An Experimental Estimation of Aromaticity Relative to That of Benzene. The Synthesis and NMR Properties of a Series of Highly Annelated Dimethyldihydropyrenes: Bridged Benzannulenes

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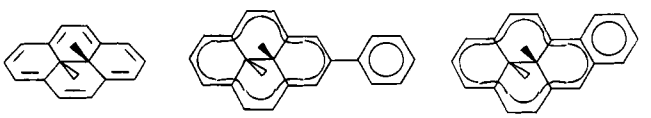
Abstract: The synthesis of 13 *trans*-dimethyldihydropyrenes (bridged [14]annulenes) fused to one or more benzene, naphthalene, phenanthrene, phenalene, or quinoxaline rings and 6 *cis*-dihydropyrene derivatives from benzenoid precursors using either a thiacyclophane route or an electrocyclic addition of a furan to an annulyne followed by deoxygenation is reported. Their ^{1}H NMR spectra are studied in detail to obtain correlations between $^3J_{H,H}$ coupling constants and the internal methyl proton chemical shifts and also between the latter and the more distant external annulene ring proton shifts. These linear correlations are then used to obtain a relationship between the relative aromaticity of benzene and the fused ring in question, such that the aromaticity of the fused ring can be estimated relative to that of a benzene ring simply from a measurement of chemical shift in the fused annulene.

The concept of "aromaticity" has now stimulated both synthetic and theoretical chemists for well over a century and probably will continue to do so. It is a concept we teach our beginning students, yet we still debate its cause (is it driven by the hexagonal geometry of benzene or by delocalization?).[1] Three recent papers[2] summarize most of the present ideas. One point that is eminently clear is that it is difficult to measure aromaticity. This is especially true for methods that try to relate some calculated or derived quantity to that which would be obtained for a hypothetical reference structure. A case in point is resonance energy estimates derived from heats of hydrogenation, where the reference structure for benzene is "cyclohexatriene", usually assumed to be equivalent to three cyclohexenes. What the appropriate reference structures are, for example, for the cyclopentadienide anion or ferrocene (both considered aromatic molecules) is far from obvious. We believe a much more useful approach to estimating aromaticity is to compare the effect that the system under study has on a probe with the effect that a benzene ring has on the same probe. The advantage is that the comparison is to a real quantity, the effect of a benzene ring. The latter, of course, is the prototype aromatic, and even if aromaticity is hard to define, most chemists have a good feel for the properties of benzene. The goal then of this paper is to place a series of aromatic compounds on a simply measured scale, in order of aromaticity, where the scale is defined relative to the effect of benzene. A secondary goal is to link the scale to an established theoretical aromaticity index such as resonance energy, at least for benzenoid systems. To establish this goal, a suitable probe molecule is required, which has a simply measured quantity related to aromaticity.



1 2 3

We suggest that the bridged annulene, **1**, *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, is one such suitable molecule. It is planar,[3] and the internal methyl groups are rigidly held close to the center of the strongly shielding zone of the ring current, such that at δ −4.25, these methyl protons show 5.22 ppm of ring current shielding, which is affected only to a very minor extent (usually <0.3 ppm) by substituents[4] but very strongly by fusion of a benzene ring, which changes dramatically the delocalization in the macrocyclic ring and hence the ring current.[5] Thus, the chemical shifts of the internal methyl protons in **2**, the phenyl substituted derivative,[6] are δ −4.03 and −4.00, shifted <0.3 ppm from **1**, while for the fused annulene **3**,[7] δ = −1.62, a shift of 2.63 ppm! In both cases, the through space deshielding of the methyl protons by the ring current of the benzene ring is very small, <0.1 ppm on the basis of calculations

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(1) Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657−4659. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Nature* **1986**, *323*, 699−701. Hiberty, P. L.; Shaik, S. S.; Ohanessian, G.; Lefour, J. M. *J. Org. Chem.* **1986**, *51*, 3908−3909. Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907−3908. Kuwajima, S.; Soos, Z. G. *J. Am. Chem. Soc.* **1987**, *109*, 107−113. Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363−374. Ohanessian, G.; Hiberty, P. C.; Lefour, J. M.; Flament, J. P.; Shaik, S. S. *Inorg. Chem.* **1988**, *27*, 2219−2224. Hiberty, P. C.; Ohanessian, G.; Shaik, S. S.; Flament, J. P. *Pure Appl. Chem.* **1993**, *65*, 35−45.

(2) Zhou, Z. *Int. Rev. Phys. Chem.* **1992**, *11*, 243−261. Jug, K.; Koster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163−169. Parkanyi, C.; Boniface, C. *Bull. Soc. Chim. Belg.* **1990**, *99*, 587−594.

(3) Crystal structure is reported below. Also, two crystal structures of derivatives of **1** have been published: Hanson, A. W. *Acta Crystallogr.* **1965**, *18*, 599−604. Hanson, A. W. *Acta Crystallogr.* **1967**, *23*, 476−481.

(4) Mitchell, R. H. *Adv. Theor. Interesting Mol.* **1989**, *1*, 135−199.

(5) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571−2578.

(6) Mitchell, R. H.; Chaudhary, M.; Dingle, T. W.; Williams, R. V. *J. Am. Chem. Soc.* **1984**, *106*, 7776−7779.

(7) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2544−2551.

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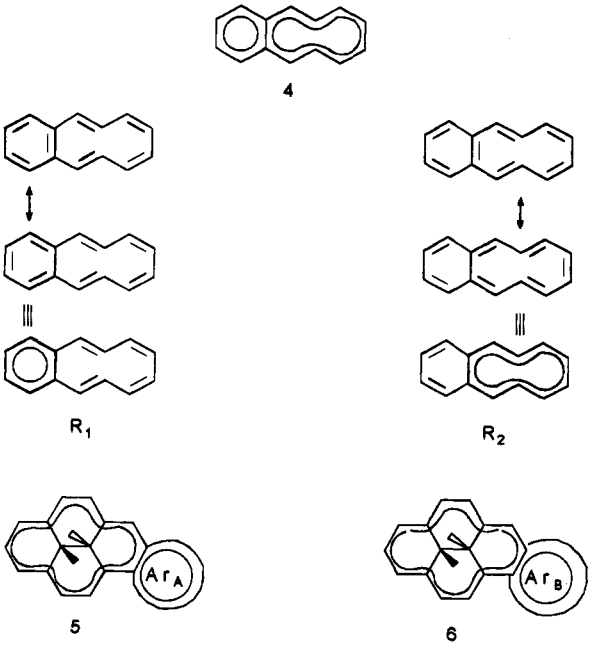
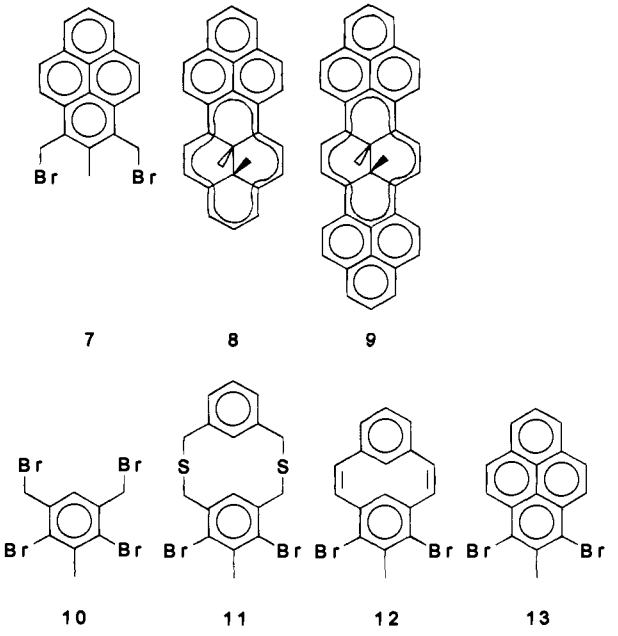
using the Memory equation.[8] From the work of Haddon,[9] Aihara,[10] and Verbruggen,[11] there can be no doubt that ring currents in annulenes are related directly to the aromaticity (resonance energy) of the annulene. The question then arises as to whether the ring current in one annulene can give information about the aromaticity of another that is fused to the first. Consider the simple fused annulene 4; this can be represented by three Kekulé structures and contains three resonance circuits. The 6π circuit $\mathbf{R_1}$ involves two of these



structures, as does the 10π circuit $\mathbf{R_2}$. Inspection of $\mathbf{R_1}$ indicates that delocalization of the 6π circuit involves bond fixation in the rest of the molecule, while inspection of $\mathbf{R_2}$ likewise indicates that delocalization of the 10π circuit involves bond fixation in the other ring. The relative contributions of these circuits will depend on the resonance energies of $\mathbf{R_1}$ vs $\mathbf{R_2}$.[12] Now consider two fused annulenes with one ring in common, and specifically the case of interest to us, annulenes **5** and **6**. We have indicated above that for **1**, the chemical shift of the methyl protons mainly depends on the ring current around the macrocyclic ring. In the fused annulenes **5** and **6**, this will depend on the delocalization of this ring[5] and hence, on the relative resonance energies of the fused rings $\mathbf{Ar_A}$ and $\mathbf{Ar_B}$. Clearly, if $\mathbf{Ar_A}$ is large, then delocalization around the 14π dihydropyrene ring will be small, the ring current will be small, and hence, the chemical shift shielding of the methyl protons will be small. Conversely, if the resonance energy of $\mathbf{Ar_A}$ is small, the dihydropyrene ring is well-delocalized and the ring current and the shielding will be large. Thus, a comparison of the relative delocalizations of the common 14π ring in **5** and **6** should be possible by comparison of the methyl chemical shifts, and hence, the relative aromaticities (resonance energies) of the fused rings $\mathbf{Ar_A}$ and $\mathbf{Ar_B}$ can be compared. For the remainder of this paper, we thus define aromaticity to equate with π-electron delocalizing ability. The more aromatic a molecule is, the greater are its π-electrons delocalized and the more it resists having its π-electrons bond-fixed. Since benzene is the prototype aromatic compound, it should be the reference comparison point, and thus for us, **5** will be the benzannulene **3**. In the decade that has elapsed since publication here[5,7,13] of our early work on the mono- and dibenzo derivatives of **1**, we have prepared many higher annelated derivatives of **1** with the goal of an experimental aromaticity scale based on simple chemical shift measurement. We present the results of these investigations here.

Syntheses

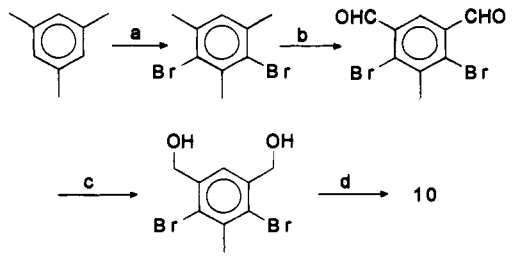
Prior to the early 1970s, because the annulenes themselves were both difficult to synthesize and were not very stable, many benzannulenes were prepared as more stable models.[14] Most of these early compounds sustained almost no macrocyclic ring current. This changed as we[15] and others[16] prepared strongly diatropic planar benzannulenes. The fact that dibenzannulenes could sustain substantial ring currents was surprising at first,[17] but as understanding of the delocalization present in such systems grew,[18] this provided the impetus for the synthesis of even more highly annelated systems. The first approach that we took to the synthesis of benzannelated derivatives of **1** was to modify our synthesis[19] of **1** itself, starting with, instead of 2,6-bis(bromomethyl)toluene, a 1,3-bis(bromomethyl)-2-methylarene such as naphthalene.[7] While this seems simple enough, the synthesis of the appropriate 1,2,3-trisubstituted aromatic compound is not always straightforward. Indeed, we had intended to use the pyrene **7** to synthesize the more highly annelated dihydropyrenes **8** and **9**. In attempts to prepare **7**, we intended to use our thiacyclophane route to pyrenes,[20] specifically by using **10** to form **11**, which should be transformable through **12** and **13** to **7**.



Pure tetrabromide **10** could not be prepared by reaction of NBS/CCl_4 on dibromomesitylene, **14**, but could be prepared by using the longer route shown in Scheme 1. Coupling of **10** with *m*-xylylenedithiol and KOH gave 75% of the *syn*-dithiacyclophane **11**. Wittig rearrangements of such cyclophanes usually[21] proceed easily to give the ring-contracted product; however, reaction of **10** in THF with lithium diiso-

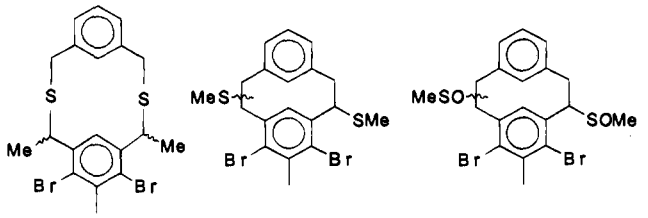
(8) Memory, J. D. *J. Magn. Reson.* **1977**, *73*, 241–244.
(9) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722–1728.
(10) Aihara, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1163–1164.
(11) Verbruggen, A. *Bull. Soc. Chim. Belg.* **1982**, *91*, 865–868.
(12) Hess, B. A., Jr.; Schaad, L. J.; Agranat, F. *J. Am. Chem. Soc.* **1978**, *100*, 5268–5271.
(13) Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2551–2559.
(14) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives*; CRC Press: Boca Raton, FL, 1987; Vols. I–III.
(15) Mitchell, R. H.; Carruthers, R. J. *Tetrahedron Lett.* **1975**, 4331–4334.

Scheme 1[a]



[a] $Br_2/CHCl_3/Fe/I_2$, 87%; (b) $CrO_3/AcOH/Ac_2O/H_2SO_4$, 0 °C, then aqueous H_2SO_4, 22%; (c) $NaBH_4$/THF, quant.; (d) 48% aqueous HBr, reflux, 87%.

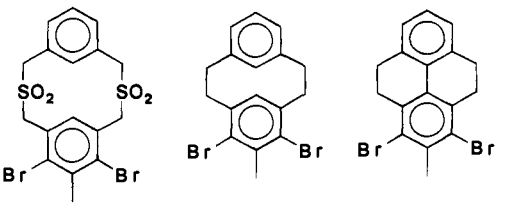
propylamide (LDA) and then CH_3I at 20 °C gave a mixture of the bridge-alkylated product **15** and the ring-contracted product **16**. Evidently, the intermediate bridge anion formed shows some stability since if the reaction is carried out below 0 °C, only **15** is obtained, whereas if the reaction is refluxed for 30 min before the addition of the CH_3I, the rearrangement takes place and 77% of **16** is formed. A Hofmann-type elimination



15 16 17

on **16** proceeded only poorly; thus, it was oxidized to bis-sulfoxide **17** using[22] bromine and aqueous $NaHCO_3$ in 77% yield, which was then thermolyzed in refluxing *N*-methyl-2-pyrrolidinone to give 65% of pyrene **13**. This pyrene turned out to be a highly insoluble compound and was thus extremely difficult to convert to **7** in useful amounts. The approach was thus modified somewhat to take advantage of the higher solvent solubility of the tetrahydropyrenes. The latter are probably most conveniently prepared by oxidation of the corresponding *anti*-[2.2]metacyclophanes.[23] Thus, thiacyclophane **11** was oxidized (H_2O_2–AcOH, 92% yield) to the bis-sulfone **18**, which was flash pyrolyzed at 650–700 °C under low pressure to give 49% of the *anti*-cyclophane **19**, internal protons at δ 4.27 and 4.41. On oxidation with Br_2 in CCl_4 in the presence of iron powder, **19** gave 98% of the tetrahydropyrene **20**. Conversion to the bis(bromomethyl) compound **24** was achieved using the sequence shown in Scheme 2, and indeed, it showed good solubility in benzene.

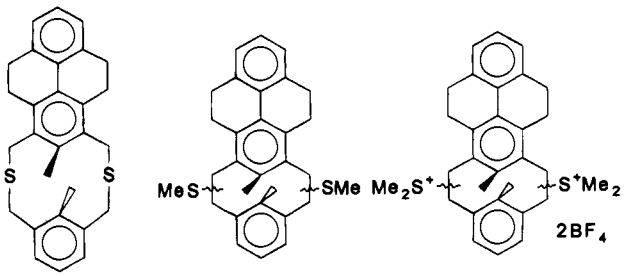
Coupling of the bis-bromide **24** with the three bis-thiols **25**,[19] **26**,[24] and **27** (prepared from **24** and thiourea) proceeded



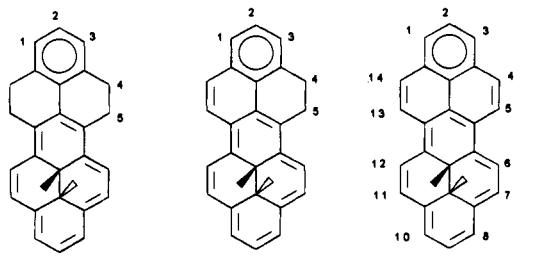
18 19 20

smoothly to give the three dithiacyclophanes **28**–**30** as a mixture of *syn* and *anti* isomers, which could be separated by careful chromatography. The yields obtained were *anti*-**28**, 67%; *syn*-**28**, 7%; *anti*-**29**, 62%; *syn*-**29**, 11%; *anti*-**30**, 60%; and *syn*-**30**, 6%. The structures were evident from their molecular ions in their mass spectra and the positions of the internal methyl protons; the three *anti* compounds showed these shielded at δ 1.38 and 1.18 (**28**), 1.50 and 0.72 (**29**), and 1.32 (**30**). In contrast, the three *syn* compounds showed these protons normal at δ 2.48 and 2.44 (**28**), 2.63 and 2.49 (**29**), and 2.14 (**30**). Full spectral data can be found in the Experimental Section.

Wittig rearrangement[21] of *anti*-**28** with *n*-BuLi in THF, followed by CH_3I, yielded quantitatively the ring-contracted cyclophane *anti*-**28A** as a mixture of stereoisomers (SCH_3 protons at δ 2.60, 2.12, and 2.08). This mixture was directly



anti-28 anti-28A anti-28B



31 32 33

remethylated with Borch reagent,[25] $(CH_3O)_2CHBF_4$, to give 87% of the sulfonium salts, *anti*-**28B**, which were subjected to a Hofmann elimination with potassium *tert*-butoxide in refluxing THF. Interestingly, the product **31** (43% yield) also contained small amounts of the dehydrogenated derivatives **32** and **33**. Dehydrogenation by metal alkoxides, although not without precedent,[26] is not very common, but **31** on further reflux with *t*-BuOK/THF gave 71% yield of **33**. Excess DDQ/benzene, at reflux, only gave a poor yield of **33**. Nevertheless, reaction of **31** with 1.1 equiv of DDQ in benzene proved to be the best route to obtain **32** (81% yield). The structures of the dihydro-

(16) See, for example: Weavers, R. T.; Sondheimer, F. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 141–142. Yasuhara, A.; Satake, T.; Iyoda, M.; Nakagawa, M. *Tetrahedron Lett.* **1975**, 895–898. Weavers, R. T.; Jones, R. R.; Sondheimer, F. *Tetrahedron Lett.* **1975**, 1043–1046. Ojima, J.; Kimura, A.; Yokoyama, T. *Chem. Lett.* **1975**, 207–210. Yasuhara, A.; Iyoda, M.; Satake, T.; Nakagawa, G. *Tetrahedron Lett.* **1975**, 3931–3934.

(17) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L. *J. Am. Chem. Soc.* **1978**, *100*, 1007–1008.

(18) Mitchell, R. H. *Isr. J. Chem.* **1980**, *20*, 294–299.

(19) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547–1557.

(20) Mitchell, R. H.; Carruthers, R. J. *Can. J. Chem.* **1974**, *52*, 3054–3056.

(21) Mitchell, R. H. *Heterocycles* **1978**, *11*, 563–586. Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 219–222.

(22) Drabowicz, J.; Midura, W.; Mikolajczyk, M. *Synthesis* **1979**, 39–40.

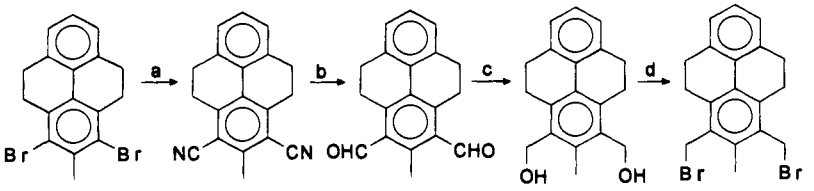
(23) Umemoto, T.; Satani, S.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1975**, 3159–3162.

(24) Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560–2571.

(25) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627–629.

