}Br_2$: C, 65.14; H, 3.90. Found: C, 65.26; H, 3.91.

***syn*-Phenanthro[9,10:10′,11′]-2-thia[2.3]metacyclophan-10-ene (8b).** A solution of the dibromide **7** (1.173 g, 2.27 mmol) in benzene (200 mL) and a solution of 95% sodium sulfide nonahydrate (0.574 g, 2.27 mmol) in water (200 mL) were prepared. These solutions, in separate rotaflow dropping funnels, were added at the same rate into vigorously stirred 95% C_2H_5OH (1 L) under nitrogen over a period of 5 h. The mixture was further stirred for 15 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 chromatographed with hexane/dichloromethane (2:1) as eluent to give **8b**, 0.398 g (45%). A sample recrystallized from benzene afforded colorless crystals of **8b**: mp 256–258 °C; ^1H NMR δ 8.90 (dd, 2 H, J = 1.6, 8.0 Hz, Ar H4, H5), 7.5–8.0 (m, 6 H, phenanthrene Ar H), 7.36 (br s, 2 H, Ar H_i), 6.6–7.1 (m, 6 H, benzene Ar H), 3.95 (s, 4 H, CH_2S); IR (KBr) 1470, 1400, 1310, 850, 790, 775, 750, 715, 695, 630 cm^{-1}; MS ($M^{\bullet+}$), m/z 388 (100), 356 (13), 354 (15), 352 (18), 337 (20), 324 (15), 149 (27). Anal. Calcd for $C_{28}H_{20}S$: C, 86.56; H, 5.19. Found: C, 86.48; H, 5.37.

Wittig Rearrangement of Thiacyclophanene 8b. A solution of *n*-butyllithium (4.59 mmol in hexane) was added dropwise to a solution of the thiacyclophanene **8b** (0.64 g, 1.65 mmol) under N_2 in dry THF (15 mL) at 0 °C. After a further 10 min, methyl iodide (2.29 mmol) from a 2 M solution in dry THF) was added. The intense color of the mixture was discharged. Water was added and the mixture extracted with dichloromethane. The organic layer was then washed, dried, and evaporated. The crude product was chromatographed on silica gel with hexane/dichloromethane (3:1) as eluent to give colorless crystals of **12**: 0.30 g (45%); mp 202–204 °C; ^1H NMR δ 8.84 (dd, 2 H, J = 1.7, 7.6 Hz, Ar H4, H5), 8.1–8.2, 7.5–7.8 (m, 6 H, phenanthrene Ar H), 7.48 (br s, 1 H, H_a), 7.19 (br s, 1 H, H_b), 6.6–6.8 (m, 6 H, benzene Ar H), 4.07 (dd, 1 H, J_{xy} = 8.8 Hz, J_{xz} = 6.6 Hz, H_x), 3.68 (dd, 1 H, J_{yx} = 8.8 Hz, J_{yz} = 13.2 Hz, H_y), 2.89 (dd, 1 H, J_{zx} = 6.6 Hz, J_{zy} = 13.2 Hz, H_z), 2.18 (s, 3 H, SCH_3); IR (KBr) 1540, 1470, 1440, 1410, 1310, 1150, 1060, 1035, 940, 785, 755, 720, 700 cm^{-1}; MS ($M^{\bullet+}$), m/z 402 (<10), 355 (38), 354 (100), 353 (70), 352 (42), 351 (16), 350 (17), 339 (10), 327 (14), 326 (12); M_r calcd for $C_{29}H_{22}S$ 402.1442, found (MS) 402.1449.

***syn*-Phenanthro[9,10:1′,2′][2.2]metacyclophan-1-ene (14b).** The cyclophanene **12** (0.62 g, 1.54 mmol) was added to 95% ethanol (30 mL) containing an excess of W-7 Raney nickel, and the mixture was heated at reflux for 2.5 h. The excess nickel was filtered and the solvent evaporated. The residue was recrystallized from a cyclohexane/ethanol mixture to give colorless crystals of *syn*-cyclophanene **14b**: 0.44 g (80%); mp 210–212 °C; ^1H NMR δ 8.84 (dd, 2 H, J = 1.9, 7.6 Hz, Ar H4, H5), 8.0–8.2, 7.3–7.8 (m, 6 H, phenanthrene Ar H), 7.09 (br s, 2 H, H_i), 6.6–6.9 (m, 6 H, benzene Ar H), 3.0–3.4 (m, 4 H, CH_2); MS ($M^{\bullet+}$), m/z 356 (100), 355 (32), 354 (10), 339 (10), 329 (12), 328 (13), 327 (11), 326 (18). Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.02; H, 5.99.

Hofmann Elimination of Sulfonium Salt 17. (a) Salt 17. A solution of the cyclophanene **12** (0.30 g, 0.75 mmol) in dichloromethane (15 mL) was added via a syringe to a stirred suspension of dimethoxycarbonium fluoroborate (0.23 g, 1.41 mmol) in dichloromethane (10 mL) at −30 °C under nitrogen. The mixture was further stirred without cooling for 2 h. Ethyl acetate (10 mL) was added, and the mixture was further stirred for 5 h. The crystalline precipitate was filtered, washed with ethyl acetate, and dried to give the salt **17**: 0.27 g (86%); mp >240 °C.

(b) Elimination. Potassium *tert*-butoxide (0.10 g, 0.89 mmol) was added to a suspension of the salt **17** (0.30 g, 0.61 mmol) in dry THF (15 mL) under nitrogen at room temperature. The reaction mixture was then heated at gentle reflux for 45 min. After the solution was cooled, dilute HCl and dichloromethane were added, and the organic layer was washed, dried, and evaporated. The residue was preadsorbed onto silica gel and chromatographed by using hexane/dichloromethane (3:1) as eluent to give the hydrocarbon **18**: 93 mg (43%); mp 250–252 °C (lit.[23] mp 258–260 °C); ^1H NMR δ 6.7–8.3 (m, Ar H); IR (KBr) 1435, 1415, 1035, 860, 820, 815, 790, 755, 745, 715 cm^{-1}; MS ($M^{\bullet+}$), m/z 352 (100), 351 (38), 350 (39), 348 (18), 328 (28). Anal. Calcd for $C_{28}H_{16}$: C, 95.42; H, 4.58. Found: C, 95.08; H, 5.00.

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