Nonplanar Aromatic Compounds.† 3. A Proposed New Strategy for the Synthesis of Buckybowls. Synthesis, Structure and Reactions of [7]-, [8]- and [9](2,7)Pyrenophanes

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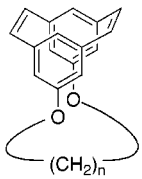
A new strategy for the synthesis of Buckybowls is presented and initial attempts to implement it are reported. This involves annulation of further rings onto polycyclic aromatic systems that prefer to be planar but have been "pre-bent" by the installation of a tether. Pyrenophane **2b** reacts with TCNE and PTAD to give 1:1 and 1:2 adducts, respectively. The less strained pyrenophane **2c** is unreactive toward TCNE but gives a 1:2 adduct with PTAD. Attempted electrophilic aromatic brominations of pyrenophane **2e** under a variety of conditions were unsuccessful, as were attempts to brominate cyclophanediene **1c**, the direct synthetic precursor of **2c**. Tether cleavage and addition reactions occurred rather than substitution. In an effort to circumvent tether cleavage problems, [7]-, [8]- and [9](2,7)pyrenophanes **22b**−**d** were prepared. However, attempted bromination and Friedel−Crafts acylations failed. Evidence for the fleeting existence of [6](2,7)pyrenophane **22a** was also obtained. Comparison of structural data (X-ray and AM1 calculations) for the pyrenophanes **22a**−**d** with their 1,*n*-dioxa analogues **2a**−**d** indicates that the nature of the tether has a strong effect on the degree of bend in the pyrene moiety and this led to the identification of trioxapyrenophane **28** as the next target in the quest for increasingly bent pyrenes.

Introduction

The discovery of the fullerenes[1] triggered a surge of interest in nonplanar polycyclic aromatic compounds, particularly those that map onto the surface of one or more of the fullerenes. Fullerene subunits whose lowest energy conformations are nonplanar have been termed "Buckybowls",[2] the curvature of which is a consequence of the presence of one or more five-membered rings. The pyramidalization of the sp^2 hybridized carbon atoms translates into a high degree of strain in these systems and this, in turn, renders them synthetically challenging targets. Most, if not all, reported synthetic approaches to Buckybowls[3] have relied upon some sort of ring closing reaction to generate the characteristic curvature. Since the starting materials in these reactions are planar, or nearly so, a considerable amount of energy is required to distort them into the conformations that are required for ring closure to occur. FVT methodology[3] has figured prominently in this regard, although reductive couplings[4] now appear to be emerging as viable nonthermolytic alternatives. However, Buckybowls must still be regarded as formidable targets.

We propose a conceptually different, three-step approach to the construction of Buckybowls: (1) bend an otherwise planar polycyclic aromatic hydrocarbon by tethering two remote positions; (2) annulate further rings so as to generate an innately curved polycyclic system; and (3) remove the tether. The purpose of "pre-bending" the starting polycyclic aromatic system is to enforce a geometry in which it is substantially more amenable to the construction of the "curvature-enforcing" rings than when it is in a planar, or nearly planar, conformation.



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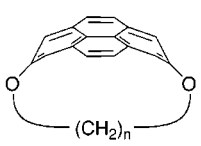
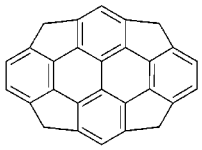
1b n=5
1c n=6
1d n=7



2a n=4
2b n=5
2c n=6
2d n=7
2e n=8



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† This series of papers was formerly titled "Curved Aromatic Compounds".

(1) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K. Huffman, D. R. *Nature* **1990**, *347*, 354−358. (c) Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917−7919. (d) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: New York, 1994.

(2) Rabideau, P. W.; Abdourazek, A. H.; Folsom, H. E.; Marcinow, Z.; Sygula, A.; Sygula, R. *J. Am. Chem. Soc.* **1994**, *116*, 7891−7892.

(3) (a) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (b) Mehta, G.; Rao, H. S. P. In *Advances in Strain In Organic Chemistry*; Halton, B., Ed.; JAI: London, 1997; Vol. 6, pp 139−187. (c) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (d) Siegel, J. S.; Seiders, T. J. *Chem. Br.* **1995**, 313−316. (e) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1424−1432. (f) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT, 1995; Vol. 3, pp 1−36. (g) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Atual. Fis.-Quim. Org.* **1999**, *11*, 138−150. (h) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

(4) (a) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, 2, 1427−1430. (b) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755. (c) Seiders, J. T.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813. (d) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800−7803. (e) Rabideau, P. W.; Sygula, A. *J. Am. Chem. Soc.* **1998**, *120*, 12666−12667.