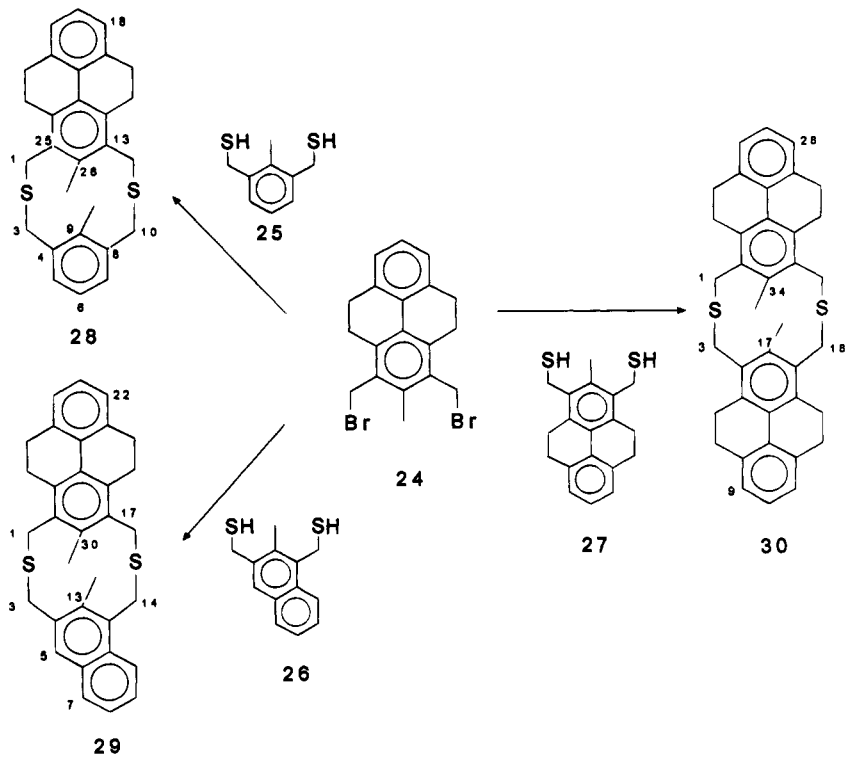
(26) Pines, H.; Schaap, L. *J. Am. Chem. Soc.* **1957**, *79*, 2956–2958. Baldwin, J. E.; Barton, D. H. R.; Sutherland, J. K. *J. Chem. Soc.* **1964**, 3312–3315. Barton, D. H. R.; Jones, D. W. *J. Chem. Soc.* **1965**, 3563–3570.

Scheme 2

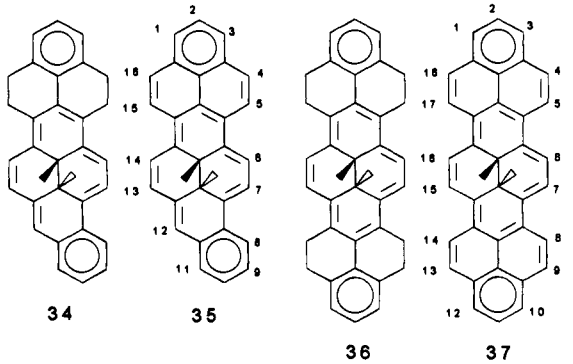


[a] CuCN/NMP, 41%; (b) DIBAH, 80%; (c) $NaBH_4$/THF, 92%; (d) 48% aqueous HBr, reflux, 74%.

Scheme 3



pyrenes **31**−**33** (note: **33** ≡ **8**) were evident from the deeply colored crystals (the initial products from the Hofmann elimination, the isomeric cyclophanedienes are colorless), from their mass spectra, and from the highly shielded internal methyl protons. Their NMR spectra are discussed below. Using the same sequence as for *anti*-**28** → **28A** → **28B** → **31**, we found *anti*-**29** gave 12% of the benzannulene **34**, which with *t*-BuOK/THF at reflux gave 70% of **35**, and *anti*-**30** likewise gave 71% of the annulene **36**, which with *t*-BuOK/THF gave only about 8% of the highly annelated annulene **37** (≡ **9**).

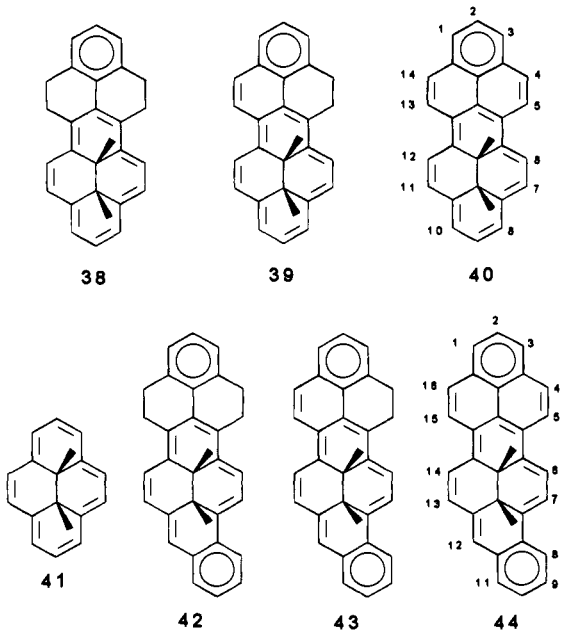


Generally, the isomeric *cis*-dimethyldihydropyrenes[19] are much rarer and less stable than the *trans* isomers. Indeed, at this time, no benzannelated *cis*-dimethyldihydropyrenes were known. The isolation of the pure *syn* isomers of **28** and **29** thus provided an opportunity to attempt their synthesis. Whereas the Wittig rearrangement[21] of dithiametacyclophanes isomerizes the *syn* to the *anti* series during the rearrangement, the Stevens rearrangement usually leaves some *syn* product. Indeed, methylation of *syn*-**28** with $(MeO)_2CHBF_4$[25] gave 99% of the bissulfonium salt, which on reaction with NaH/THF gave 37% of *syn*-**28A**, which on remethylation and Hofmann elimination of Me_2S using *t*-BuOK/THF as with the *anti* series gave 30% yield of the novel *cis*-dihydropyrene **38**,together with small amounts of the dehydrogenated products **39** and **40**. As expected, the internal methyl protons of **38** at δ −1.82 and −1.89 are similar to the parent **41** at δ −2.06.[19] Dehydrogenation of **38** to **40** can be achieved in 28% yield with DDQ/benzene.

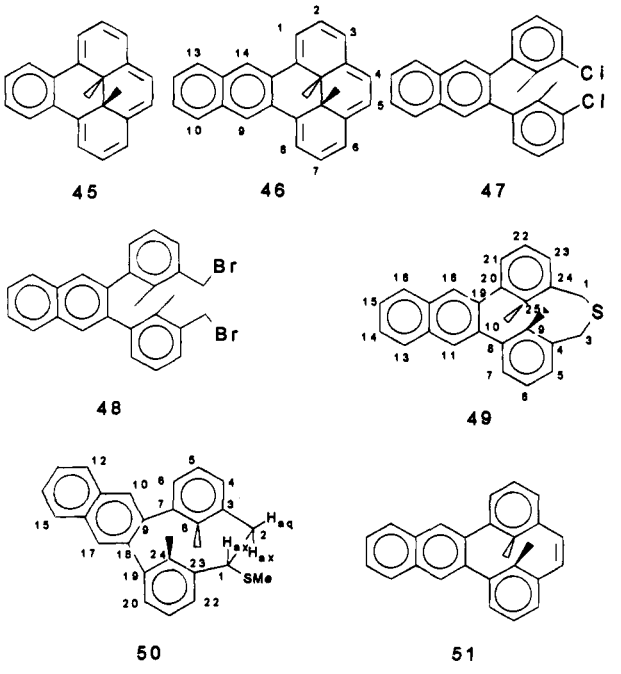
Similar reaction of *syn*-**29** gave 77% of *syn*-**29A**, 50% of *syn*-**29B**, and 23% of **42**, with some **43** and **44**. Dehydrogenation of **42** with *t*-BuOK/THF gave 30% of **44**. The NMR properties of these are discussed below.

[*e*]-Fused Dihydropyrenes. The previous synthesis of the [*e*]-fused dihydropyrene, **45**, started from a suitably substituted *ter*-aryl.[13] We required the naphth-fused analogue, **46**, and thus started the synthesis with 2,3-dibromonaphthalene.[27] This, in a nickel-catalyzed coupling reaction with the mono-Grignard reagent of 2,6-dichlorotoluene, gave 27−54% of the *ter*-aryl

(27) Synthesis: Danish, A. A.; Silverman, M.; Tajima, Y. A. *J. Am. Chem. Soc.* **1954**, *76*, 6144−6150. Purification: Prill, E. A. *J. Am. Chem. Soc.* **1947**, *69*, 62−63.

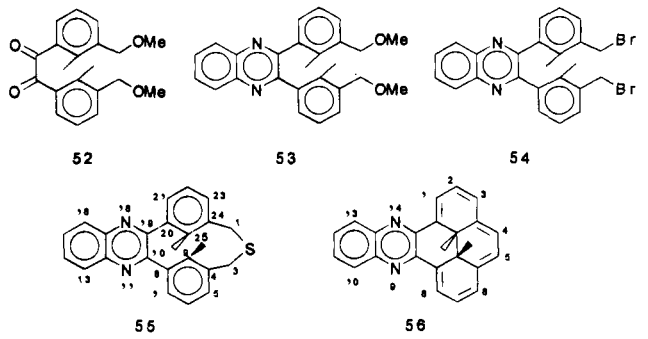


47, which was then taken through the same sequence as for **20** → **24** in Scheme 2, in overall 71% yield to give the dibromide **48**.



This was coupled in 27% yield with Na_2S to give only the *anti*-thiacyclophane **49**, mp 198–200 °C, internal methyl protons shielded at δ 0.95. Wittig rearrangement with LDA then gave 94% of a single isomer, **50**, with the SMe group pseudoequatorial, evident from the 11 Hz diaxial bridge hydrogen coupling constant. Remethylation (90%), followed by *t*-BuOK/THF-induced Hofmann elimination, proceeded in 90% yield to give the red-purple dihydropyrene **46**. Like[13] the benzannelated isomer **45**, tungsten light completely bleached a solution of **46** to the colorless cyclophanediene **51**, which reverted to **46** on standing or warming.

Starting from our recently reported[28] benzil derivative, **52**, we found that condensation with *o*-phenylenediamine yielded 90–95% of the quinoxaline **53**, which with BBr_3 at −78 °C



gave 80% of the dibromide **54**. Since this was rather insoluble in benzene or ethanol it was coupled with Na_2S as a suspension in benzene/ethanol/DMF/water with $CsCO_3$ as the base and gave a good yield of 60% of the thiacyclophane **55**. The structure of the latter was evident from its NMR and MS data but was also backed by a crystal structure.[29] Then, in the same way as for **49** above, this was converted into the rather unstable green dihydropyrene **56**. The two [*e*]-fused dihydropyrenes, **46** and **56**, showed rather similar NMR spectra, with their internal methyl protons at δ −0.74 and −0.72, respectively. The effect of the two nitrogen atoms on the spectrum of **46** is discussed in the NMR section below.

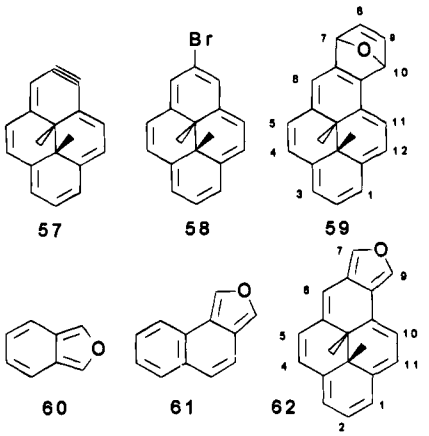
Syntheses from a Reactive Intermediate. The above routes to dihydropyrenes, which involve the synthesis of a suitably substituted bis(bromomethyl)arene, followed by cyclization to the dithiacyclophane, ring contraction, and elimination of Me_2S, have proved very successful. However, the sequence involved is long, and for each new system, a new starting bromide is required. If a preformed dihydropyrene nucleus could in some way be fused onto the benzannelating arene, the sequence might be substantially shortened. We have investigated two routes, both of which use a Diels–Alder reaction between an acetylene and a diene to make the annelating ring. We report the details here where the acetylene is incorporated into the dihydropyrene as the aryne **57**. Reaction of the bromide **58**, obtainable from the parent **1** using NBS/DMF,[30] with 5 equiv of sodium amide and a catalytic amount of *t*-BuOK in THF with a large excess of furan, trapped[31] the aryne **57** as the adduct **59** in 62% yield. Deoxygenation of adduct **59** was achieved in 90% yield with $Fe_2(CO)_9$ in refluxing benzene to give the benzo[*a*]dihydropyrene **3**. This synthesis of **3** uses a shorter route than the original,[7] in higher yield, but more importantly demonstrates the use of the reactive intermediate, **57**. This same intermediate was generated in the presence of the three annelated furans **60**–**62** and formed adducts with all three, and these all in turn gave new dihydropyrenes, indicating the generality of the method. Thus, isobenzofuran **60** (generated from 1-methoxyphthalan with $NaNH_2$/THF) gave 42% of adduct **63**, which with $Fe_2(CO)_9$ gave 70% of the naphthoannelated dihydropyrene **64**. The less symmetrical naphthofuran **61** can condense both ways around and thus gave 47% of the 1:1 mixture of adducts **65** and **66**, which on deoxygenation gave 44% of the two phenanthrodihydropyrenes **67** and **68**. Surprisingly, more of **67** was isolated than **68**, so the former could be obtained in pure form, mp 209–210 °C, and its structure confirmed by an X-ray determination. More equal amounts of **67** and **68** are formed when deoxygenation occurs using a large excess of $NaNH_2$ in the original trapping reaction, and then a combination of chromatography

(28) Mitchell, R. H.; Iyer, V. S. *Tetrahedron Lett.* **1993**, *34*, 3683–3686.

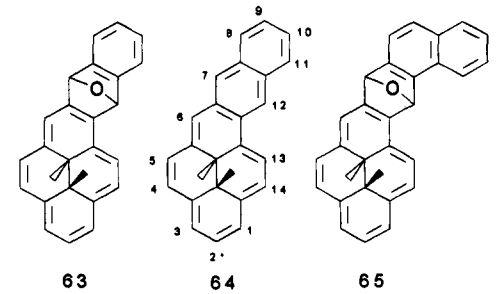
(29) The crystal data summary can be found in the Experimental Section, and full data are deposited in the supplementary material.

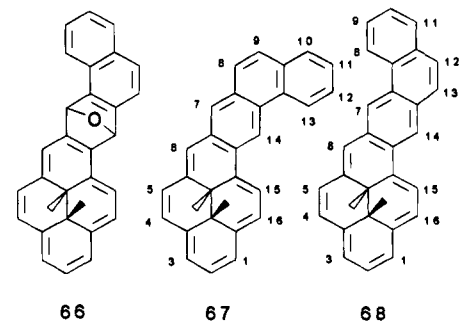
(30) Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733–4735.

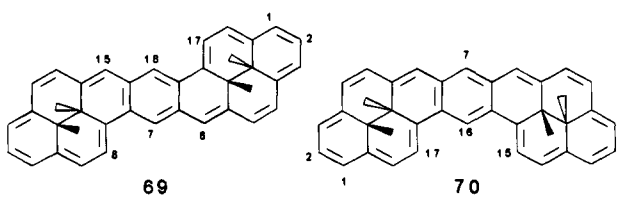
(31) Mitchell, R. H.; Zhou, P. *Tetrahedron Lett.* **1990**, *31*, 5277–5280.



and crystallization, with hand picking of the needles (**68**) away







from the cubes (**67**), allows a pure enough sample of **68** to be obtained to accurately assign all its ^{1}H NMR peaks. The dihydropyrenofuran **62** was obtained[32] in 78% yield by the action of 3,6-dipyridyltetrazine[33] on the adduct **59**. This was stable and thus could be purified and then reacted with aryne **57** to give a mixture of adducts that were directly deoxygenated to the two possible dihydropyrenes, the transoid isomer **69** (isolated in greater amount when $Fe_2(CO)_9$ was used to deoxygenate) and the cisoid isomer **70** (isolated preferentially when sodium/THF was used to deoxygenate). The stereochemistry of the methyl groups between the two dihydropyrene units is not known. These compounds were stable enough to obtain NMR spectra and mass spectra but not to separate in pure forms or characterize completely.

NMR Spectra Correlations

To achieve the goals of this paper, we have to show that the measured quantity, chemical shift, does indeed correlate with what is generally recognized to be aromaticity. Aromatic molecules are generally considered to be bond-delocalized, and bond alternation or fixation is considered to indicate reduced aromaticity. In our earlier paper,[5] we showed that the observed chemical shift for the internal methyl protons for **1** and its mono- and dibenzannelated derivatives correlated linearly with the average calculated bond order deviation from a perfect annulene. Thus, the more the bonds were calculated to alternate in the dihydropyrene ring, the less shielding was observed for the chemical shift of the methyl protons, indicating a smaller ring current in the dihydropyrene ring. The equation derived did quite well in predicting other annelated systems; for example, the calculated chemical shifts for the compounds **32**, **33**, and **35** were δ −2.75, −3.97, and −1.73, while those found experimentally were −2.8, −4.2, and −1.4, in amazing agreement considering the simplicity of the assumptions. There can be no doubt that the chemical shift measured for the internal protons does indeed reflect the delocalization around the macrocyclic ring, at least as estimated from bond order *calculations*. We did, however, want to obtain some experimental evidence for this bond fixation in annelated annulenes. After more than 20 years of trying, we have now obtained suitable crystals of the parent, **1**, to obtain a satisfactory X-ray structure. The compound crystallizes as two distinct molecules though the parameters are almost the same (see Experimental Section), and an ORTEP drawing is shown in Figure 1. The largest torsional angle around the perimeter is only 4°, and thus, the molecule is virtually planar. Bond alternation is almost absent around the perimeter, with bond lengths running between 1.38 and 1.40 Å. Unfortunately, we have not been as successful with its annelated derivatives. While we were able to grow crystals sufficiently well to initiate study on **46**, **64**, and **67** (all of which are chiral), the refinement obtained only proved the carbon skeleton and was not good enough to obtain accurate bond lengths. We thus turned to coupling constants. Cremer and Gunther[34] point out that in the absence of suitable X-ray C−C bond length data or ^{13}C−^{13}C coupling constant measurements, the best experimental indicator of bond lengths in aromatic systems are $^3J_{cis}$ values. Since the latter can be perturbed by steric effects, we considered the best set in structure

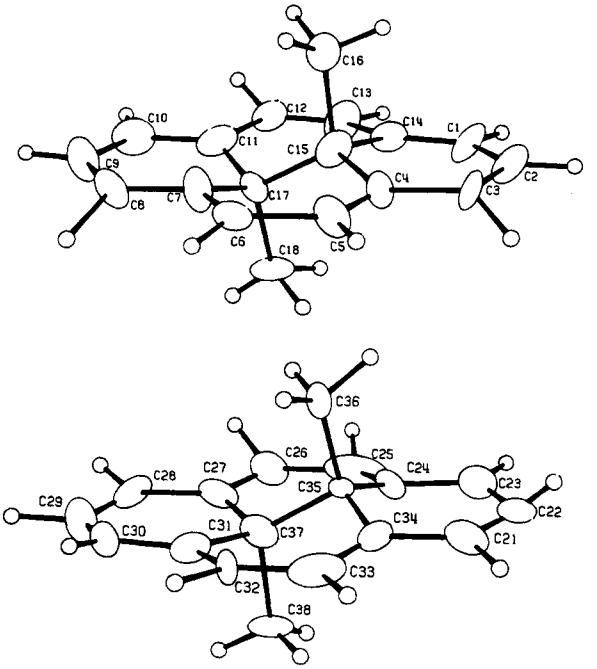


Figure 1. ORTEP drawing of the two molecules in the cell of **1**.

(32) Mitchell, R. H.; Zhou, P. *Tetrahedron Lett.* **1992**, *33*, 6319−6322.
(33) Geldard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318−319.
(34) Cremer, D.; Gunther, H. *Liebigs Ann. Chem.* **1972**, *763*, 87−108.

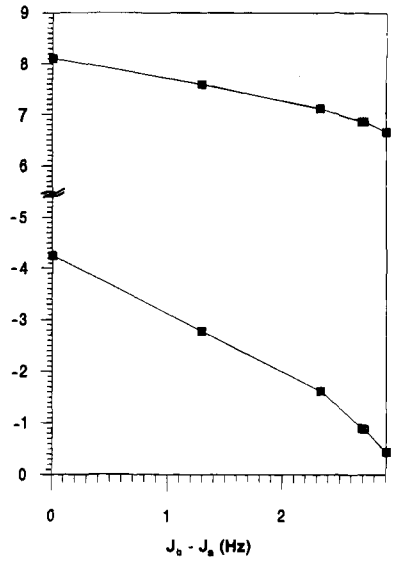


Figure 2. Plot of $\delta(H_{dis})$ [top] and $\delta(Me_{av})$ [bottom] against the difference in coupling constants $J_b - J_a$ (Hz) for the [*a*]-fused compounds analyzed.

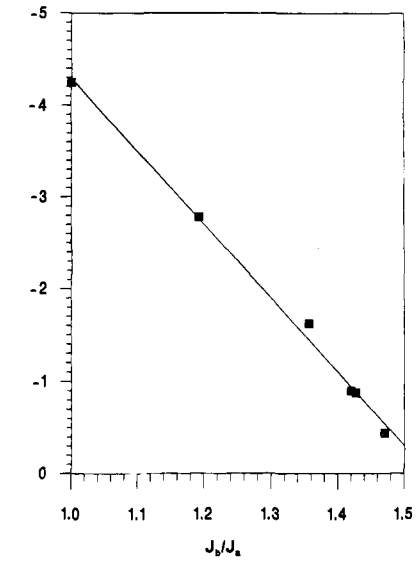
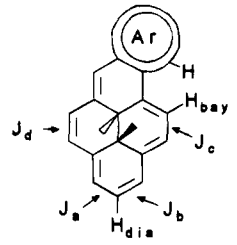


Figure 3. Plot of $\delta(Me_{av})$ against the ratio of coupling constants J_b/J_a for the [*a*]-fused compounds analyzed.

A to consider would be J_a and J_b. For the [*a*]-annelated



A

dihydropyrenes, this avoids any steric problems caused by the bay proton, H_{bay}, interacting with the corresponding annelating ring one. The values of J_a, J_b, $\delta(H_{dis})$, and $\delta(Me_{av})$ for **1**, for the [*a*]-annelated **3**, **32**, **33**, **64**, **67**, and **68**, and for the [*e*]-annelated **45**, **46**, and **56**, which are used in the following analysis,[35,36] are collected in the supplementary material as tables of NMR data. If we take $J_b - J_a$ as a measure of the degree of bond alternation, then Figure 2 clearly shows that as $J_b - J_a$ increases, the ring current falls. This is clear *experimental* evidence that as the bonds become more alternating, the ring current and hence the chemical shift of the internal methyl protons fall. The change in ring current, while not so dramatic, is also reflected in the chemical shift of the protons H_{dis}. If instead of the difference, the ratio of the two coupling constants J_b/J_a is plotted against the internal methyl chemical shift (see Figure 3), then a reasonably linear relationship appears to hold (eq 1).

$$\delta(Me_{av}) = 7.99(J_b/J_a) - 12.29 \qquad (r^2 = 0.996) \quad (1)$$

This is not changed significantly by attempting to include a steric correction to J_a or J_b for the *peri* interaction of the protons adjacent to H_{dis}. The ratio of coupling constants J_b/J_a is in fact

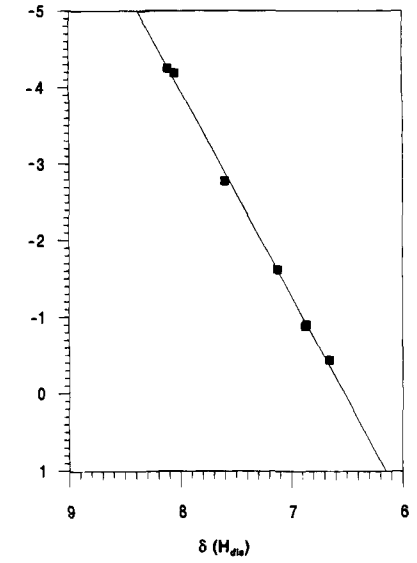


Figure 4. Plot of $\delta(Me_{av})$ against $\delta(H_{dis})$ for the [*a*]-fused compounds analyzed.

linearly related to the ratio J_d/J_c for the compounds **3**, **67**, and **64** (which all have similar steric effects) by $J_b/J_a = 1.769(J_d/J_c) - 1.023$ ($r^2 = 0.9994$), which indicates that although the measured coupling constants may vary around the molecule, the ratio of the appropriate pairs is probably a very reasonable measure of bond fixation in the molecule. The three [*e*]-fused annulenes, **45**, **46**, and **56**, also follow the same trend (data in table in the supplementary material). However, further analysis will have to await the synthesis of additional examples.

In using the chemical shift of either the distant external proton, H_{dis}, or the internal methyl protons, Me_{av}, to represent the ring current and hence the aromaticity of the molecule, we rely on the assumption that the observed shifts are only changed by a change in ring current. Our calculations of the through space deshielding effect of the fused Ar ring of **A** on either H_{dis} or Me_{av}, based on the Memory equation,[8] are at most 0.1 ppm for Me_{av} and less for H_{dis}. Also, H_{dis} should not suffer any serious steric deshielding. If these assumptions are true, then clearly $\delta(H_{dis})$ should correlate with $\delta(Me_{av})$ for the systems under study. Figure 4 shows a plot of $\delta(Me_{av})$ vs $\delta(H_{dis})$ for seven of the [*a*]-fused dihydropyrenes studied. From the correlation coefficient, $r^2 = 0.998$, it is clear that the two chemical shifts

(35) Generally, the assignment of protons in **A** is relatively straightforward since the bay protons are the most deshielded, and then, solution using the coupling constants to identify partners finds the rest. H_{dis} is usually the most upfield proton. COSY and NOESY spectra were used where necessary to confirm couplings and proton identity.

(36) In the case of **32**, J_b could not be determined since the two protons overlap in chemical shift. However, for **3**, **67**, and **64**, J_b/J_a varies linearly with J_d/J_c. Since for **32**, J_d, J_c, and J_a could all be measured, J_b could be estimated to within 0.1 Hz.

Table 1. Bond Localization Energies Relative to Benzene (RBLE) Based on Dewar Resonance Energies (RE)

arene	RE (eV)	fusion bond	residual arene	RBLE
benzene	0.869	any	none	1.00
naphthalene	1.323	1−2	benzene	0.52
		2−3	none	1.52
anthracene	1.600	1−2	naphthalene	0.32
		2−3	none	1.84
tetracene	1.822	1−2	anthracene	0.26
		2−3	none	2.10
phenanthrene	1.933	1−2	naphthalene	0.70
		2−3	benzene	1.22
		9−10	biphenyl	0.27
biphenylene	1.346	2−3	benzene	0.55
azulene	0.169	any	none	0.19

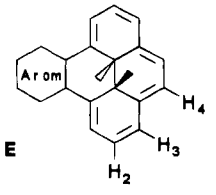
change linearly with respect to each other, and thus, it is likely that only the ring current is having a substantial effect on these two particular shifts. The relationship between $\delta(Me_{av})$ and $\delta(H_{dis})$ is

$$\delta(Me_{av}) = 17.515 - 2.685\delta(H_{dis}) \quad (2)$$

This relationship is important, because if in future annelated systems the observed chemical shifts for the two protons do not correspond, it would be indicative of some additional effect; e.g. if charge is distributed over the π-system, this would be expected to affect H_{dis} more than the internal methyl protons. Similar relationships hold for the other external protons; however, as they get closer to the annelating ring, and thus are more subject to anisotropic effects, the correlations are not so good. For the [*e*]-fused dihydropyrenes, **E**, using compounds **1**, **45**, and **46**, assignment of protons is trivial, since H_4 is a singlet, H_2 is a double doublet, and H_1 is deshielded (mostly sterically) from H_3, which are both doublets. The relationships found for the three protons H_2, H_3, and H_4 are instructive:

$$\delta(Me_{av}) = 19.239 - 2.899\delta(H_2) \quad (r^2 = 0.9987)$$
$$= 16.014 - 2.351\delta(H_3) \quad (r^2 = 0.9999)$$
$$= 12.283 - 1.909\delta(H_4) \quad (r^2 = 0.9984)$$

These three hydrogens are not equally sensitive to changes

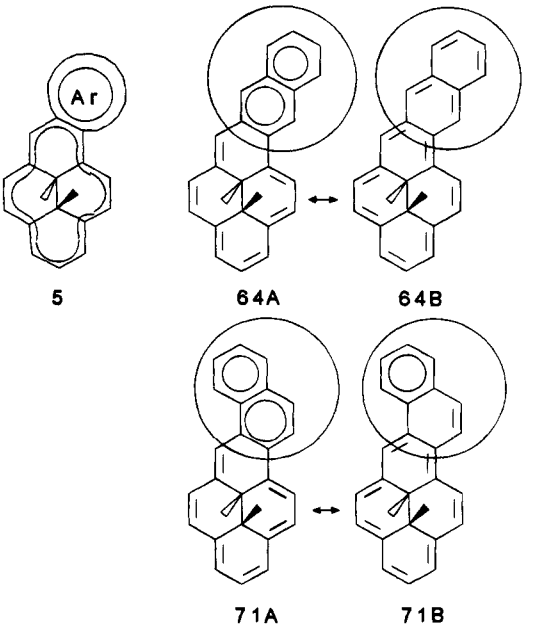


in the ring current, with $H_2 < H_3 < H_4$, reflecting, presumably, at least in part, the increasing distance from the center of the ring current. Haddon[37] has applied the Biot−Savart Law to ring current analysis for a variety of annulenes. For the parent **1**, he calculated ring current geometry factors for the three types of ring protons and the methyl protons. His values would lead to slopes of 2.38, 2.08, and 1.96 in the above three relationships. In the [*a*]-series, **A**, even though H_{dis} is furthest from the center of the macrocyclic ring, and is thus least sensitive to changes in the ring current, it is the least likely to be affected sterically and, hence, was used in this study. From Haddon's geometry factors, one would expect the methyl protons to be 2.38 times more sensitive to the ring current than the proton H_{dis}. From eq 2 the found value is 2.65, in reasonable agreement (clearly distance from the center of the ring current is not the only factor but looks to be the most important one).

(37) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613−3633.

Relative Aromaticities

We are now in a position to compare the relative aromaticities of the annelating aromatic ring for structures of type **5**. This comparison should be valid for any monocyclic annelating aromatic ring or for any polycyclic system that cannot form localized 6π rings in **both** of the Kekulé structures that delocalize the dihydropyrene ring. Thus, for the dihydropyrene ring to delocalize, i.e. **64A** ↔ **64B**, the full resonance energy



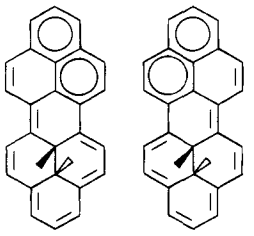
(RE) of the naphthalene ring is lost in structure **64B**. The bonds in the naphthalene ring (in the circle) in **64B** cannot be written in any way involving a normal Kekulé structure, which places a benzenoid sextet within the circle. In **71**, however, which is also a naphthannelated dihydropyrene, a benzenoid sextet does exist in both structures **71A** and **71B**. Thus, for the dihydropyrene ring to delocalize, the total resonance energy of naphthalene is not lost but rather that of naphthalene less benzene (strictly styrene). Thus, in measuring the aromaticity of the annelating ring (naphthalene) in **71**, the value for benzene will have to be added back. An alternative way of viewing this is that for the dihydropyrene ring to delocalize, the common fusion bond must be considered to be localized in the annelating aromatic. Thus, the aromaticity determined will reflect the energy necessary to localize this bond. In the case of naphthalene, if fusion is at the 2−3 bond, then localization of this bond costs the whole resonance energy of naphthalene. However, if fusion is at the 1−2 bond, then the localization energy cost is equivalent to the resonance energy of naphthalene less that of benzene. We will call this quantity the bond localization energy (BLE) of the aromatic compound being studied, and it has a different value for each type of bond in the aromatic compound being studied. Thus, in this study, the relative aromaticities of benzene and naphthalene can be found by examination of compounds **3**, **64**, and **32** (a derivative of **71**) and of **45** and **46**. The relevant data are found in Table 1. The relative aromaticity (RA) can be derived by calculating the change in ring current in **1**, when annelated by **Ar**, relative to

the change in ring current caused by benzannelation (**Bz**):

$$\frac{\text{aromaticity of annelating ring}}{\text{aromaticity of benzene}} = \frac{\text{change in chemical shift } \delta(\text{Ar}) \text{ from shift in } \mathbf{1}}{\text{change in chemical shift } \delta(\mathbf{3} \text{ or } \mathbf{45}) \text{ from shift in } \mathbf{1}}$$

$$\text{RA} = \Delta\delta(\text{Ar})/\Delta\delta(\text{Bz}) \qquad (3)$$

For **64**, $\Delta\delta$(Ar) for the methyl protons is 3.81 ppm, while for **3**, $\Delta\delta$(**3**) is 2.63 ppm, and thus the ratio (RA) is 1.45; for **46** and **45**, the corresponding values are 3.51 and 2.40 ppm, respectively, leading to a RA of 1.46. Thus, the measured aromaticity of naphthalene relative to benzene is about 1.46. A further estimate can be derived from **32**, where the values found are 1.47 and 2.63 ppm, leading to a ratio of 0.56, to which has to be added back the value for benzene (1.00) or more strictly styrene (0.99), and then a value of about 1.55 is obtained. The relative aromaticity of naphthalene to benzene based on Dewar resonance energies[38] is 1.52, in good agreement with those found. If the above analysis is correct, then compound **33** should show the **same** ring current as in dihydropyrene **1** since in both Kekulé structures **33A** and **33B**, there is always a



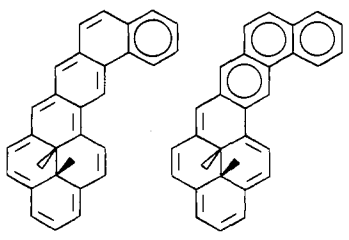
33A **33B**

delocalized naphthalene ring (i.e. the BLE for this annelating system is zero). Indeed they do. The chemical shifts of the internal methyl protons for **1** and **33** are −4.25 and −4.20 and −4.29, respectively. Moreover, the distant protons, H_{dis} (see **A**, above), should also be, and are approximately at the same shift, 8.11 and 8.24 for **1** and **33**, respectively. Consider now the phenanthrene-fused dihydropyrenes **67** and **68**. These are fused along the 2−3 bond of phenanthrene, and the BLE here is equivalent to the RE of phenanthrene less the RE of benzene because a benzene ring (the residual aromatic) is always present in both structures **67A** and **67B**. Thus, in this case, the measured aromaticity (RA) should correspond to the calculated value (RBLE) which should be

$$\frac{\text{RE(phenanthrene)} - \text{RE(benzene)}}{\text{RE(benzene)}}$$

$$= (1.933 - 0.869)/0.869$$

$$= 1.22 \qquad \text{(based on Dewar resonance energies)}^{38}$$



67A **67B**

The internal methyl protons for **67** are at δ −0.90, and from eq 3, the measured aromaticity (RA) is thus 4.25 − 0.90/2.63 = 1.27. Using the distant protons, H_{dis} (in **A**), that appear at δ 6.865, we found that the measured aromaticity is (8.11 − 6.865)/(8.11 − 7.12) = 1.26. Both are in excellent agreement with the calculated value. Thus, it would seem that using benzene, naphthalene, and phenanthrene as calibrants for the annelating ring, we are able to use chemical shifts to make a reasonable experimental estimate of relative aromaticity. Using these aromatic compounds to calibrate our scale, we then should be able to extend these measurements to other systems. To this end, Table 1 gives RBLE (bond localization energies relative to benzene)[39] based on Dewar resonance energies (RE)[38] for several of the common aromatic compounds that are of interest as possible annelating rings in **5**.

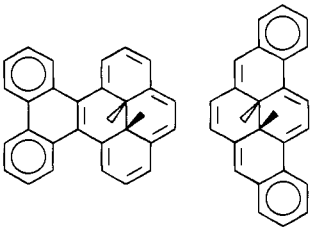
Table 2. Relative Aromaticity Data Arranged in Decreasing Ring Current Order δ(Me)

compd	annelating arene	δ(Me)	$\delta(H_{dis})$	RA(Me)	RA(H_{dis})	RBLE
1	none	−4.25	8.11	0	0	0
33	*a*	−4.24	8.24	0.00	0.13	0
37	*a*	−4.08		0.06		*a*
72	9,10-phenanthrene	−3.32[40]		0.39[b]		0.27
32	1,2-naphthalene	−2.78	7.60	0.56	0.52	0.52
45	benzene	−1.85	7.25	1.00	1.00	1.00
3	benzene	−1.62	7.12	1.00	1.00	1.00
34	benzene	−1.41		1.08		1.00
35	benzene[a]	−1.38		1.09		1.00[a]
67	2,3-phenanthrene	−0.88	6.86	1.28	1.26	1.22
68	2,3-phenanthrene	−0.90	6.865	1.27	1.26	1.22
46	2,3-naphthalene	−0.74	6.91	1.46[b]	1.40[b]	1.52
56	2,3-naphthalene[c]	−0.72	7.05	1.47[b]	1.23[b]	1.52
64	2,3-naphthalene	−0.44	6.66	1.45	1.46	1.52
73	benzene × 2	0.02		1.62		2.00

[a] The annelating aromatic is difficult to define; however, the effective RBLE for **33** is zero (see text above) and for **35** would be close to 1.00. For **37**, it is more difficult to determine, and while it might not be zero, it probably would not be large because of the symmetry of the structures. [b] Based on comparison to **45**. [c] Strictly 2,3-quinoxaline, but according to Wiberg,[40] essentially the same as naphthalene.

These values can now be used to compare with the values estimated from the chemical shifts of the internal methyl protons and, where present, the distant protons H_{dis} (**A** above) for the compounds synthesized in this paper. This data is given in Table 2.

Compound **72**, reported by Lai,[41] is included for completeness, but the value of RA measured is larger than that expected (RBLE). There is distortion of the dihydropyrene perimeter



72 **73**

by steric interactions between the phenanthrene ring hydrogens and those on the dihydropyrene. These would lead to a methyl proton chemical shift at a lower field than expected, i.e. reduced ring current in the macrocyclic ring, and this would lead to an aromaticity value (RA) for the annelating ring that is larger than expected. Compound **73** was prepared by us previously.[24] It can be seen that the data determined from H_{dis} agrees well with

(38) Dewar, M. J. S.; De Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789−795.
(39) Determined as discussed for **67**.
(40) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178−4190.
(41) Lai, Y. H.; Chen, P.; Peck, T. G. *Pure Appl. Chem.* **1993**, *65*, 81−87.

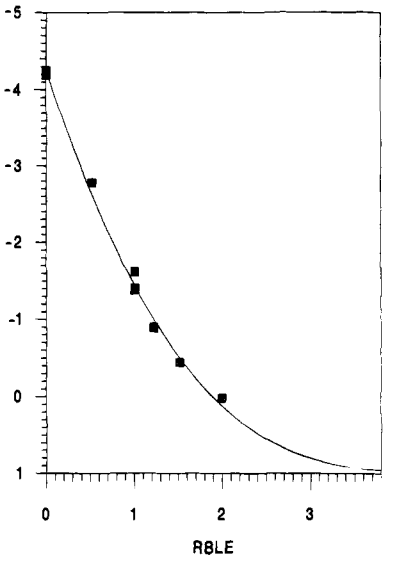


Figure 5. Plot of $\delta(Me_{av})$ against RBLE (see text) for the [*a*]-fused compounds in Table 2.

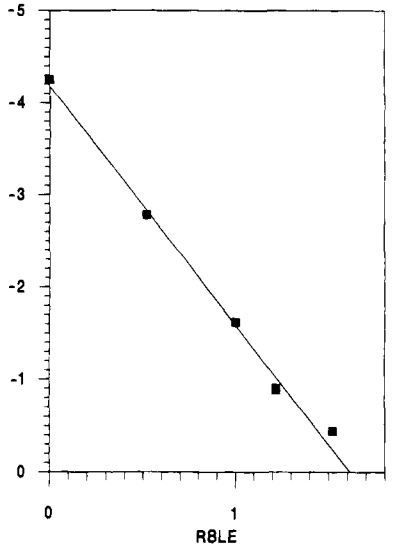


Figure 6. Plot of $\delta(Me_{av})$ against RBLE for compounds **1**, **32**, **3**, **67**, **68**, and **64**.

that from Me_{av}, except for compound **56**. Here, however, H_{dis} is deshielded somewhat by the ring nitrogen, which reduces the value observed for RA somewhat.

For the compounds in Table 2,

$$RA(Me) = 0.978(RBLE) + 0.04 \qquad (r^2 = 0.991) \quad (4)$$

Thus, essentially, the relative aromaticity (RA), as defined in eq 3 above, is almost equal to the ratio of the relative resonance energies of the system under comparison (eq 4).

A plot of $\delta(Me_{av})$ vs RBLE is shown in Figure 5 for all the [*a*]-series compounds in Table 2.

Clearly, the chemical shift of the internal methyl protons increases smoothly as the resonance energy of the annelating ring increases. When the resonance energy of the annelating ring (RBLE) becomes very large, the ring current in the dihydropyrene ring is 0 and the curve must become horizontal at a chemical shift of 0.97. Exactly where this occurs is not known but is of obvious interest. Our future work will attempt to provide data in this region (RBLE > 2). For 0 < RBLE < 1.8, the graph is reasonably linear and for the principal examples, **1**, **32**, **3**, **67**, **68**, and **64**, is expanded in Figure 6. In this region,

$$\delta(Me_{av}) = 2.59(RBLE) - 4.18 \qquad (r^2 = 0.992) \quad (5)$$

Clearly then, synthesis of compounds of type **5** and measurement of their internal methyl proton chemical shift and use of a transform of eq 5,

$$RBLE = [4.18 + \delta(Me_{av})]/2.59$$

give an experimental measurement of resonance energy relative to that of benzene = 1 for aromatics where RBLE is between 0 and 1.8 (see Table 1). If the annelating ring is a monocyclic system, then RBLE represents the relative aromaticity of the ring to benzene; if the ring is polycyclic, then the relative aromaticity must be calculated from RBLE as defined above. Subsequent papers will report application of this equation to systems where the annelating aromatic compound is biphenylene, cyclopentadienide, metaloarenes such as the metallocenes, azulene, and other bridged annulenes.

Similar equations can be derived for the other protons or for the other series. For example, in the [*e*]-fused series, **E** above, RBLE = [4.22 + $\delta(Me_{av})$]/2.32; however, we have less data available in this series.

Until now, sparse data have been available in the *cis*-dihydropyrene series. The relevant data for the methyl protons are given in Table 3 for compounds **38**–**44**.

While agreement is still reasonable between RA and RBLE, greater deviation is observed. It should be noted that average chemical shifts for the methyl protons have been used, and there is a considerably greater deviation between the shifts for the two methyl groups in the *cis* series, in which the molecule is saucer-shaped, than for the almost planar *trans* series. For example, in the *cis* compound **40**, the methyl protons are at δ −1.85 and −2.14 [$\Delta\delta = 0.29$], while in the corresponding *trans* compound **33**, they are at δ −4.19 and −4.28 [$\Delta\delta = 0.09$]. For the *cis*-dihydropyrene series, the relationship between δ(Me) and RBLE is:

$$\delta(Me_{av})_{cis} = 1.71(RBLE) - 1.95 \qquad (r^2 = 0.979) \quad (6)$$

However, there is somewhat more scatter than there is for the *trans* series, and thus, this should only be *used* if the *trans* isomer is not available.

Conclusions

We have described the synthesis of 13 annelated *trans*-dihydropyrenes and 6 *cis*-dihydropyrenes from benzenoid precursors. These higher annelated benzannulenes show good stability in the solid state (some samples show little decomposition after 12 years in a freezer), and all show measurable diamagnetic ring currents in the macrocyclic ring. They also undergo electrophilic substitution.[42] Such systems are thus truly regarded as benzannulenes rather than benzene rings joined by double bonds. We have shown that the chemical shift of the internal methyl protons correlates with the degree of bond alternation around the macrocyclic [14]annulene ring as measured by $^3J_{H,H}$ coupling constants. Linear correlations are observed between the chemical shifts of the internal methyl protons and the more distant nonsterically affected external ring protons. Both of these shifts thus mostly depend on the ring current, and hence, both can be used to estimate the aromaticity of the fused ring relative to a benzene ring. Good correlations are found between the measured aromaticity and Dewar resonance energies for the fused ring when the fused ring has a bond localization energy of between 0 and 1.8 benzene rings.

(42) Mitchell, R. H.; Yan, J. S. H. *Tetrahedron Lett.* **1979**, 1289–1290. Electrophilic substitution of **3** and **33** will be reported elsewhere.

Table 3. Relative Aromaticity Data for *cis*-Dihydropyrenes **38**–**44**

compd	annelating arene	$\delta(Me_{av})$	RA(Me)	RBLE
41	none	−2.06	0	0
38	none	−1.86	0.10	0
40	none	−1.95	0.06	0
39	1,2-naphthalene	−1.22	0.42	0.52
42	benzene	−0.02	1.02	1
44	benzene	−0.12	0.97	1
43	benzene + 1,2-naphthalene	0.47	1.27	1.52

Systems with larger resonance energies than 1.8 times that of benzene can be studied by fusion along an appropriate bond such that the bond localization energy lies between 0 and 1.8 benzene units. Thus, by using the simple aromatic compounds benzene and naphthalene as calibrants, we found a simple experimental method, which only involves measurement of chemical shift and which permits the estimation of aromaticity of other fused rings relative to the effect of a benzene ring.

Experimental Section

Melting points were determined on a Reichert 7905 melting point apparatus integrated to a chrome–alumel thermocouple. Infrared spectra, major peaks only, calibrated with polystyrene were recorded on a Bruker IFS25 FT-IR or on a Perkin-Elmer 283 spectrometer as KBr disks unless otherwise stated. Ultraviolet–visible spectra were recorded on a Cary 5 or a Perkin-Elmer Lambda-4B spectrometer in cyclohexane. Proton NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32, at 250 MHz on a Bruker WM 250, or at 360 MHz on a Bruker AMX 360 using $CDCl_3$ as solvent and either TMS as internal standard or the $CHCl_3$ peak at 7.24 ppm. Carbon NMR spectra were recorded at 62.9 MHz or at 90.6 MHz in $CDCl_3$ using the solvent peak at 77.0 ppm for calibration. Mass spectra were recorded on a Finnigan 3300 gas chromatograph–mass spectrometer using methane gas for chemical ionization (CI) or electron impact (EI) at 70 eV. Exact mass measurements used a Perkin-Elmer-Hitachi RMU-6E or a Kratos Concept-H instrument with perfluorokerosene as the calibrant. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous $MgSO_4$, Na_2SO_4, or K_2CO_3 as appropriate. SiGel refers to Merck silica gel, 70–230 mesh. PE refers to distilled petroleum ether, bp 30–60 °C.

2,4-Dibromo-1,3,5-trimethylbenzene. Bromine (680 g, 218 mL, 4.25 mol) was added dropwise over 4 h to a mechanically stirred mixture of mesitylene (250 g, 290 mL, 2.08 mol), iron powder (7.5 g), and iodine crystals (15 mg) in chloroform (300 mL) with exclusion of moisture. After an additional hour, the reaction mixture was filtered through Celite, which was washed with additional chloroform (300 mL). The filtrate was washed with water, aqueous $NaHSO_3$, aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and water, dried, and evaporated. The product was fractionally distilled at 0.2 Torr to give 506 g (87%) of the dibromide as a solid. Crystallization of a sample from ethanol gave colorless crystals: mp 62–64 °C (lit.[43] mp 64 °C); ^{1}H NMR (90 MHz) δ 6.98 (s, 1H), 2.60 (s, 3H), 2.31 (s, 6H); ^{13}C NMR (15.1 MHz) δ 137.1 (C-3), 136.7 (C-1,5), 129.6 (C-6), 124.7 (C-2,4), 24.9 (C-3-CH_3), 23.8 (C-1,5-CH_3); IR 1450, 1375, 1215, 1045, 1030, 960, 850, 630 cm^{-1}.

4,6-Dibromo-5-methylisophthalaldehyde. A mixture of 2,4-dibromo-1,3,5-trimethylbenzene (100 g, 0.360 mol), glacial acetic acid (1200 g, 1.144 L), and acetic anhydride (1224 g, 1.132 L) was stirred at 20 °C for 0.5 h. This mixture was then cooled to 0 °C, and concentrated sulfuric acid (170 mL) was added dropwise over 1 h with stirring, while the temperature was maintained below 5 °C. Then at 0 °C, CrO_3 (200 g, 2 mol) was added in portions such that the temperature did not rise above 15 °C. After a further 15 min of stirring, the reaction mixture was poured into three 4 L beakers, $^2/_3$-filled with chipped ice–water. After the mixture was stirred well and left to stand for 4 h, the solids were separated and washed with cold water. These were then suspended in 2% aqueous $NaHCO_3$ (1 L) and stirred vigorously for 30 min. The solid was separated, washed well with water, and air-dried to give 110 g of yellow powder. This, ethanol (400 mL), water (350 mL), and concentrated sulfuric acid (30 mL) were then heated under reflux with stirring for 45 min. The mixture was filtered hot, and the solid was washed well with water until it was neutral. This solid was then extracted with dichloromethane (1.2 L), and the extract was washed, dried, concentrated, and filtered through a short SiGel column. Recrystallization of the evaporated eluate from CCl_4 gave 24.2 g (22%) of the product as pale yellow needles: mp 172–174 °C; ^{1}H NMR (90 MHz) δ 10.43 (s, 2H), 8.23 (s, 1H), 2.74 (s, 3H); ^{13}C NMR (15.1 MHz) δ 190.8, 141.0, 134.5, 133.6, 128.3, 23.4; IR 1690, 1565, 1275, 1170, 1055, 995, 990, 722 cm^{-1}; EI MS *m/z* 308, 306, 304 (1:2:1, M^+). Anal. Calcd for $C_9H_6Br_2O_2$: C, 35.33; H, 1.98. Found: C, 35.51; H, 1.99.

2,6-Dibromo-3,5-bis(hydroxymethyl)toluene. A solution of 4,6-dibromo-5-methylisophthalaldehyde (62 g, 0.20 mol) in THF (1.9 L) was added slowly to a stirred slurry of $NaBH_4$ (6.3 g, 0.17 mol) in THF (50 mL) at 20 °C. After 20 h, the mixture was cooled in an ice–salt bath, and 1:1 concentrated aqueous HCl–water was added dropwise carefully until the resulting solution was slightly acidic. The aqueous layer was saturated with NaCl and extracted with ether (8 × 200 mL). The combined extracts were washed once with water, dried, and concentrated. Benzene (1.2 L) was added to the product, and water was removed using a Dean–Stark trap (about 2 h reflux). The product was obtained by hot filtration and was washed once with benzene (100 mL) to give a quantitative yield of the dialcohol as 63 g of free-flowing white powder. Recrystallization from methanol–benzene gave colorless crystals: mp 192–194 °C; IR 3330 (broad), 1395, 1070, 1005, 980, 960, 885 cm^{-1}; EI MS *m/z* 312, 310, 308 (1:2:1, M^+). Anal. Calcd for $C_9H_{10}Br_2O_2$: C, 34.87; H, 3.25. Found: C, 34.78; H, 3.22.

2,6-Dibromo-3,5-bis(bromomethyl)toluene. 2,6-Dibromo-3,5-bis(hydroxymethyl)toluene (80 g, 0.26 mol) was added to a well-stirred mixture of concentrated sulfuric acid (7 mL) and concentrated hydrobromic acid (48%, 300 mL, 2.6 mol), and the mixture was heated under reflux for 22 h. After the mixture was cooled, cold water (250 mL) was added, and the mixture was extracted with benzene (6 × 250 mL). The extracts were washed with water, aqueous $NaHCO_3$ until neutral, and water, dried, and evaporated to yield 97.4 g (87%) of product. A sample was recrystallized from cyclohexane as colorless crystals: mp 120–122 °C; ^{1}H NMR (90 MHz) 7.42 (s, 1H), 4.56 (s, 4H), 2.64 (s, 3H); ^{13}C NMR (15.1 MHz) δ 140.1, 137.0, 130.3, 127.4, 33.6, 25.2; IR 1215, 1040, 980, 890, 885, 850, 725, 680, 730 cm^{-1}; EI MS *m/z* 440, 438, 436, 434, 432 (1:4:6:4:1, M^+). Anal. Calcd for $C_9H_8Br_4$: C, 24.80; H, 1.85. Found: C, 25.12; H, 1.81.

5,7-Dibromo-6-methyl-2,11-dithia[3.3]metacyclophane (11). A solution of 2,6-dibromo-3,5-bis(bromomethyl)toluene (21.8 g, 50 mmol) and *m*-xylylenedithiol[19] (8.5 g, 50 mmol) in deoxygenated benzene (900 mL) was added dropwise over 60–70 h at 20 °C to a well-stirred deoyxgenated solution of KOH (8 g, 85%, 120 mmol, dissolved in 80 mL of water, which was then added to 1.9 L of ethanol). When the addition was complete, the solution was stirred for an additional 2 h. The solvent was then evaporated, and water, aqueous HCl until acidic, and dichloromethane were added to the residue. The organic extract (1 L) was washed, dried, and evaporated, and the residue was chromatographed over SiGel using dichloromethane as the eluant. Recrystallization from cyclohexane gave 16.65 g (75%) of the cyclophane **11** as colorless crystals: mp 172–173 °C; ^{1}H NMR (90 MHz) δ 7.28 (bs, 1H), 7.0–6.9 (m, 3H), 6.62 (s, 1H), 3.76 (s, 4H), 3.73 (s, 4H), 2.45 (s, 3H); ^{13}C NMR (15.1 MHz) δ 137.2, 135.3, 131.9, 131.1, 128.3, 127.3 (C-14,16), 124.8, 38.6, 38.2, 24.6; IR 1048, 1038, 975, 895, 800, 720 cm^{-1}; EI MS *m/z* 444 (M^+, correct isotope pattern). Anal. Calcd for $C_{17}H_{16}Br_2S_2$: C, 45.96; H, 3.63. Found: C, 36.36; H, 3.57.

1,3-Dibromo-2-methylpyrene (13). This was prepared using the sequence **11** → **16** → **17** → **13** as follows. A solution of lithium diisopropylamide [prepared from *n*-BuLi (0.14 mol in 80 mL of hexane) and diisopropylamine (20 mL, 0.14 mol)] in dry THF (400 mL) was added over 45 min to a refluxing solution of the thiacyclophane **11** (20 g, 45 mmol) under N_2 in dry THF (400 mL). After further reflux for 30 min, the mixture was cooled to 20 °C, and methyl iodide (38.4 g, 0.27 mol) was added. After the mixture was stirred for 10 min, water, 2 M aqueous HCl, and dichloromethane were added. The organic extract was washed, dried, and evaporated. Filtration of the product through SiGel using dichloromethane gave 16.47 g (77%) of

(43) Varma, P. S.; Subrahmanian, T. S. *J. Indian. Chem. Soc.* **1936**, *13*, 192–193.

16 as a mixture of stereoisomers: ^{1}H NMR (90 MHz) δ 7.6−6.4 (m, ArH), 5.4−4.3 (m, internal ArH and CHS), 4.0−2.0 (m, CH_2), 2.68 (s, $ArCH_3$), 1.88 and 1.85 (s, SCH_3); EI MS *m/z* 472 (M^+, $C_{19}H_{20}Br_2S_2$). This mixture of isomers (16 g, 34 mmol) was dissolved in dichloromethane (500 mL) and stirred vigorously with 10% aqueous $KHCO_3$ (500 mL), and then bromine (70 mmol) in dichloromethane (50 mL) was added slowly over 30 min. Stirring was continued for a further 30 min, and then more dichloromethane (1 L) was added to extract the product. The extract was washed, dried, concentrated, and filtered through SiGel using dichloromethane and then methanol to yield the bis-sulfoxide product, **17**, as a buff-colored solid, 13.2 g (77%), as a mixture of stereoisomers; in their ^{1}H NMR spectra, only the singlets of the $ArCH_3$ protons of **17** at δ 2.94 and the $SOCH_3$ protons at δ 2.77 and 2.74 were clearly assignable. CI MS *m/z* 505 (MH^+ for $C_{19}H_{20}Br_2O_2S_2$ = M). This mixture of isomers was heated under reflux in *N*-methyl-2-pyrrolidinone (400 mL) for 20 h, cooled, poured into 2 M aqueous HCl, and extracted with dichloromethane (3 × 1 L). The organic layer was washed, dried, and evaporated, and the residue was chromatographed over SiGel using dichloromethane−PE (3:7) as the eluant to give 6.4 g (65%) of pyrene **13** as a yellow product. Recrystallization from benzene gave pale yellow crystals: mp 238−240 °C; ^{1}H NMR (90 MHz, CD_2Cl_2) δ 8.51 (d, J = 9.3 Hz, 2H), 8.18 (d, J = 9.3 Hz, 2H), 8.36−7.97 (m, 3H), 3.13 (s, 3H); IR 1415, 1372, 1334, 1129, 1080, 1024, 975, 833, 815, 695 cm^{-1}; CI MS *m/z* 375 (MH^+, 1:2:1 pattern). Anal. Calcd for $C_{17}H_{10}Br_2$: C, 65.58; H, 2.70. Found: C, 54.63; H, 2.41.

Bis-sulfone 18. Hydrogen peroxide (30%, 50 mL) was added to a solution of cyclophane **11** (5 g, 11.3 mmol) in acetic acid (150 mL, dissolved hot, then cooled). The mixture was then stirred under reflux for 18 h. After the mixture was cooled, the product was filtered, washed with water, aqueous $NaHCO_3$, and water and then dried at 80 °C under vacuum for 6 h to yield 5.28 g (92%) of sulfone **18** as a shiny white powder: mp 325−327 °C dec; ^{1}H NMR (90 MHz, CF_3COOD, poorly soluble) δ 7.5−7.2 (m, 5H), 4.95 and 4.70 (s, 4H each), 2.59 (s, 3H); IR 1405, 1315, 1295, 1230, 1155, 1130, 1105, 1035, 975, 910, 884, 848, 815, 694, 495, 468 cm^{-1}; CI MS *m/z* 509 (MH^+, correct isotope pattern). Anal. Calcd for $C_{17}H_{16}Br_2O_4S_2$: C, 40.17; H, 3.17. Found: C, 40.14; H, 3.06.

4,6-Dibromo-5-methyl[2.2]metacyclophane (19). The bis-sulfone **18** (1 g, 1.97 mmol) in a porcelain boat (9 × 1.5 × 1 cm) was placed in a Pyrex tube (31 × 2.5 cm) sealed at one end. The open end was connected through a cold finger to a vacuum system and was evacuated to 0.05 Torr. The tube was placed in a 15 cm tube furnace preheated to 650 °C so that the boat was in the hot zone. Immediately, product began to collect on the ice−water-cooled cold finger, and the reaction was complete in <2 min. After removal from the furnace and cooling, the product was extracted with dichloromethane from the entire tube and cold finger. The extract was evaporated, and the residue was extracted with hot hexane. The cooled hexane extract was chromatographed over SiGel to give 366 mg (49%) of cyclophane **19**, which was recrystallized from benzene−ethanol as colorless crystals: mp 115−117 °C; ^{1}H NMR (250 MHz) δ 7.27 (AB_2, 1H, H-13), 7.03 (AB_2, 2H, H-12,14), 4.37 and 4.24 (s, 1H each, H-8,16), 3.60 (dt, J = 12.6 and 3.5 Hz, 2H, H-2_{eq},9_{eq}), 2.99 (dt, J = 12.5 and 3.5 Hz, 2H, H-1_{eq},-10_{eq}), 2.67 (s, 3H), 2.21 (dt, J = 12.3 and 3.2 Hz, 2H, H-2_{ax},9_{ax}), 1.87 (dt, J = 12.2 and 3.2 Hz, 2H, H-1_{ax},10_{ax}); ^{13}C NMR (15.1 MHz) δ 138.5, 137.3, 137.1, 136.1, 129.4, 125.7, 123.8, 41.8, 38.1, 25.3; IR 1440, 1430, 1380, 1178, 1165, 1038, 972, 947, 868, 853, 790, 727, 716, 708, 620, 602 cm^{-1}; EI MS *m/z* 380 (M^+, 1:2:1 isotope pattern). Anal. Calcd for $C_{17}H_{16}Br_2$: C, 53.71; H, 4.24. Found: C, 53.81; H, 4.29.

1,3-Dibromo-4,5,9,10-tetrahydro-2-methylpyrene (20). A solution of bromine (5.43 g, 33.9 mmol) in dry CCl_4 (125 mL) was added to a stirred mixture of cyclophane **19** (10 g, 26.3 mmol), iron powder (0.5 g), and CCl_4 (500 mL) under N_2 in the dark. After the mixture was stirred for 80 h, the solids were filtered and washed with CCl_4 (100 mL). The combined filtrate was washed with water, aqueous $NaHSO_3$, water, $NaHCO_3$, and water, dried, and evaporated. Chromatography of the orange product over SiGel using PE as the eluant gave 9.74 g (98%) of the product **20** as a pale yellow powder. A sample was recrystallized from cyclohexane as pale yellow crystals: mp 128−130 °C; ^{1}H NMR (90 MHz) δ 7.3−7.0 (m, 3H), 3.2−2.7 (m, 8H), 2.68 (s, 3H); EI MS *m/z* 378 (M^+, 1:2:1 pattern). NMR indicated that traces of **19** were present, but this material could be used satisfactorily in the next step.

1,3-Dicyano-4,5,9,10-tetrahydro-2-methylpyrene (21). Cuprous cyanide (3 g) was added to a solution of the dibromide **20** (10.35 g, 27.38 mmol) in *N*-methyl-2-pyrrolidinone (130 mL) and was refluxed under N_2. Further portions of cuprous cyanide (4, 4, and 6.2 g) were added after 4, 12, and 25 h reaction time. The mixture was then refluxed a further 3 h, cooled to 100 °C, and poured into water−concentrated aqueous NH_3 (1:1, 600 mL). This mixture was stirred for 24 h, and then the solids were filtered and air-dried. These solids were extracted well with dichloromethane (4 × 300 mL) in a blender, and the extract was washed, dried, and evaporated. The residue was chromatographed over SiGel using dichloromethane−PE (1:1) as the eluant and gave 3.02 g (41%) of pale yellow product **21**. Recrystallization from benzene−ethanol gave colorless crystals: mp 224−226 °C; ^{1}H NMR (250 MHz) δ 7.27−7.21 (AB_2, 1H), 7.15−7.12 (AB_2, 2H), 3.20−3.14 (A_2B_2, 4H), 2.98−2.88 (A_2B_2, 4H), 2.78 (s, 3H); ^{13}C NMR (62.9 MHz) δ 144.0, 143.2, 134.9, 131.0, 129.3, 126.6, 115.7, 112.5, 27.5, 27.2, 20.2; IR 2225, 1435, 798, 772 cm^{-1}; EI MS *m/z* 270 (M^+). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.41; H, 5.22; N, 10.37. Found: C, 84.22; H, 5.12; N, 10.33.

1,3-Diformyl-4,5,9,10-tetrahydro-2-methylpyrene (22). A solution of DIBAH (11.25 g, 79.2 mmol) in hexane (75 mL) was added dropwise with stirring under N_2 to a solution of dicyanide **21** (8.47 g, 31.37 mmol) in benzene (250 mL) at 20 °C. After a further 24 h of stirring, methanol (100 mL) was cautiously added with ice cooling, and then water−concentrated HCl (1:1, 200 mL) and then benzene (500 mL) were added. The organic layer was washed, dried, and evaporated to give 6.93 g (80%) of the dialdehyde **22**. A portion was recrystallized from CCl_4 as colorless crystals: mp 147−149 °C; ^{1}H NMR (250 MHz) δ 10.69 (s, 2H), 7.23−7.17 (AB_2, 1H), 7.17−7.12 (AB_2, 2H), 3.21−3.15 (A_2B_2, 4H), 2.92−2.80 (A_2B_2, 4H), 2.74 (s, 3H); ^{13}C NMR (62.9 MHz) δ 194.2, 141.2, 139.5, 135.3, 132.9, 130.9, 126.1, 128.1, 125.8, 27.5, 25.0, 15.5; IR 1682, 1548, 1430, 1298, 1065, 875, 770 cm^{-1}; EI MS *m/z* 276 (M^+). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 81.79; H, 5.90.

1,3-Bis(hydroxymethyl)-4,5,9,10-tetrahydro-2-methylpyrene (23). A solution of the dialdehyde **22** (6.86 g, 24.86 mmol) in undried THF (200 mL) was added dropwise to a stirred slurry of $NaBH_4$ (1.88 g, 50 mmol) in THF (50 mL) at 20 °C. After the mixture was stirred for 24 h and cooled in ice, water−concentrated HCl (1:1, 100 mL) was added slowly. The aqueous layer was saturated with NaCl and extracted with ether (7 × 200 mL). The organic layers were combined and evaporated to give 6.39 g (92%) of diol **23**. Recrystallization from CCl_4 gave colorless crystals: mp 180−182 °C; ^{1}H NMR (90 MHz) δ 7.09 (bs, 3H), 4.80 (s, 4H), 3.1−2.7 (m, 8H), 2.54 (s, 3H), 1.52 (s, 2H, exchanged with D_2O); IR 3280 (b), 1025, 990, 765 cm^{-1}; EI MS *m/z* 280 (M^+). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 80.86; H, 7.39.

1,3-Bis(bromomethyl)-4,5,9,10-tetrahydro-2-methylpyrene (24). The dialcohol **23** (6.34 g, 22.64 mmol) was added to a mixture of aqueous HBr (48%, 300 mL, 2.6 mol) and concentrated sulfuric acid (2 mL), and the mixture was stirred under reflux for 7 h. After the mixture was cooled, ice−water (200 mL) was added, and the mixture was extracted with dichloromethane (6 × 200 mL). The extract was washed with water, aqueous $NaHCO_3$, and water until neutral, dried, and evaporated. Chromatography over SiGel using dichloromethane−PE (3:7) as the eluant gave 6.79 g (74%) of the bromide **24**. Recrystallization of a sample from cyclohexane gave colorless crystals: mp 208−210 °C; ^{1}H NMR (90 MHz) δ 7.09 (bs, 3H), 4.60 (s, 4H), 2.89 (bs, 8H), 2.48 (s, 3H); ^{13}C NMR (15.1 MHz) δ 135.9, 135.0, 131.6, 130.1, 129.9, 127.3, 125.7, 29.3, 27.8, 24.7, 15.1; IR 1458, 1203, 799, 763, 663, 560, 550 cm^{-1}; EI MS *m/z* 406 (M^+, 1:2:1 isotope pattern). Anal. Calcd for $C_{19}H_{18}Br_2$: C, 56.18; H, 4.47. Found: C, 56.48; H, 4.55.

4,6-Dicyano-5-methyl[2.2]metacyclophane.[44] From bromide **20** (22.8 g, 60 mmol), CuCN (20.2 g, 225 mmol), and *N*-methyl-2-

pyrrolidinone (100 mL), exactly as described for dicyanide **21** above, was obtained 14.24 g (87%) of 4,6-dicyano-5-methyl[2.2]metacyclophane as colorless crystals from benzene–ethanol: mp 201–202 °C; ^{1}H NMR (250 MHz) δ 7.38 (t, J = 7.5 Hz, 1H), 7.14 (dd, J = 7.5 and 1.5 Hz, 2H), 4.33 (bs, 1H, H-16), 4.28 (s, 1H, H-8), 3.70–3.56 (m, 2H, H-2_{eq},9_{eq}), 3.37–3.23 (m, 2H, H-1_{eq},10_{eq}), 2.83 (s, 3H), 2.34–2.06 (12 lines, 4H, H_{ax}); ^{13}C NMR (62.9 MHz) δ 146.8, 146.3, 137.8, 135.7, 135.6, 130.2, 126.1, 115.6, 111.3, 40.3, 39.5, 20.1; IR 2220, 1231, 1180, 1170, 1080, 1050, 952, 872, 798, 760, 720, 710 cm^{-1}; EI MS m/z 272 (M^+). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.59; H, 5.90; N, 10.22.

4,6-Diformyl-5-methyl[2.2]metacyclophane.[44] From 4,6-dicyano-5-methyl[2.2]metacyclophane (14 g, 51.5 mmol) and DIBAH (19 g, 134 mmol) in benzene (250 mL), exactly as described for dialdehyde **22** above, was obtained 12.77 g (89%) of 4,6-diformyl-5-methyl[2.2]-metacyclophane as pale yellow crystals from CCl_4: mp 128–130 °C; ^{1}H NMR (250 MHz) δ 10.71 (s, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.10 (dd, J = 7.4 and 1.5 Hz, 2H), 4.35 (bs, 1H, H-16), 4.34 (s, 1H, H-8), 4.01 (dt, J = 12.1 and 3.5 Hz, 2H, H-2_{eq},9_{eq}), 3.21 (dt, J = 12.5 and 3.6 Hz, 2H, H-1_{eq},10_{eq}), 2.84 (s, 3H), 2.20 (td, J = 12.1 and 2.9 Hz, 2H, H-2_{ax},9_{ax}), 1.84 (td, J = 12.1 and 3.2 Hz, 2H, H-1_{ax},10_{ax}); ^{13}C NMR (62.9 MHz) δ 193.0, 144.9, 142.7, 138.7, 138.2, 135.3, 132.1, 129.7, 125.7, 40.2, 38.0, 15.5; IR 1690, 1245, 1182, 1070, 950, 798, 770, 720, 710 cm^{-1}; EI MS m/z 278 (M^+). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.73; H, 6.31.

4,6-Bis(hydroxymethyl)-5-methyl[2.2]metacyclophane.[44] From 4,6-diformyl-5-methyl[2.2]metacyclophane (12.63 g, 45.4 mmol) and $NaBH_4$ (3.44 g, 90.9 mmol) in THF (250 + 50 mL), exactly as described for dialcohol **23** above, was obtained 12.48 g (97%) of 4,6-bis(hydroxymethyl)-5-methyl[2.2]metacyclophane as colorless crystals from CCl_4: mp 214–216 °C; ^{1}H NMR (90 MHz) δ 7.3–6.9 (m, 3H), 4.81 (s, 4H), 4.34 and 4.23 (s, 1H each, H-8,16), 3.2–2.7 (m, 4H, H_{eq}), 2.55 (s, 3H), 2.5–1.7 (m, 4H, H_{ax}), 1.44 (s, 2H, exchanges with D_2O); IR 3400 (b), 1178, 1070, 1000, 988, 950, 788, 715 cm^{-1}; EI MS m/z 282 (M^+). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.86. Found: C, 80.37; H, 7.87.

4,6-Bis(bromomethyl)-5-methyl[2.2]metacyclophane.[44] From 4,6-bis(hydroxymethyl)-5-methyl[2.2]metacyclophane (12.3 g, 43.62 mmol), aqueous HBr (48%, 300 mL, 2.6 mol), and concentrated H_2SO_4 (2 mL), exactly as described for **24** above, was obtained 10.17 g (57%) of 4,6-bis(bromomethyl)-5-methyl[2.2]metacyclophane as colorless crystals from cyclohexane: mp 191–192 °C; ^{1}H NMR (250 MHz) δ 7.34 (t, J = 7.4 Hz, 1H), 7.11 (dd, J = 7.7 and 1.5 Hz, 2H), 4.73 and 4.68 (AB, J = 10.4 Hz, 4H, CH_2Br), 4.43 (bs, 1H, H-16), 4.12 (s, 1H, H-8), 3.49 (dt, J = 12.9 and 3.7 Hz, 2H, H-2_{eq},9_{eq}), 3.16 (dt, J = 12.1 and 3.5 Hz, 2H, H-$1_{eq}10_{eq}$), 2.55 (s, 3H), 2.38 (td, J = 12.1 and 2.9 Hz, 2H, H-2_{ax},9_{ax}), 1.95 (td, J = 12.5 and 3.3 Hz, 2H, H-1_{ax},10_{ax}); ^{13}C NMR (62.9 MHz) δ 138.6, 138.4, 137.5, 136.5, 136.2, 132.0, 129.3, 125.6, 39.3, 38.0, 29.0, 14.9; IR 1248, 1209, 1200, 1175, 1078, 955, 873, 788, 781, 760, 715, 706, 682, 615, 578, 543, 490 cm^{-1}; EI MS m/z 408 (M^+, 1:2:1 isotope pattern). Anal. Calcd for $C_{19}H_{20}Br_2$: C, 55.90; H, 4.94. Found: C, 56.45; H, 5.20.

1,3-Bis(mercaptomethyl)-4,5,9,10-tetrahydro-2-methylpyrene (27). A solution of bromide **24** (2.1 g, 5.2 mmol) and thiourea (0.98 g, 13 mmol) in 95% ethanol (40 mL) was stirred under reflux for 3 h. After the solution was cooled, about half the solvent was evaporated and the remainder cooled in a freezer. The precipitated bis-thiouronium salt was collected and dried to give 2.88 g (quantitative) of white powder. This salt was added to a deoxygenated (bubbling N_2 for 30 min) solution of KOH (15 g, 85%, 0.23 mol) in water (50 mL) under N_2 and was refluxed for 7 h. After it was ice-cooled, concentrated H_2SO_4–water (1:1, 60 mL) was added slowly. The liberated thiol was then extracted into ether (4 × 150 mL). The extract was washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated. The yellow residue was chromatographed over SiGel using first PE and then PE–dichloromethane (1:1) as the eluants to give 1.6 g (quantitative) of the bis-thiol **27**. A sample was recrystallized from benzene–hexane: mp 146–148 °C; ^{1}H NMR (250 MHz) δ 7.18–7.07 (m, 3H), 3.85 (d, J = 6.4 Hz, 4H), 3.00–2.84 (AA′BB′, 8H), 2.51 (s, 3H), 1.64 (t, J = 6.4 Hz, 2H, SH); ^{13}C NMR (62.9 MHz) δ 135.4, 135.0, 133.1, 133.5, 131.0, 129.9, 127.2, 125.8, 28.5, 25.1, 23.4, 15.7; IR 2555, 1450, 1440, 1245, 1240, 765, 680 cm^{-1}; EI MS m/z 312 (M^+). Anal. Calcd for $C_{19}H_{20}S_2$: C, 73.03; H, 6.45. Found: C, 73.30; H, 6.38.

9,26-Dimethyl-2,11-dithia(1,3)-benzeno(1,3)-4,5,9,10-tetrahydropyreno[3.3]cyclophane (28). A solution of the bromide **24** (3.00 g, 7.39 mmol) and dithiol **25**[19] (1.36 g, 7.39 mmol) in deoxygenated benzene (800 mL) was added dropwise over 75 h, at 20 °C under N_2, to a vigorously stirred solution prepared by dissolving KOH (85%, 5.1 g, 72 mmol) in deoxygenated water (100 mL) and adding deoxygenated ethanol (1.9 L). The solvent was then evaporated, and the residue was acidified (dilute aqueous H_2SO_4) and then was extracted with dichloromethane (6 × 150 mL). The extract was washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated. The residue was chromatographed over SiGel using dichloromethane–PE (3:7) as the eluant. Eluted first was *anti*-**28**, 2.113 g (67%), which on recrystallization from benzene–cyclohexane gave white needles: mp 252–254 °C; ^{1}H NMR (90 MHz) δ 7.5–7.0 (m, 6H), 3.78 (bs, 4H), 3.67 (s, 4H), 3.4–2.6 (m, 8H), 1.38 and 1.18 (s, 3H each); ^{13}C NMR (15.1 MHz) δ 139.6, 137.8, 135.9, 135.2, 135.1, 130.8, 130.2, 129.7, 128.2, 126.6, 125.5, 32.4, 28.4, 28.0, 25.8, 15.7, 15.0; IR 1465, 1455, 1435, 1209, 1203, 785, 768, 730, 715 cm^{-1}; EI MS m/z 428 (M^+). Anal. Calcd for $C_{28}H_{28}S_2$: C, 78.46; H, 6.58. Found: C, 78.08; H, 6.63.

Eluted next was *syn*-**28**, 231 mg (7.3%), colorless crystals from cyclohexane: mp 198–200 °C; ^{1}H NMR (90 MHz) δ 7.08 (bs, 3H, H-5,6,7), 6.91 (d, J = 7.2 Hz, 2H, H-18,20), 6.40 (t, J = 7.2 Hz, 1H, H-19), 4.19 (AB, J = 15 Hz, 2H), 4.01 (s, 4H), 3.77 (AB, J = 15 Hz, 2H), 3.2–2.6 (m, 8H), 2.48 and 2.44 (s, 3H each); ^{13}C NMR (15.1 MHz) δ 136.3, 135.3, 135.0, 134.0, 132.8, 130.9, 130.7, 128.5, 128.0, 126.3, 125.3, 34.9, 31.1, 27.9, 25.5, 18.5, 16.8; EI MS m/z 428 (M^+). Anal. Calcd for $C_{28}H_{28}S_2$: C, 78.46; H, 6.58. Found: C, 78.70; H, 6.21.

13,30-Dimethyl-2,15-Dithia(1,3)-naphtho(1,3)-4,5,9,10-tetrahydropyreno[3.3]cyclophane (29). From bromide **24** (1.00 g, 2.46 mmol) and dithiol **26**[24] (0.576 g, 2.46 mmol) in benzene (900 mL) and KOH (85%, 1.69 g, 26 mmol) in water (100 mL) and ethanol (800 mL), exactly as described for **28** above, was obtained, eluted first, 730 mg (62%) of *anti*-**29**, white needles from benzene–cyclohexane: mp 226–227 °C; ^{1}H NMR (250 MHz) δ 8.29 (d, J = 8.4 Hz, 1H, H-10), 7.97 (s, 1H, H-5), 7.81 (d, J = 7.9 Hz, 1H, H-7), 7.58–7.43 (m, 2H, H-8,9), 7.25–7.08 (m, 3H, H-22,23,24), 4.40–3.58 (4 sets AB, 8H, CH_2S), 3.42–2.74 (m, 8H), 1.55 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (62.9 MHz) δ 138.1, 138.0, 135.6, 135.3, 135.2, 132.7, 132.2, 131.0, 130.9, 130.3, 130.2, 129.0, 128.9, 128.2, 126.8, 126.1, 125.8, 125.2, 125.0, 123.9, 32.4, 28.6, 28.0, 26.4, 26.0, 16.3, 15.4; CI MS m/z 479 (MH^+). Anal. Calcd for $C_{32}H_{30}S_2$: C, 80.29; H, 6.31. Found: C, 79.95; H, 6.05.

Eluted next was 130 mg (11%) of *syn*-**29** as colorless crystals from benzene–cyclohexane: mp 204–206 °C; ^{1}H NMR (250 MHz) δ 8.01 (d, J = 8.5 Hz, 1H, H-10), 7.80–6.76 (m, 7H), 4.80–3.53 (4 sets AB, 8H, CH_2S), 3.15–2.03 (m, 8H), 2.65 and 2.51 (s, 3H each); ^{13}C NMR (62.9 MHz) δ 135.4, 134.7, 134.5, 134.2, 132.6, 132.2, 131.9, 131.2, 131.0, 130.3, 129.4, 128.5, 128.3, 127.9, 127.4, 126.3, 126.2, 125.6, 125.0, 124.9, 124.6, 124.5, 124.2, 35.7, 31.6, 31.0, 28.6, 28.0, 25.9, 25.2, 18.8, 18.1; CI MS m/z 479 (MH^+). Anal. Calcd for $C_{32}H_{30}S_2$: C, 80.29; H, 6.31. Found: C, 79.79; H, 6.32.

17,34-Dimethyl-2,19-dithiabis{(1,3)-4,5,9,10-tetrahydropyreno}-[3.3]cyclophane (30). From bromide **24** (2.00 g, 4.93 mmol) and dithiol **27** (1.54 g, 4.93 mmol) in benzene (900 mL) and KOH (85%, 3.38 g, 51 mmol) in water (190 mL) and ethanol (1.61 L), exactly as described for **28** above, was obtained, eluted first, 1.49 g (54%) of *anti*-**30**, pale yellow crystals from benzene–cyclohexane: mp 289–291 °C (turns orange); ^{1}H NMR (250 MHz) δ 7.34–7.00 (m, 6H), 3.85 and 3.80 (AB, J = 14 Hz, 8H, CH_2S), 3.38–3.26 (m, 4H), 3.04–2.81 (m, 12H), 1.34 (s, 6H); ^{13}C NMR (62.9 MHz) δ 139.2, 135.5, 131.1, 130.5, 129.1, 126.9, 125.8, 28.7, 26.4, 16.0; IR 1438, 1428, 1412, 1208, 1202, 802, 788, 769, 758 cm^{-1}; CI MS m/z 557 (MH^+). Anal. Calcd for $C_{38}H_{36}S_2$: C, 81.97; H, 6.52. Found: C, 82.17; H, 6.30.

Eluted next was a mixture of *anti*-**30** and *syn*-**30** (about 1:1, 314 mg, 11.5%), from which the pure *syn* isomer could not be isolated. By

(44) The sequence **19** → **24** was also investigated in an alternate order by first converting **19** to the corresponding dinitrile, reducing it to the dialdehyde, then to the dialcohol, and then converting it to the bis-(bromomethyl) compound. This sequence was sucessful; however, oxidation of the metacyclophane to the tetrahydropyrene **24** with Br_2/Fe or with $FeCl_3$ did not give products that were as easy to obtain in their pure form as by the other route.

subtraction, the ^{1}H NMR spectral data for *syn*-**30** (90 MHz) δ 7.05 (s, ArH), 3.75 (s, CH_2S), 3.5−2.6 (m, CH_2CH_2), 2.14 (s, CH_3).

Wittig Rearrangement of *anti*-Dithiacyclophanes 28, 29, and 30. *n*-BuLi (11.3 mmol) in hexane (7.1 mL) was added using a syringe to a stirred solution of the dithiacyclophane **28** (2.07 g, 4.84 mmol) in dry THF (150 mL) under N_2 at 20 °C. After 10 min, methyl iodide (1.5 mL, excess) was added until the deep reddish color was discharged, followed by water, dilute aqueous HCl, and dichloromethane. The aqueous layer was extracted with dichloromethane (5 × 150 mL), and the combined extracts were washed, dried, and evaporated to a yellow orange product. This was chromatographed over SiGel using dichloromethane−PE (3:7) as the eluant to give 2.18 g (99%) of mixed isomers of *anti*-**28A**: ^{1}H NMR (90 MHz) δ 7.9−6.9 (m, 6H), 4.2−1.8 (m, ca. 14H), 2.26, 2.10, 2.08 (s, total 6H, SCH_3), 1.05−0.53 (series of s, total 6H, *anti*-CH_3); EI MS *m/z* 456 (M^+). This material was used directly to prepare *anti*-**28B**.

This same procedure was used for *anti*-**29**. From *n*-BuLi (3.44 mmol) in hexane (1.43 mL), *anti*-**29** (705 mg, 1.48 mmol), and THF (100 mL), was obtained 436 mg (59%) of mixed isomers of *anti*-**29A**, used directly in the subsequent step to make *anti*-**29B**.

For *anti*-**30**, the following procedure was preferred. Thiacyclophane **30** (1.146 g, 2.061 mmol) in dichloromethane (250 mL) was added to a stirred suspension of $(CH_3O)_2CH^+BF_4^-$ (ref 25) (1.3 g of 80% oil, 6.2 mmol) in dichloromethane (20 mL) at −30 °C under N_2. After the mixture was stirred for 20 h, half the solvent was evaporated and ethyl acetate (40 mL) was added to dissolve excess methylating agent, and the mixture was stirred for 1 h. The white powder was then collected, dried (1.26 g), and added to a stirred solution of *t*-BuOK (560 mg, 5 mmol) in dry THF (100 mL) under N_2 at 20 °C. After the solution was stirred for 1 h, dilute aqueous HCl was added and then dichloromethane. The aqueous layer was extracted with dichloromethane (6 × 100 mL), and the combined extracts were washed well with water, dried, and evaporated to give 914 mg (94%) of mixed isomers of *anti*-**30A**, used diectly in the subsequent step to make *anti*-**30B**.

***trans*-12b,12c-Dimethyl-4,5,12b,12c,14,15-hexahydrodibenzo[*cd,lm*]perylene (31).** The mixed Wittig isomers, *anti*-**28A** (1.97 g, 4.33 mmol) in dichloromethane (25 mL), were added with stirring to a suspension of $(CH_3O)_2CHBF_4$[25] (2.46 g of 80% oil, 12 mmol) in dichloromethane (5 mL) held at −30 °C under N_2. This mixture was stirred without further cooling for 20 h. Ethyl acetate (40 mL) was then added, and stirring continued for 1.5 h. The precipitated sulfonium salt was collected and stirred with a further portion of ethyl acetate (50 mL) for 2 h to dissolve any remaining methylating agent to give 2.48 g (87%) of the salt, *anti*-**28B** (mp 197−202 °C, dec turns red). This salt (3.75 mmol) was then added to a solution of *t*-BuOK (1.47 g, 13.1 mmol) in dry THF (100 mL) under N_2 and was refluxed for 1 h. After the solution was cooled, benzene (250 mL) was added, and then dilute aqueous HCl was added until acidic. The aqueous layer was further extracted with benzene (3 × 250 mL), and the combined extracts were washed, dried, and evaporated. The red residue was chromatographed over deactivated (5% water) SiGel using PE as the eluant to yield 579 mg (43%) of **31**. A sample was recrystallized from cyclohexane as dark red crystals that decomposed on attempted melting: ^{1}H NMR (360 MHz) δ 8.81 (d, J = 8.07 Hz, H-6,12), 8.51 (d, J = 8.0 Hz, H-7,11), 8.41 (d, J = 7.7 Hz, H-8,10), 7.94 (t, J = 7.7 Hz, H-9), 7.34−7.17 (m, H-1,2,3), 3.99−3.83 (m, H-5,5′,13,13′), 3.24−3.10 (m, H-4,4′,14,14′), −3.85 and −3.92 (s, CH_3). These assignments were confirmed by a COSY spectrum, coupling between H-6/H-7 and H-8/H-9, and a NOESY spectrum, interaction between H-3/H-4 and H-5/H-6: EI MS *m/z* 360 (M^+, base peak, with strong peaks corresponding to the loss of one and two methyl groups, each set showed four peaks of almost equal intensity corresponding to the sequential loss of four hydrogens).

The recrystallized sample of **31** always contained small amounts of the dehydrogenated products, **32** and **33**, readily visible by their internal methyl proton peaks (see below). This material should be kept in the freezer in the solid state.

***trans*-12b,12c-Dimethyl-4,5,12b,12c-tetrahydrodibenzo[*cd,lm*]perylene (32).** The annulene **31** (62 mg, 0.17 mmol) and DDQ (43 mg, 0.19 mmol) were refluxed in dry benzene (40 mL) for 3 h under N_2. After the solution was cooled and concentrated, chromatography over SiGel (deactivated with 5% water) using PE as the eluant gave a mixture of **31**, **32**, and **33**. The desired **32** was separated by preparative HPLC on a Varian Model 5000 liquid chromatograph using an MCH-10 column [reverse phase, CH_3CN-H_2O (85:15)] to obtain 50 mg (81%) of pure **32** as red-brown crystals: mp about 120 °C (dec); ^{1}H NMR (360 MHz) δ 9.03 (d, J = 8.99 Hz, H-13), 8.79 (d, J = 7.04 Hz, H-12), 8.61 (d, J = 9.05 Hz, H-6), 8.20 (d, J = 9.05 Hz, H-7), 8.10 (d, J = 8.99 Hz, H-14), 8.04 (d, J = 8.60 Hz, H-1), 7.99 (d, J = 7.04 Hz, H-11), 7.93 (d, J = 6.71 Hz, H-10), 7.92 (d, J = 7.45 Hz, H-3), 7.60 (m, H-2,9), 7.56 (m, H-1), 4.40−4.20 and 3.60−3.37 (m, H-4,4′,5,5′), −2.78 (s, CH_3); COSY couplings were observed between H-1/2, H-2/3, H-6/7, H-8/9, H-9/10, H-11/12, and H-13/14; ^{13}C NMR (62.9 MHz) δ 138.6, 138.1, 137.2, 133.4, 132.4, 131.0, 129.4, 128.6, 128.2, 127.1, 126.4, 126.2, 125.9, 125.3, 125.1, 125.0, 123.6, 122.6, 122.1, 122.0, 121.9, 118.0, 30.1, 29.9, 25.3, 16.3, 16.0; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 232 (12 600), 260 (5800), 376 (31 900), 409 (10 900), 484 (3070), 514 (2390); CI MS *m/z* 359 (MH^+). This material should be kept in the freezer in the solid state.

***trans*-12b,12c-Dimethyl-12b,12c-dihydrodibenzo[*cd,lm*]perylene (33).** The annulene **31** (335 mg, 0.93 mmol) and *t*-BuOK (2.6 g, 23 mmol) were refluxed in dry THF (200 mL) for 17 h (smaller scale experiments required shorter times) under N_2. After the solution was cooled, benzene (100 mL) was added, and the resultant mixture was acidified with dilute aqueous HCl and further extracted with benzene (2 × 50 mL). The extract was washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated. The residue was preadsorbed on Celite and chromatographed on SiGel using PE as the eluant to give 270 mg (82%) of orange-red solid. A sample was recrystallized from benzene−methanol to give **33** as dark red-brown crystals: mp 198−199 °C; ^{1}H NMR (360 MHz) δ 9.70 (d, J = 7.96 Hz, H-6,12), 9.50 (d, J = 9.33 Hz, H-5,13), 8.90 (d, J = 7.96 Hz, H-7,11), 8.75 (d, J = 7.68 Hz, H-8,10), 8.30 (d, J = 9.33 Hz, H-4,14), 8.24 (t, J = 7.68 Hz, H-9), 8.23 (d, J = 7.52 Hz, H-1,3), 8.01 (t, J = 7.52 Hz, H-2), −4.20 and −4.29 (s, CH_3); COSY couplings were observed between H-1/2, H-4/5, H-6/7, and H-8/9; NOESY interactions between H-5/6 (strong) and H-7/8 (weak); ^{13}C NMR (90.56 MHz) δ 136.6, 132.0, 131.1, 127.3 (C-4,14), 126.8, 126.1 (C-2), 125.3 (C-1,3), 125.1, 124.2 (C-5,13), 123.6 (C-7,8,10,11), 123.1 (C-9), 122.0, 118.9 (C-6,12), 30.3, 30.1, 14.0 (assigned by ^{1}H−^{13}C HETCORR); UV (cyclohexane) λ_{max} (ϵ_{max}) nm 254 (19 900), 272 (99 700), 306 (10 700), 396 (53 400), 416 (203 000), 446 (29 900), 465 (23 100), 495 (26 300); IR (KBr) 1640, 838, 815, 810, 630 cm^{-1}; EI MS *m/z* 356 (M^+). Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.33; H, 5.70.

***trans*-14b,14c-Dimethyl-4,5,14b,14c,15,16-hexahydrobenzo[*rst*]naphtho[8,1,2-*cde*]pentaphene (34).** From the mixed Wittig isomers, *anti*-**29A** (435 mg, 0.86 mmol), dichloromethane (10 mL), and $(CH_3O)_2CHBF_4$ (608 mg of 80% oil, 3 mmol), exactly as described for **31** above, was obtained 503 mg (82%) of salt *anti*-**29B**. This in THF (50 mL) with *t*-BuOK (278 mg, 2.48 mmol), as for **31** above, gave 36 mg (12%) of dark red **34**: ^{1}H NMR (90 MHz) 8.8−7.0 (m, 12H, ArH), 4.0−2.8 (m, 8H, CH_2CH_2), −1.41 (s, 6H, internal CH_3); CI MS *m/z* 411 (MH^+, $C_{32}H_{26}$). A small amount of dehydrogenated product (next step) was always present.

***trans*-14b,14c-Dimethyl-14b,14c-dihydrobenzo[*rst*]naphtho[8,1,2-*cde*]pentaphene (35).** The annulene **34** (36 mg, 0.09 mmol) and *t*-BuOK (246 mg, 2.2 mmol) were refluxed in dry THF (70 mL) for 6 h under N_2. After it was cooled, the mixture was acidified with dilute aqueous HCl and was extracted with benzene (3 × 75 mL). The organic layers were washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated. The residue was preabsorbed on Celite and chromatographed over SiGel using PE as the eluant to give 29 mg (70%) of dark red **35**: mp 219−221 °C; ^{1}H NMR (360 MHz) δ 8.76−8.72 (m, H-8), 8.72 (d, J = 8.89 Hz, H-5), 8.37 (d, J = 9.29 Hz, H-14), 8.22 (d, J = 9.68 Hz, H-15), 8.15 (d, J = 6.92 Hz, H-6), 8.14 (d, J = 6.92 Hz, H-7), 8.03 (d, J = 8.89 Hz, H-4), 7.98−7.96 (m, H-11), 7.90 (s, H-12), 7.89−7.87 (m, H-3), 7.81 (d, J = 9.29 Hz, H-13), 7.72−7.68 (m, H-9,10), 7.67−7.61 (m, H-1,2), 7.43 (d, J = 9.68 Hz, H-16), −1.35 and −1.40 (s, CH_3); COSY couplings were observed between H-2/3, H-4/5, H-6/7, H-8/9, H-10/11, H-13/14, H-15/16, and NOESY interactions between H-3/4, H-5/6, H-7/8, H-11/12, H-12/13, H-14/15, and H-16/1; ^{13}C NMR (62.9 MHz) δ 137.5, 135.4, 134.4, 133.1, 132.7, 130.5, 128.6, 128.4, 127.8, 127.5, 127.4, 127.34, 127.28, 126.8, 126.5, 126.2, 125.3, 125.0, 124.7, 124.4, 124.2, 123.5, 123.0, 121.6, 117.4, 117.1, 37.2, 36.9, 17.8, 17.6; UV (cyclohexane) λ_{max} (ϵ_{max}) nm

226 (26 600), 264 (14 000), 296 (11 400), 410 (69 100), 427 (89 800), 505 (5100), 535 (6700), 575 (5100); CI MS *m/z* 407 (MH^+, $C_{32}H_{22}$).

***trans*-16b,16c-Dimethyl-4,5,8,9,13,14,16b,16c,17,18-decahydrobenzo[*rst*]dinaphtho[8,1,2-*cde*:2′,1′,8′-*klm*]pentaphene (36) and *trans*-16b,16c-Dimethyl-16b,16c-dihydrobenzo[*rst*]dinaphtho[8,1,2-*cde*:2′,1′,8′-*klm*]pentaphene (37).** A solution of the mixed Stevens isomers, *anti*-**30A** (901 mg, 1.54 mmol) in dichloromethane (80 mL), was added to $(CH_3O)_2CHBF_4$ (924 mg of 80% oil,[25] 4.57 mmol) at −30 °C under N_2 and stirred for 20 h without further cooling. The mixture was concentrated to half its volume, then ethyl acetate (40 mL) was added, and stirring continued for 5 h. Filtration, followed by washing the precipitate with more ethyl acetate (10 mL), gave a pinkish salt, *anti*-**30B**, 687 mg (57%). This salt was suspended in dry THF (150 mL) under N_2, and *t*-BuOK (351 mg, 3.13 mmol) was added. This was heated to reflux and stirred for 1 h. After the mixture was cooled, dilute aqueous HCl and then benzene (100 mL) was added. The aqueous layer was further extracted with benzene (4 × 150 mL), and the combined organic layers were washed with water, saturated aqueous $NaHCO_3$, and water, dried, and evaporated. The red product was preadsorbed on Celite and chromatographed on SiGel using PE as the eluant to give 302 mg (71%) of a mixture containing some **36** and some of its dehydrogenated products. This material was directly dehydrogenated in the next step. The above red material was suspended in dry THF (150 mL), *t*-BuOK (1.7 g, 15 mmol) was added, and then the mixture was refluxed under N_2 for 21 h. After the mixture was cooled, benzene and dilute aqueous HCl were added, and the aqueous layer was further extracted with benzene (5 × 150 mL). The organic layers were washed, dried, and evaporated, and the product was preadsorbed on Celite and chromatographed over SiGel using PE as the eluant. The dark red product (25 mg, 8%) was a mixture of **37** and its 4,5,17,18-tetrahydro derivative. We were not able to obtain pure forms of either. For **37**: ^{1}H NMR (250 MHz) δ 9.94 (s, H-6,7,-15,16), 9.64 (d, *J* = 9.3 Hz, H-5,8,14,17), 8.39 (d, *J* = 9.3 Hz, H-4,9,-13,18), ~8.3 (H-1,3,10,12), 8.08 (H-2,11), −4.08 (s, CH_3). For 4,5,17,18-tetrahydro-**37**: ^{1}H NMR (250 MHz) δ 9.73 (d, *J* = 8.3 Hz, H-7,15), 9.53 (d, *J* = 9.3 Hz, H-8,14), 9.21 (d, *J* = 8.3 Hz, H-6,16), 8.30 (d, *J* = 9.3 Hz, H-9,13), 8.22 (d, *J* = 7.7 Hz, H-10,12), 8.02 (t, *J* = 7.7 Hz, H-11), 7.39 (t, *J* = 7.8 Hz, H-2), 7.28 (d, *J* = 7.8 Hz, H-1,3).

***cis*-12b,12c-Dimethyl-4,5,12b,12c,14,15-hexahydrodibenzo[*cd*,*lm*]perylene (38).** A solution of *syn*-**28** (210 mg, 0.49 mmol) in dichloromethane (7 mL) was added slowly with stirring to a suspension of $(CH_3O)_2CHBF_4$ (278 mg, 80% oil,[25] 1.37 mmol) in dichloromethane at −30 °C under N_2. The mixture was then stirred without cooling for 5 h. Ethyl acetate (5 mL) was then added to dissolve the excess methylating agent, and after the mixture was stirred for 0.5−1 h, the white powder (306 mg, 99%) was collected. This bis-sulfonium salt of *syn*-**28** was added to a suspension of NaH (35 mg, 1.46 mmol) in dry THF (60 mL) under N_2 and was stirred for 45 h. After acidification with dilute aqueous HCl and extraction into dichloromethane (4 × 50 mL), the extract was washed, dried, and evaporated. The residue was chromatographed over SiGel using dichloromethane−PE (2:8) as the eluant and gave 81 mg (37%) of *syn*-**28A**, CI MS *m/z* 457 (MH^+). These were remethylated by dissolving them in dichloromethane (5 mL) and adding them to $(CH_3O)_2CHBF_4$ (99 mg) in dichloromethane (2 mL) as before, which after ethyl acetate washing yielded 97 mg (84%) of the bis-salt *syn*-**28B** as a white powder. This was suspended in dry THF (60 mL) under N_2, and then *t*-BuOK (57 mg, 0.51 mmol) was added. After the mixture was stirred for 1 h, benzene (100 mL) was added, and the organic layer was washed, dried, and concentrated. This was then chromatographed over SiGel using PE as the eluant to yield 16 mg (30%) of **38** as almost black crystals: mp 164−167 °C; ^{1}H NMR (90 MHz) 8.99 (d, *J* = 9 Hz, H-6,12), 8.68 (d, *J* = 9 Hz, H-7,11), 8.18 (d, *J* = 6 Hz, H-8,10), 7.50 (t, *J* = 6 Hz, H-9), 7.17 (bs, H-1,2,3), 4.2−2.7 (m, H-4,5,13,14), −1.82 and −1.89 (s, CH_3); CI MS *m/z* 361 (MH^+). ^{1}H NMR also indicated that a small amount of **39**, internal methyl protons at δ −0.99 and −1.04, was present.

***cis*-12b,12c-Dimethyl-12b,12c-dihydrodibenzo[*cd*,*lm*]perylene (40).** A mixture of **38** (16 mg, 0.04 mmol) and DDQ (30 mg, 0.13 mmol) in dry benzene (40 mL) was refluxed for 2 h under N_2. The solution was cooled, concentrated, and chromatographed over SiGel using PE as the eluant to give **40** as a pale green solid, 3.8 mg (28%): ^{1}H NMR (250 MHz) δ 9.71 (d, *J* = 8.8 Hz, H-6,12), 9.31 (d, *J* = 9.1 Hz, H-5,-13), 8.96 (d, *J* = 8.8 Hz, H-7,11), 8.45 (d, *J* = 9.1 Hz, H-4,14), 8.39 (d, *J* = 7.4 Hz, H-8,10), 8.22−8.18 (m, H-1,2,3), 7.96 (t, *J* = 7.4 Hz, H-9), −1.85 and −2.14 (s, CH_3); CI MS *m/z* 357 (MH^+); UV (cyclohexane) λ_{max} (ϵ_{max}) nm 263 (5500), 276 (4900), 310 (2800), 322 (3200), 386 (9100), 407 (30 500), 432 (8100), 437 (9100), 468 (5000), 494 (3200).

***cis*-14b,14c-Dimethyl-4,5,14b,14c,15,16-hexahydrobenzo[*rst*]naphtho[8,1,2-*cde*]pentaphene (42).** From *syn*-**29** (128 mg, 0.268 mmol) in dichloromethane (15 mL) and methylating reagent (160 mg), exactly as described above for **38**, was obtained 141 mg (77%) of the bis-salt of *syn*-**29**. This with NaH (15 mg, 0.6 mmol) in THF (80 mL) gave 105 mg (quantitative) of *syn*-**29A**. These were remethylated (150 mg reagent) in dichloromethane (10 mL) and gave 76 mg (50%) of greenish powder, *syn*-**29B**. This with *t*-BuOK (42 mg, 0.38 mmol) in dry THF (40 mL), as above, gave, after chromatography, 10 mg (23%) of red **42**: ^{1}H NMR (250 MHz) δ 8.52−7.00 (m, ArH), 3.8−2.6 (m, H-4,5,-15,16), −0.08 and −0.21 (s, CH_3) [these appeared at 26.8 and 25.0 in the ^{13}C NMR spectrum, 62.9 MHz]; small singlets at δ 0.49 and 0.45 assigned to **43** could also be seen.

***cis*-14b,14c-Dimethyl-14b,14c-dihydrobenzo[*rst*]naphtho[8,1,2-*cde*]pentaphene (44).** *t*-BuOK (100 mg, 0.89 mmol) was added to a solution of **42** (10 mg, 0.02 mmol) in dry THF (30 mL) under N_2, and the mixture was refluxed for 30 min. After the mixture was cooled, benzene and dilute aqueous HCl were added. The benzene layer was washed, dried, and concentrated and then chromatographed over SiGel using PE as the eluant to give red **44** (3 mg, 30%): ^{1}H NMR (250 MHz) δ 8.42−7.19 (m, ArH), −0.10 and −0.14 (s, CH_3); UV (cyclohexane) λ_{max} (ϵ_{max}) 252 nm (13 000), 262 (13 000), 283 (9300), 295 (10 200), 335 (6700), 352 (10 600), 403 (35 700), 466 (7300), 473 (7500), 487 (6000), 520 (5400).

2,3-Dibromonaphthalene. The method of Danish[27] was suitable for 100 g preparations: mp 139−141 °C; ^{1}H NMR (250 MHz) δ 8.11 (s, H-1,4), 7.73−7.67 (m, H-5,8), 7.52−7.47 (m, H-6,7); ^{13}C NMR (62.9 MHz) δ 133.0, 132.2, 127.1, 126.8, 121.9.

2,3-Bis(3-chloro-2-methylphenyl)naphthalene (47). A solution of 2,6-dichlorotoluene (Aldrich, 60.4 g, 48.2 mL, 0.375 mol) in dry THF (100 mL) was added dropwise over 1 h to a well-stirred frothy mixture of gently warmed (~35 °C) Mg turnings (9.12 g, 0.375 mol), 1,2-dibromoethane (1.5 mL, 17 mmol), and dry THF (200 mL) under N_2 in oven-dried glassware, such as to maintain a gentle reflux. The mixture was then refluxed for a further 2−3 h until most of the Mg dissolved. The mono-Grignard reagent thus formed was cooled to −20 °C and added over 45 min to a well-stirred solution of 2,3-dibromonaphthalene (32.0 g, 0.112 mol) and Ni(acac)$_2$ (2.33 g, 9 mmol) in dry THF (400 mL) under N_2. [Note: This addition could be performed in reverse, naphthalene to Grignard, and also gave variable yield.] This reaction mixture was then refluxed for 3 h. After the mixture was cooled and the THF evaporated, the residue was dissolved in ether (800 mL) and 3 M aqueous HCl (100 mL). The organic layer was washed, dried, and evaporated. The resulting brown oil was preadsorbed onto SiGel (50 g) and chromatographed over SiGel using PE as the eluant to yield 11−22 g (27−54%) of *ter*-aryl **47**. A portion was recrystallized from DMSO as white needles: mp 155−156 °C; ^{1}H NMR (250 MHz) δ 7.91−7.87 (m, 2H), 7.79 (s, 1H), 7.76 (s, 1H), 7.59−7.53 (m, 2H), 7.27−7.21 (m, 2H), 7.02−6.97 (m, 4H), 2.15 (bs, 6H, CH_3); ^{13}C NMR (62.9 MHz) δ 142.6, 142.1, 138.7, 138.4, 135.0, 134.7, 134.2, 132.5, 132.3, 129.9, 129.7, 129.2, 128.3, 128.1, 128.0, 127.7, 126.5, 125.8, 125.5, 18.4, 17.9 (*syn* and *anti* isomers present[45]); IR (KBr) 1546, 1419, 1046, 1013, 993, 889, 883, 795, 785, 775, 750, 743, 715, 707, 472 cm^{-1}; CI MS *m/z* 377 (MH^+). Anal. Calcd for $C_{24}H_{18}Cl_2$: C, 76.40; H, 4.81. Found: C, 76.29; H, 4.86.

Eluted subsequently was 10-chloro-11*H*-benzo[*b*]fluorene, 270 mg (1%), as white crystals from $CHCl_3$: mp 198−200 °C; ^{1}H NMR (250 MHz) δ 8.16 (s, 1H), 7.96 (s, 1H), 7.93−7.77 (m, 3H), 7.50−7.29 (m, 4H), 4.07 (s, H-11,11); ^{13}C NMR (62.9 MHz) δ 143.0, 141.8, 140.2, 139.9, 133.4, 132.9, 131.4 (4 °C), 128.6, 128.2, 127.9, 127.3, 125.6, 123.5, 118.8, 118.5 (=CH), 36.0; IR (KBr) 862, 775, 735, 717 cm^{-1}; CI MS *m/z* 251 (MH^+). Anal. Calcd for $C_{17}H_{11}Cl$: C, 81.44; H, 4.42. Found: C, 81.45; H, 4.48.

2,3-Bis(3-cyano-2-methylphenyl)naphthalene. A mixture of **47** (18.8 g, 50 mmol) and CuCN (20 g, 220 mmol) in 1-methyl-2-

(45) Use of VT NMR spectra to obtain rotation barriers between the *syn* and *anti* isomers will be discussed elsewhere.

pyrrolidinone (100 mL) was refluxed for 12 h under N_2 with mechanical stirring. A further portion of CuCN (10 g, 110 mmol) was added, and reflux continued for a further 12 h. The reaction mixture was cooled to about 100 °C and was poured onto ice (400 g) and concentrated aqueous ammonia (30%, 800 mL). After it was mixed thoroughly, the insoluble solid was separated, washed well with dilute aqueous ammonia, and extracted as thoroughly as possible into dichloromethane (~1 L). The extract was washed, dried, and evaporated. The residue was preadsorbed onto SiGel and chromatographed over SiGel. PE first eluted small amounts (<10%) of unchanged **47**; PE–dichloromethane (7:3) then eluted any mononitrile, 2-(3-chloro-2-methylphenyl)-3-(3-cyano-2-methylphenyl)naphthalene, usually about 300 mg (4%): mp 161–163 °C from ethanol; ^{1}H NMR (250 MHz) δ 7.90–6.90 (m, 12H), 2.30, 2.28, 2.09 (s, 6H total) (mixed isomers); ^{13}C NMR (62.9 MHz) δ 142.2–113.2 (41 peaks), 19.2, 18.7, 18.4, 17.9 (CH_3, *syn* and *anti* isomers[45]); IR (KBr) 2211 cm^{-1}; CI MS *m/z* 368 (MH^+). Anal. Calcd for $C_{25}H_{18}ClN$: C, 81.62; H,4.93. Found: C, 81.30; H, 4.99.

Eluted next was the desired dinitrile, 15.2 g (85%), as white crystals from benzene–methanol: mp 181–183 °C; ^{1}H NMR (250 MHz) δ 7.91–7.09 (m, 12H), 2.27 (s, 6H); ^{13}C NMR (62.9 MHz) δ 141.7–113.4 (23 peaks), 19.2, 18.7 (CH_3, *syn* and *anti* isomers[45]); IR (KBr) 2211, 787, 740, 715, 475, 445 cm^{-1}; CI MS *m/z* 359 (MH^+). Anal. Calcd for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06. Found: C, 87.21; H, 5.16.

2,3-Bis(3-formyl-2-methylphenyl)naphthalene. A solution of DIBAH (2.6 g, 18 mmol) in hexane (17 mL) was added to the dinitrile (immediately above, 3.0 g, 8.4 mmol) in vigorously stirred dry benzene (50 mL) under N_2 at 20 °C over about 30 min. After the mixture was stirred for 24 h, the viscous gel was quenched cautiously, using ice-bath cooling, with methanol (5 mL), methanol–water (1:1, 5 mL), and dilute aqueous HCl (5 mL). Benzene (150 mL) was then added, and the extract was washed, dried, and evaporated. The residue was filtered through a short column of SiGel using dichloromethane as the eluant to give the product dialdehyde, 2.75 g (90%), as white crystals from benzene or CCl_4: mp 204–206 °C; ^{1}H NMR (250 MHz) δ 10.21, 10.19 (s, 2H total, CHO *syn* and *anti* isomers[45]), 7.91–7.16 (m, 12H), 2.40, 2.37 (s, 6H total, CH_3); ^{13}C NMR (62.9 MHz) δ 192.8 (bs, CHO, isomers), 142.5–125.1 (21 peaks), 17.0, 16.5 (CH_3, isomers); IR (KBr) 1663, 1230, 741 cm^{-1}; CI MS *m/z* 365 (MH^+). Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.58; H, 5.42.

2,3-Bis(3-(hydroxymethyl)-2-methylphenyl)naphthalene. The dialdehyde (immediately above, 2.75 g, 7.5 mmol) in THF (15 mL) was added to a stirred suspension of $NaBH_4$ (0.23 g, 6 mmol) in wet THF (15 mL) at 20 °C and was stirred for 20 h. Water (5 mL) and 10% aqueous HCl (5 mL) were then added, and the aqueous layer was saturated with NaCl and extracted with dichloromethane. The extract was washed, dried, and evaporated to yield 2.72 g (98%) of product dialcohol. A portion was recrystallized from benzene as white crystals: mp 155–157 °C; ^{1}H NMR (250 MHz) δ 7.88–7.00 (m, 12H), 4.59 and 4.56 (s, CH_2OH, *syn* and *anti* isomers[45]), 2.07 and 1.97 (s, CH_3, isomers), 1.56 (s, OH, exchanges with D_2O); ^{13}C NMR (62.9 MHz) δ 141.7–124.6 (22 peaks, isomers[45]), 63.78, 63.67 (CH_2O), 16.4, 15.9 (CH_3); IR (KBr) 3350 (broad), 1004, 987, 879, 785, 736, 716 cm^{-1}; CI MS *m/z* 369 (MH^+). Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.70; H, 6.55.

2,3-Bis(3-(bromomethyl)-2-methylphenyl)naphthalene (48). A mixture of concentrated aqueous HBr (48%, 1.5 mL) and concentrated H_2SO_4 (0.5 mL) was added to a solution of the bis-alcohol (immediately above, 1.0 g, 2.7 mmol) in benzene (10 mL) and was stirred at 20 °C for 18 h. The mixture was cooled in an ice bath, cold water (20 mL) was added, and the mixture was extracted with benzene (3 × 15 mL). The organic layer was washed with water, 10% aqueous $NaHCO_3$ solution, and water, dried, and evaporated to yield 1.23 g (92%) of **48**. A portion was recrystallized from benzene–PE as white crystals: mp 148–149 °C; ^{1}H NMR (250 Mz) δ 7.90–6.94 (m, 12H), 4.44 and 4.41 (s, CH_2Br, *syn* and *anti* isomers[45]), 2.14 and 2.07 (s, CH_3, isomers); ^{13}C NMR[45] (62.9 MHz) δ 142.0, 141.5, 139.4, 139.1, 136.0, 135.3, 132.5, 132.3, 130.8, 129.5, 129.1, 129.0, 128.9, 127.8, 127.7, 126.4, 126.3, 125.2, 125.0, 33.2, 33.1, 16.5, 16.1; IR (KBr) 1195, 995, 880, 803, 792, 735, 715, 560, 470 cm^{-1}; CI MS *m/z* 493 (MH^+). Anal. Calcd for $C_{26}H_{22}Br_2$: C, 63.18; H, 4.49. Found: C, 63.60; H, 4.54.

***anti*-9,25-Dimethylnaphtho[10,11-*b*]-2-thia[2.3]metacyclophan-10-ene (49).** A solution of bromide **48** (1.15 g, 2.33 mmol) in benzene (100 mL) was added dropwise at the same rate as a solution of $Na_2S{\cdot}9H_2O$ (0.60 g, 2.53 mmol) [dissolved in N_2-purged water (32 mL) to which was then added N_2-purged ethanol (68 mL)] through separate dropping funnels to vigorously stirred N_2-purged 95% ethanol (300 mL) under N_2 over about 24 h. The solvent was then evaporated, and water (250 mL) and dichloromethane (250 mL) were added to the residue. The organic layer was washed, dried, and evaporated, and the residue was preadsorbed onto SiGel and chromatographed over SiGel using dichloromethane–PE (1:3) as the eluant to give 230 mg (27%) of exclusively the *anti* isomer **49**. A portion was crystallized from cyclohexane as white crystals: mp 198–200 °C; ^{1}H NMR (250 MHz) δ 8.12 (s, H-11,18), 7.96–7.92 (m, H-13,16), 7.56–7.51 (m, H-14,15), 7.41–7.38 (m, 2H), 7.25–7.15 (m, 4H), 3.84 and 3.69 (AB, J = 13.0 Hz, H-1,1,3,3), 0.96 (s, CH_3-9,25); ^{13}C NMR (62.9 MHz) δ 140.5, 139.6, 139.4, 134.4, 133.2, 131.6, 129.8, 127.8, 127.7, 126.2, 125.9, 30.5, 17.5; IR (KBr) 892, 877, 785, 737, 722, 716, 471 cm^{-1}; CI MS *m/z* 367 (MH^+). Anal. Calcd for $C_{26}H_{22}S$: C, 85.20; H, 6.05. Found: C, 84.87; C, 6.12.

Wittig Rearrangement of Thiacyclophane 49 To Give [2.2]-Cyclophane (50). A solution of LDA [from diisopropylamine (0.17 mL) and *n*-BuLi (0.15 mL, 1.6 mmol in hexane)] in dry THF (10 mL) was added over 10 min to a stirred solution of thiacyclophane **49** (150 mg, 0.4 mmol) in dry THF (15 mL) under argon. After the mixture was stirred for an additional 15 min, excess methyl iodide (280 mg, 2 mmol) was added, which discharged the color. Water (100 mL) and dichloromethane (100 mL) were then added, and the organic layer was washed, dried, and evaporated. The yellow residue was chromatographed over SiGel using PE–dichloromethane (3:2) as the eluant to give 150 mg (94%) of product **50**. Recrystallization from cyclohexane gave colorless crystals: mp 143–144 °C; ^{1}H NMR (250 MHz) δ 8.18 (s, H-10,17), 7.95–7.90 (m, H-12,15), 7.82 (dd, J = 7.1 and 1.8 Hz, H-22), 7.56–7.49 (m, H-13,14), 7.29–7.05 (m, 5H), 3.83 (dd, J = 11.0 and 3.0 Hz, H-1_{ax}), 3.22 (dd, J = 12.0 and 3.0 Hz, H-2_{eq}), 2.53 (dd, J = 12.0 and 11.0 Hz, H-2_{ax}), 2.18 (s, SCH_3), 0.68 (s, CH_3-8,24); ^{13}C NMR (62.9 MHz) δ 141.1, 140.8, 140.6, 140.5, 139.0, 138.5, 136.8, 136.3, 133.4, 131.3, 130.6, 128.5, 127.8, 127.5, 126.3, 125.9, 125.6, 124.7, 54.4, 45.4, 16.9, 16.8, 15.7; IR (KBr) 1416, 885, 874, 787, 765, 736, 707, 554, 474 cm^{-1}; CI MS *m/z* 381 (MH^+). Anal. Calcd for $C_{27}H_{24}S$: C, 85.22; H, 6.36. Found: C, 84.92; H, 6.47.

***trans*-14c,14d-Dimethyl-14c,14d-dihydrodibenzo[*de*,*qr*]naphthacene (46).** Borch's reagent,[25] $(CH_3O)_2CHBF_4$ (0.13 g, 0.76 mmol), was added to a solution of **50** (0.16 g, 0.4 mmol) in dichloromethane (10 mL) at −30 °C under N_2, and this was then stirred without further cooling for 10 h. Ethyl acetate (5 mL) was then added, and stirring continued until the precipitate could be collected easily as 180 mg (90%) of white powder. This sulfonium salt was suspended in dry THF (30 mL) under argon, *t*-BuOK (60 mg, 0.6 mmol) was added, and then the mixture was refluxed for 25 min. After the mixture was cooledd, the solvent was evaporated, and the residue was extracted with distilled PE (30 mL). This was washed, dried, and evaporated, and the residue was chromatographed on SiGel (deactivated with 5% water) using N_2-purged PE as the eluant to give 108 mg (90%) of the dihydropyrene **46**. Recrystallization from methanol gave lustrous red-purple crystals: mp 103–105 °C; ^{1}H NMR (C_6D_6, 250 MHz) δ 8.94 (s, H-9,14), 8.01–7.90 (m, H-10,13), 7.73 (d, J = 6.6 Hz, H-1,8), 7.43–7.39 (m, H-11,12), 7.03 (d, J = 9.0 Hz, H-3,6), 6.72 (s, H-4,5), 6.70 (dd, J = 9.0 and 6.6 Hz, H-2,7), −0.49 (s, CH_3); ^{13}C NMR (THF-d_8; 250 MHz) δ 140.3, 136.8, 132.6, 129.2, 128.6, 127.0, 126.4, 124.2, 123.8, 123.0, 118.4, 38.8, 19.2; IR (KBr) 785, 727 cm^{-1}; CI MS *m/z* 333 (MH^+); EI MS (rel intensity) *m/z* 332 (M^+, 37), 317 (M − CH_3, 98), 302 (M − $2CH_3$, 100); UV (cyclohexane) λ_{max} (ϵ_{max}) nm 260 (45 600), 275 sh (33 600), 312 sh (19 600), 320 (33 400), 350 sh (14 700), 369 sh (25 900), 380 (49 700), 399 (66 800), 526 sh (4200), 550 (4600), 580 sh (3550). Anal. Calcd for $C_{26}H_{20}$: M = 332.156. Found: M = 332.153.

1,1′-Oxalylimidazole. Oxalyl chloride (6.6 g, 0.1 mol) in dry THF (25 mL) was added dropwise to a solution of imidazole (7.07 g, 0.05 mol) and diisopropylethylamine (18.36 mL, 0.1 mol) in dry THF (200 mL) under N_2. After the mixture was stirred for 1 h, the precipitate was removed under a blanket of argon and washed with a further quantity of dry THF (50 mL). The filtrate contained the product, which can be used directly in the next reaction. Evaporation of a small portion of filtrate yielded a very hygroscopic white solid: IR (KBr) 3110, 1595,

1420, 1300, 1080, 1060, 900, 880, 830, 760, 630 cm^{-1}; CI MS *m/z* 191 (MH^+). See also ref 28.

1,2-Bis(3-(methoxymethyl)-2-methylphenyl)ethanedione (52). 1,1'-Oxalylimidazole (52 mmol, 143 mL THF solution, prepared as immediately above) was added dropwise to a solution of (3-(methoxymethyl)-2-methylphenyl)magnesium chloride[46] (105 mmol, prepared from 18.0 g of the chlorobenzene) at −40 °C under argon. After a further 15 min of stirring, solid EDTA (10 g) was added, and the reaction mixture was allowed to warm to 25 °C, when saturated aqueous NH_4Cl (50 mL) was added. The organic layer was separated, the aqueous layer was extracted with ether (2 × 100 mL), and the combined organic layers were dried over Na_2SO_4 (note: $MgSO_4$ severely reduces the yield), and evaporated. The residue was chromatographed over SiGel using PE−ether (8:2) as the eluant to give firstly, any unreacted ether (3 g, 17%), and secondly, the yellow dione **52**, 8.1 g (50%), as yellow needles from methanol: mp 69 °C; ^1H NMR (250 MHz) δ 7.59−7.21 (m, 6H, ArH), 4.51 (s, 4H, CH_2O), 3.43 (s, 6H, OCH_3), 2.60 (s, 6H, CH_3); ^{13}C NMR (62.9 MHz) δ 196.8, 139.6, 138.6, 133.4, 132.9, 132.1, 125.6, 72.6, 58.4, 15.8; IR (KBr) 1674, 1582, 1450, 1225, 1193, 1116, 913, 784, 743, 725, 645 cm^{-1}; CI MS *m/z* 327 (MH^+, weak), 163 (M/2, strong). Anal. Calcd for $C_{20}H_{22}O_2$: C, 73.59; H, 6.79. Found: C, 73.38; H, 6.71.

2,3-Bis(3-(methoxymethyl)-2-methylphenyl)quinoxaline (53). A mixture of 1,2-phenylenediamine (320 mg, 3 mmol), the dione **52** (600 mg, 1.84 mmol), and molecular sieves (4 Å, 5 g) in anhydrous ethanol (150 mL) were refluxed for 30 h under N_2. After the mixture was cooled to 25 °C, the sieves were removed, and the solvent was evaporated, the residue was chromatographed on SiGel using PE−ethyl acetate (7:3) as the eluant to give the quinoxaline **53** as colorless crystals (after trituration with ethyl acetate), 601 mg (82%): mp 151 °C; ^1H NMR (250 MHz) δ 8.21−8.17 (m, H-5,8), 7.83−7.79 (m, H-6,7), 7.28−7.02 (m, H-4′,5′,6′,4″,5″,6″), 4.41 (s, 4H, CH_2O), 3.27 (s, 6H, OCH_3), 2.08 (s, 6H, CH_3); ^{13}C NMR (62.9 MHz) δ 155.5, 140.9, 138.7, 136.8, 134.8, 130.0, 129.5, 129.2, 128.7, 125.0, 72.9, 57.7, 15.9. Anal. Calcd for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.57; N, 7.02. Found: C, 78.43; H, 6.58; N, 7.02.

2,3-Bis(3-(bromomethyl)-2-methylphenyl)quinoxaline (54). The ether **53** (1.00 g, 2.5 mmol) in dry dichloromethane (15 mL) was added to a stirred solution of BBr_3 (2.50 g, 10 mmol) in dry dichloromethane (100 mL) at −70 °C under argon. The solution turned orange in color. The mixture was allowed to warm to 25 °C, was stirred for 10 h, and was quenched with ice cold water (20 mL). A solution of K_2CO_3 was added to bring the pH of the aqueous layer to 8. The organic layer was separated, dried, and evaporated, and the residue was recrystallized from dichloromethane−heptane to yield 1.00 g (80%) of **54** as colorless needles: mp 250−251 °C; ^1H NMR (250 MHz) δ 8.22−8.18 (m, H-5,8), 7.86−7.82 (m, H-6,7), 7.27−7.06 (m, H-4′,5′,6′,4″,5″,6″), 4.44 (s, 4H, CH_2Br), 2.15 (s, 6H, CH_3); ^{13}C NMR (62.9 MHz) δ 154.9, 141.0, 139.2, 136.6, 135.7, 130.8, 130.5, 130.3, 129.3, 125.7, 32.3, 16.0; IR (KBr) 1210, 1021, 795, 770, 720, 519, 494 cm^{-1}; EI MS *m/z* 498 (M^+). Anal. Calcd for $C_{24}H_{20}Br_2N_2$: C, 58.09; H, 4.06; N, 5.65. Found: C, 58.08; H, 4.05; N, 5.66.

***anti*-9,25-Dimethylquinoxalino[10,11-*b*]-2-thia[2.3]metacyclophan-10-ene (55).** A solution of the bromide **54** (1.40 g, 2.8 mmol) in benzene−95% EtOH−DMF (55:35:5 by volume, 100 mL, thoroughly purged with argon) was added through one dropping funnel at the same rate as a solution prepared by dissolving $Na_2S·9H_2O$ (0.67 g, 2.8 mmol) in argon-purged H_2O (20 mL) and then adding argon-purged 95% EtOH (80 mL) in a second addition funnel to vigorously stirred 95% EtOH (300 mL) under argon over 6 h. The mixture was stirred for a further 12 h and then was evaporated. The residue was extracted with dichloromethane (300 mL) and water (100 mL). The organic layer was dried and evaporated, and the residue was chromatographed over SiGel using PE−chloroform (7:3) as the eluant to give 0.62 g (60%) of the thiacyclophane **55**. A sample was recrystallized from toluene−95% EtOH to give bright yellow needles: mp 233−234 °C; ^1H NMR (250 MHz) δ 8.23−8.19 (m, H-13,16), 7.82−7.78 (m, H-14,15), 7.46−7.23 (m, H-5,6,7,21,22,23), 3.84 and 3.72 (AB, *J* = 13 Hz, H-1,1,3,3), 1.03 (s, CH_3-9,25); ^{13}C NMR (62.9 MHz) δ 155.3, 141.5, 139.5, 136.2, 134.7, 131.7, 129.9, 129.3, 126.6, 30.6, 17.6; CI MS *m/z* 369 (MH^+); UV (CH_3CN) λ_{max} (ϵ_{max}) nm 246 (380 000), 349 (105 000). Anal. Calcd for $C_{24}H_{20}N_2S$: C, 78.22; H, 5.47; N, 7.60. Found: C, 78.07; H, 5.48; N, 7.57.

Wittig Rearrangement of Thiacyclophane 55. LDA (0.4 mL, 1.5 M solution in hexane, excess) was added dropwise to a stirred solution of thiacyclophane **55** (100 mg, 0.27 mmol) in dry THF (10 mL) at 0 °C under argon. The solution turned deep brown immediately. After the solution was stirred at 25 °C for 15 min, MeI (0.8 mL, excess) was added, and the stirring continued for an additional 3 h. It was then quenched with water (10 mL) and extracted with chloroform (3 × 100 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl (50 mL), water (50 mL), and saturated aqueous NaCl (50 mL), dried, and evaporated. The resulting brown solid was chromatographed on SiGel using pentane−chloroform (8:2) as the eluant to give a product analogous to **50**, *anti*-8,24-dimethyl-1_{ax}-(methylthio)quinoxalino[9,10-*b*][2.2]metacyclophan-9-ene, 88 mg (85%), as light yellow crystals from toluene−ethanol: mp 122−124 °C; ^1H NMR (250 MHz, CD_2Cl_2) δ 8.19−8.14 (m, H-12,15), 7.91 (d, *J* = 7.5 Hz, H-22), 7.83−7.76 (m, H-13,14), 7.47−7.14 (m, H-4,5,6,20,21), 3.87 (dd, *J* = 11 and 3 Hz, H-1_{ax}), 3.27 (dd, *J* = 12 and 3 Hz, H-2_{eq}), 2.56 (dd, *J* = 12 and 11 Hz, H-2_{ax}), 2.19 (s, SCH_3), 0.75 (s, CH_3-8,24); ^{13}C NMR (62.9 MHz, CD_2Cl_2) δ 156.3, 156.2, 141.9, 141.1, 137.3, 136.9, 136.2, 135.9, 131.5, 130.8, 130.6, 130.1, 129.6, 126.9, 126.8, 126.5, 54.2, 45.2, 17.4, 17.2, 15.9; CI MS *m/z* 383 (MH^+). Anal. Calcd for $C_{25}H_{22}N_2S$: C, 78.50; H, 5.80; N, 7.32. Found: C, 78.12; H, 5.74; N, 7.21.

***trans*-14c,14d-Dimethyl-14c,14d-dihydrophenanthro[4,5-*abc*]phenazine (56).** Borsch's reagent,[25] $(CH_3O)_2CHBF_4$ (150 mg, 80% oil, 0.9 mmol, excess), in dichloromethane (5 mL) was added to a stirred solution of the Wittig product from immediately above (80 mg, 0.2 mmol) in dichloromethane (25 mL) at −30 °C under argon. The reaction mixture was then stirred without further cooling for 12 h. Ethyl acetate (20 mL) was added to the mixture, and the stirring continued for a further 12 h. The greenish precipitate that formed was filtered and washed with ethyl acetate (20 mL) to give a crude salt, 85 mg (90%). The salt was quite unstable and, hence, was used immediately. *t*-BuOK (117 mg, 95%, 1 mmol) was added to a stirred suspension of the salt (80 mg, 0.15 mmol) in dry THF (50 mL) at 25 °C under argon. The reaction mixture was then refluxed for 6 h. It was cooled to 25 °C and extracted with ether (100 mL, thoroughly purged with argon) and degassed water (25 mL). The organic layer was washed with degassed water (25 mL) and degassed saturated aqueous NaCl (25 mL) and dried, and the solvent evaporated without heat. The solid residue was dissolved in ether (2 mL) and quickly chromatographed on SiGel (deactivated with 10% H_2O) using degassed ether as the eluant. Both the solvent and the SiGel slurry were purged well with argon, and the column was protected from fluorescent light. The green fraction was evaporated to yield the dihydropyrene **56**, 5 mg (10%) as a green solid, mp ~70 °C dec. The solid decomposed very rapidly in the presence of light and oxygen, resulting in many polar products (at least 10, by TLC). Solutions of **56** in degassed chlorinated solvents were sufficiently stable only to record proton spectra: ^1H NMR (250 MHz, CD_2Cl_2) δ 8.76 (d, *J* = 6.5 Hz, H-1,8), 8.35−8.31 (m, H-10,13), 7.91−7.87 (m, H-11,12), 7.31 (d, *J* = 8.9 Hz, H-3,6), 7.06 (dd, H-2,7), 7.01 (s, H-4,5), −0.72 (s, CH_3-14c,d); EI MS (rel intensity) *m/z* 336 (M^+, $C_{24}H_{18}N_2$, 10), 321 ($M - CH_3$, 40), 306 ($M - 2CH_3$, 100).

2-Bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (58). This is a modification of our original procedure.[30] A solution of NBS (0.77 g, 4.3 mmol, not recrystallized from water) in dry DMF (50 mL) was added slowly to a stirred solution of dihydropyrene **1** (1.0 g, 4.3 mmol) in dry DMF (50 mL) at 0 °C. After 5 min, the mixture was poured into ice−water and extracted with diethyl ether. The ether layer was washed well with water to remove the DMF, dried, concentrated and preadsorbed on SiGel, and then chromatographed over SiGel using PE as the eluant to give 1.1 g (80%) of **58** as green crystals from PE: mp 110−111 °C (lit.[30] mp 111−112 °C); ^1H NMR (250 MHz) δ 8.70 (s, H-1,3), 8.65−8.50 (m, 6H), 8.07 (t, J = 8 Hz, H-7), −4.07 and −4.08 (s, CH_3-10b,c).

Trapping of Dihydropyryne 57 To Give Adduct 59. Sodium amide (63 mg, 1.6 mmol) and *t*-BuOK (5 mg) were added to a solution of bromide **58** (100 mg, 0.32 mmol) and furan (1 mL) in THF (5 mL) under N_2 at 20 °C, and the solution was stirred for 6 h. Methanol was added to decompose any remaining amide, and then the solvent was

(46) Mitchell, R. H.; Lai, Y. H. *J. Org. Chem.* **1984**, *49*, 2534−2540.

evaporated. The residue was extracted with ether, and the extract was concentrated and preadsorbed on SiGel and chromatographed using PE–ether (9:1). Any unchanged bromide was eluted first, and then the adduct **59**, 59 mg (62%) was eluted as a 1:1 mixture of isomers. Thus, in the ^{1}H NMR spectrum, the internal methyl protons appeared at δ −3.29, −3.34, −3.45, and −3.51; those at −3.34 and −3.51 belonged to one isomer and the other two peaks to the other isomer. The isolated alkene hydrogens were centered at δ 7.05 in one isomer and at 7.21 in the other. One of the isomers could be fractionally crystallized from dichloromethane–heptane: mp 171–173 °C; ^{1}H NMR (250 MHz) δ 8.31 and 8.23 (AB, J = 8.6 Hz, H-11,12), 8.20 (d, J = 8.2 Hz, H-3), 8.19 (s, H-6), 8.13 (d, J = 7.0 Hz, H-1), 8.11 and 8.04 (AB, J = 7.0 Hz, H-4,5), 7.72 (dd, H-2), 7.05 (dd, J = 5.6 and 1.8 Hz, H-8), 7.00 (dd, J = 5.6 and 1.7 Hz, H-9), 6.52–6.51 (m, H-10), 6.15–6.14 (m, H-7), −3.34 and −3.51 (s, CH_3); ^{13}C NMR (62.9 MHz) δ 142.0, 141.5, 141.1, 140.7, 138.0, 137.9, 137.4, 137.1, 128.5, 127.4, 125.1, 125.0, 122.9, 122.0, 119.0, 116.3, 82.9, 80.5, 33.2, 32.4, 15.6, 14.9; IR (KBr) 1350, 1320, 1270, 990, 900, 860, 830, 820, 730, 700, 680, 650 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 238 (6400), 339 (83 600), 356 (23 800), 380 (30 700), 454 (5000), 479 (5400); CI MS m/z 299 (MH^+). Anal. Calcd for $C_{22}H_{18}O$: C, 88.64; H, 6.09. Found: C, 88.31; H, 6.29.

Deoxygenation of Adduct 59 to *trans*-12b,12c-Dimethyl-12b,12c-dihydropyrene (3). A mixture of the adduct **59** (54 mg, 0.18 mmol) and $Fe_2(CO)_9$ (79 mg, 0.22 mmol) in benzene (5 mL) was refluxed under N_2 for 20 min. The mixture was cooled and chromatographed on SiGel using PE as the eluant to give 46 mg (90%) of reddish brown **3**, which on recrystallization from PE gave the following: mp 116–117 °C (lit.[7] mp 115–116 °C); ^{1}H NMR (250 MHz, expanded data point set for aromatics) δ 8.77–8.70 (m, H-10), 8.09 and 7.36 (AB, J = 6.58 Hz, H-11 and H-12), 8.05–7.94 (m, H-7), 7.88 (s, H-6), 7.68 and 7.61 (AB, J = 8.83 Hz, H-4 and H-5), 7.70–7.64 (m, H-8,9), 7.50 (d, J = 8.85 Hz, H-1), 7.35 (d, J = 6.52 Hz, H-3), 7.13 (dd, J = 8.85 and 6.52 Hz, H-2), −1.618 and −1.626 (s, CH_3; at 360 MHz, $\Delta\delta$ = 0.0066 ppm).

Benzoisofuran Adduct 63. Sodium amide (350 mg, 9 mmol) was added to a solution of 1-methoxyphthalan[47] (1.2 g, 8 mmol) in THF (10 mL) under N_2 at 20 °C. After the mixture was stirred for 8 h, bromide **58** (100 mg, 0.32 mmol) was added, and stirring continued for a further 12 h. A few milliliters of methanol was then added, and the total mixture was preadsorbed onto SiGel and chromatographed using PE–ether to elute the green and red fractions. Removal of solvent also removed excess 1-methoxyphthalan and benzofuran, and the residue remaining was rechromatographed on SiGel. PE eluted first any red naphthodihydropyrene **64** (up to 21 mg, 20%, properties given in next experiment), and then PE–ether (50:1) eluted the green adduct **63** (usually about 26 mg, 23%) as a mixture of isomers. The combined yields of **63** and **64** indicate that about 43% of the adduct **63** must have been formed. Fractional recrystallization of the mixture of adducts from chloroform–PE gave one isomer: mp 203–204 °C; ^{1}H NMR (250 MHz) δ 8.52 and 8.49 (AB, J = 8.5 Hz, H-13,14), 8.35 (d, J = 8.1 Hz, H-3), 8.32 (d, J = 7.4 Hz, H-1), 8.28 and 8.23 (AB, J = 7.2 Hz, H-4,5), 7.86 (dd, H-2), 7.43–7.39 (m, H-8,11), 6.96 (s, H-12), 6.96–6.89 (m, H-9,10), 6.59 (s, H-7), −3.66 and −4.01 (s, CH_3); ^{13}C NMR (62.9 MHz) δ 148.0, 147.5, 141.6, 138.1, 137.7, 137.0, 127.1, 126.0, 125.9, 124.8, 124.7, 123.3, 123.1, 122.9, 122.4, 120.1, 120.0, 118.7, 116.0, 83.6, 81.1, 32.3, 31.3, 14.9, 14.4; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 243 (9900), 278 (5600), 345 (106 000), 383 (38 600), 456 (6000), 478 (7500); CI MS m/z 349 (MH^+). Anal. Calcd for $C_{26}H_{20}O$: M = 348.152. Found: M = 348.158.

***trans*-14b,14c-Dimethyl-14b,14c-dihydronaphtho[2,1,8-*qra*]naphthacene (64).** The adduct **63** (26 mg, 0.075 mmol) and $Fe_2(CO)_9$ (27 mg, 0.075 mmol) were refluxed under N_2 in dry, N_2-purged benzene (5 mL) for 5 min. The mixture was cooled, and a small amount of SiGel was added and then evaporated to dryness, followed immediately by chromatography on SiGel using PE to elute the first red fraction, 18 mg (70%) upon evaporation. The combined yield from this and the previous experiment is about 40 mg (37%) of **64**. Recrystallization from dichloromethane–heptane gave red crystals: mp 182–183 °C; ^{1}H NMR (360 MHz) δ 8.90 (s, H-12), 8.19 (s, H-7), 8.07–7.99 (m, H-8,11), 7.69 and 6.81 (AB, J = 6.4 Hz, H-13 and H-14), 7.56–7.51 (m, H-9,10), 7.18 and 7.07 (AB, J = 9.1 Hz, H-4,5), 6.97 (d, J = 9.0 Hz, H-1), 6.77 (d, $J \sim$ 6.3 Hz, H-3), 6.66 (dd, H-2), −0.44 (s, CH_3-14b,c, no detectable shift difference); ^{13}C NMR (62.9 MHz) δ 141.0, 139.9, 138.3, 134.1, 132.5, 132.0, 129.6, 128.1, 127.8, 127.4, 126.9, 126.2, 126.1, 125.8, 125.6, 124.3, 124.2, 122.1, 121.1, 117.5, 38.9, 38.0, 19.5, 18.6; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 253 (18 900), 343 (61 000), 358 (73 400), 373 (46 800), 394 (27 100), 487 (4100), 517 (4400), 552 (2700); CI MS m/z 333 (MH^+). Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.97; H, 6.11. An X-ray structure determination clearly indicated the carbon skeleton but would not complete to give satisfactory (<13%) refinement. The crystal system was orthorhombic, space group *Pccn* (No. 56) with a = 24.392 Å, b = 23.785 Å, and c = 6.140 Å.

Naphthoisofuran Adducts 65 and 66. 3,6-Dipyrid-2-yltetrazine[33] (205 mg, 0.92 mmol) [48] (160 mg, 0.84 mmol) in chloroform (2 mL) under N_2, and then the solution was stirred at 40–50 °C for 15 min. After evaporation at 20 °C under N_2, the residue was filtered through SiGel using PE–ether (5:1) and again evaporated at 20 °C to give light yellow crystals. These were dissolved in THF (5 mL), and to this solution under N_2 were added the bromide **58** (100 mg, 0.32 mmol), sodium amide (66 mg, 1.69 mmol), and a few milligrams of *t*-BuOK. This mixture was then stirred for 2 h, and then maleic anhydride (165 mg, excess) was added to remove any unchanged isofuran. After 5 min, a few milliliters of methanol was added, and the mixture was preadsorbed onto SiGel and chromatographed, collecting the green fraction to yield 60 mg (47%) of a 1:1 mixture of adducts **65** and **66**: CI MS m/z 399 (MH^+). This material was used directly in the next step. If larger amounts of sodium amide and longer times were used, deoxygenation also occurred to give approximately 1:1 mixtures of **67** and **68** (see below).

***trans*-16b,16c-Dimethyl-16b,16c-dihydrobenzo[*a*]naphtho[2,1,8-*lmn*]naphthacene (67) and *trans*-16b,16c-Dimethyl-16b,16c-dihydrobenzo[*a*]naphtho[2,1,8-*hij*]naphthacene (68).** The mixed adducts **65** and **66** from above (60 mg, 0.15 mmol) and $Fe_2(CO)_9$ (82 mg, 0.23 mmol) in N_2-purged benzene (5 mL) were refluxed under N_2 for 5 min. After the mixture was cooled, a small amount of SiGel was added, and the solvents were removed, and then chromatography on SiGel using PE as the eluant gave a red solid (25 mg, 44%) as a 4.5:1 mixture by ^{1}H NMR of **67** and **68**. (Note: **65** and **66** were present in equal amounts.) The major isomer, **67**, could be obtained in pure form by recrystallization from heptane as red *cubes*: mp 209–210 °C; ^{1}H NMR (360 MHz) δ 9.90 (s, H-14), 8.99–8.97 (m, H-13), 8.31 (s, H-7), 8.07 and 7.10 (AB, J = 6.5 Hz, H-15 and H-16), 7.94–7.89 (m, 2H), 7.78 (s, H-6), 7.78–7.71 (m, 2H), 7.66–7.61 (m, 1H), 7.42 and 7.32 (AB, J = 9.0 Hz, H-4,5), 7.22 (d, J = 9.0 Hz, H-1), 7.03 (d, J = 6.4 Hz, H-3), 6.87 (dd, H-2), −0.878 and −0.882 (s, CH_3); ^{13}C NMR (62.9 MHz) δ 140.5, 139.5, 138.2, 134.3, 132.1, 131.3, 130.6, 129.6, 128.7, 127.5, 127.2, 126.73, 126.67, 126.0, 124.1, 123.8, 122.8, 122.2, 121.2, 117.5, 117.2, 37.9, 37.2, 18.9, 18.0; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 265 (19 600), 279 (22 900), 355 (66 700), 369 (86 600), 383 (69 300), 403 (35 600), 485 (5800) 511 (6300); EI MS m/z 382 (M^+). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.69; H, 5.75. An X-ray structure determination was attempted and clearly showed the carbon skeleton but would not refine beyond 13%. The crystal system was tetragonal, space group $P4_2/n$ (No. 86) with a = 17.311 Å, b = 17.304 Å, and c = 13.606 Å.

Accumulation of mixed fractions, together with those from the trapping reaction in which a large excess of sodium amide was used (see above), followed by collection of the rear part of the red chromatography band and recrystallization from heptane produced two kinds of crystals, cubes and needles, which could be separated by hand picking. The cubes were identical to **67**; the needles proved to be **68**: ^{1}H NMR (360 MHz) δ 9.10 (s, H-7), 9.03 (s, H-14), 8.88 (d, J = 8 Hz, H-8), 7.95 and 7.78 (AB, J = 8.9 Hz, H-13 and H-12), 7.95 and 7.07 (AB, J = 6.5 Hz, H-15 and H-16), 7.91–7.88 (m, H-11), 7.88 (s, H-6), 7.74–7.69 (m, H-9), 7.66–7.61 (m, H-10), 7.44 and 7.32 (AB, J = 9.0 Hz, H-4,5), 7.20 (d, J = 9.0 Hz, H-1), 7.03 (d, J = 6.0 Hz, H-3), 6.86 (dd, H-2), −0.896 and −0.899 (s, CH_3).

***trans*-11b,11c-Dimethyl-11b,11c-dihydropyreno[1,2-c]furan (62).** 3,6-Dipyrid-2-yl-*s*-tetrazine[33] (55 mg, 0.25 mmol) was added to a

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solution of adduct **59** (59 mg, 0.20 mmol) in chloroform (2 mL) under N_2, and the mixture was stirred at 40−50 °C for 15 min. The mixture was evaporated to dryness at 20 °C, preadsorbed from ether onto SiGel, and chromatographed using PE−ether (10:1) as the eluant under a pressure of N_2. The first red fraction, on evaporation at 20 °C, gave 42 mg (78%) of **62**. This material changes color to green on warming and is sensitive to light and oxygen but is reasonably stable in N_2-purged solutions or at −20 °C in the solid state: ^{1}H NMR (250 MHz) δ 8.11 (s, H-9), 7.81 (d, J = 1.38 Hz, H-7), 7.01 (s, H-6), 6.78 and 6.39 (AB, J = 6.5 Hz, H-10 and H-11), 6.75 and 6.68 (AB, J = 9.37 Hz, H-4,5), 6.60 (d, J = 9.76 Hz, H-1), 6.42 (d, J = 5.66 Hz, H-3), 6.35 (dd, H-22); ^{13}C NMR (62.9 MHz) δ 140.9, 140.4, 138.9, 137.2, 137.0, 128.8, 127.3, 126.7, 126.5, 124.0, 122.1, 121.0, 120.6, 117.1, 116.8, 114.4, 40.5, 40.4, 20.0, 19.6; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 313 (66 600), 328 (74 000), 343 (61 700), 358 sh (38 500), 470 sh (6400), 494 (6850), 530 sh (4800); CI MS (rel intensity) m/z 273 (100, MH^+ for $C_{20}H_{16}O$).

Reaction of Pyryne 57 and Isofuran 62 To Give Bis(dihydropyreno)benzenes 69 and 70. Sodium amide (70 mg, 1.8 mmol) and a few milligrams of t-BuOK were added to a solution of bromide **58** (100 mg, 0.32 mmol) and the isofuran **62** (50 mg, 0.18 mmol) in THF (5 mL) under N_2. After the mixture was stirred for 2 h, a few milliliters of methanol was added, the solvent was evaporated, and the residue was preadsorbed onto SiGel from ether. Chromatography using PE−ether (20:1) as the eluant gave 44 mg (49%) of the adduct as a mixture of isomers (12 methyl peaks between δ −3.5 and −5.0 in the ^{1}H NMR spectrum). This mixture was dissolved in THF (10 mL), then sodium (10 mg, 0.4 mmol) was added, and the mixture was stirred at 20 °C for 14 h. The solvent was removed in a N_2 stream, and the residue was dissolved in THF-d_8 and filtered through glass wool under N_2. ^{1}H NMR indicated peaks at δ −1.18, −1.19, −1.20, and −1.21 corresponding to isomers of **70** and at −1.58 and −1.62 corresponding to **69** in a ratio of about 5:1. When $Fe_2(CO)_9$ was used as a deoxygenator (see **67** and **68** above), the ratio of products was reversed. Evaporation yielded a red solid that gave CI MS (rel intensity) m/z 487 (100, MH^+ for $C_{38}H_{30}$). Further chromatography to attempt to separate the isomers **69** and **70** only resulted in decomposition. The ^{1}H NMR peaks at δ −1.2 could be assigned to **70** because only that isomer shows the 1H downfield singlet due to H-16, which is doubly sterically deshielded by H-15 and H-17 and appears at δ 10.1; in contrast, that for H-7 or H-16 of **69** is at about δ 8.7. Both compounds' aromatic protons extend to δ 7.0, and both are a mixture of isomers of different methyl orientations between the two dihydropyrene rings, though *trans* within each dihydropyrene ring.

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Supplementary Material Available: Tables of NMR data [$\delta(Me_{av})$, $\delta(H_{dis})$, J_a, J_b, ΔJ, and J_b/J_a] for the compounds **1**, **3**, **32**, **33**, **45**, **46**, **56**, **64**, **67**, and **68**, full X-ray crystal data for **55** and **1**, and ORTEP diagrams and tables of atomic parameters for **55** and **1** (23 pages); tables of observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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