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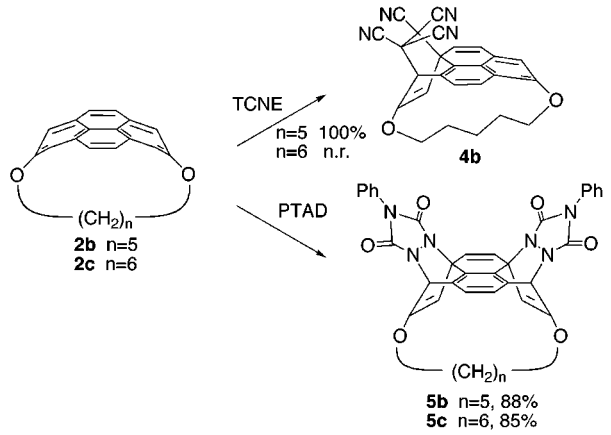
Scheme 1



In preparing 1,7-dioxa[7](2,7)pyrenophane **2b**[5a] and 1,8-dioxa[8](2,7)pyrenophane **2c**[5b] from the corresponding cyclophanedienes **1a** and **1b**, we have demonstrated that severe nonplanarity can be imparted to the normally planar pyrene system by the incorporation of a tether between the 2 and 7 positions. Since pyrene is a repeating subunit around the equators of D_{5h} C_{70}, D_{6h} C_{84}, D_{5d} C_{80}[6] and in the still hypothetical Buckybowl pinakene **3**,[7] these results constitute the first successful completion of step 1 of the strategy outlined above. If pinakene is the target Buckybowl, then step 2 would be the elaboration of **2**, or some other pyrenophane, into a tethered version of **3**. The first task leading toward the accomplishment of step 2 is the preparation of functionalized pyrenophanes and we now report the results of our initial attempts to do so.

Results and Discussion

Reactions of 1,*n*-Dioxa[*n*](2,7)pyrenophanes 2b and 2c. With gram quantities of pyrenophanes **2b** and **2c** in hand, a study of their chemistry was undertaken. In view of the propensity for strained cyclophanes to undergo cycloaddition reactions,[8] the behavior of **2b** and **2c** toward reactive dienophiles was investigated first. As we reported earlier, the reaction of **2b** with tetracyanoethene (TCNE) afforded 1:1 adduct **4b** (Scheme 1).[5a] Precedent for the observed orientation of addition can be found in cycloadditions of other small cyclophanes, such as the reactions between [6]paracyclophane with TCNE[9] and [2.2]paracyclophane with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).[10] Pyrenophane **2c** does not react with TCNE in benzene at room temperature or at reflux. That **2b** and **2c** react with TCNE in yields of ca. 100% and 0%, respectively, suggests that there is a significant difference in their strain energy. AM1 calculations predict that this difference is of the order of 15 kcal/mol.[11]

Addition of PTAD to **2b** in benzene at room temperature (Scheme 1) resulted in rapid fading of the red color of the dienophile until 2 equiv had been added, after which the color persisted. A significant amount of starting material was still present after the addition of 1 equiv of PTAD (TLC analysis) and a white precipitate formed during the addition. The mass of this product corresponded to an 88% yield of a 2:1 PTAD−pyrenophane adduct, but its very low solubility in common organic solvents and immobility on silica frustrated attempts to fully purify and characterize it. Nevertheless, quite clean ^{1}H and ^{13}C NMR spectra were obtained, although the latter was very weak. Assuming that the first equivalent of PTAD reacted to give an adduct analogous to **4b**, then there is only one possible 2:1 adduct that is consistent with the NMR spectra, namely **5b**. Steric effects likely preclude addition of the second equivalent of PTAD to either of the central rings and the retention of an aromatic sextet in **5b** is presumably responsible for the orientation of addition to the terminal ring. Other orientations of addition to this ring leave the product with no aromatic character.

In contrast to TCNE, PTAD did react with pyrenophane **2c**. This reaction was clearly slower that that of **2b**, as attested to by the persistence of the red color for over 3 h. As before, a 2:1 adduct was obtained, presumably **5c**, but it was even less soluble than **5b**. This compound also showed signs of instability, a pink color developing when heated with $CHCl_3$ (presumably retro Diels−Alder reaction) and a brown-yellow color forming upon attempted dissolution in DMSO. Only a ^{1}H NMR spectrum could be obtained for **5c** and it was very similar to that of **5b**. In line with the trend observed so far, the higher homologue **2d**,[12] having two extra carbon atoms in the tether, showed only traces of reaction with PTAD after 5 days.

In order for **2b** and **2c** to serve as precursors to larger, bowl-shaped polycyclic aromatic structures, methods of introducing functionality needed to be found. Bromination was selected for investigation, owing to the potential offered by an aryl bromide for further elaboration using palladium-catalyzed cross-coupling methodology.[13] Although there is precedent for halogenation of [*n*]cyclophanes,[14] there is also precedent for addition occurring instead of substitution when the arene is particularly strained.[15] This being the case, the comparatively less strained pyrenophane **2e** was used for preliminary investigations, but attempted brominations with Br_2, Br_2·dioxane complex,[16] pyridinium perbromide,[17] and NBS

(5) (a) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J., Mannion, M. R. *Chem. Eur. J.* **1999**, *5*, 1823−1827. (b) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J., Mannion, M. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1320−1321.

(6) Wang, C. R.; Sugai, T.; Kai, T.; Tomiyama, T.; Shinohara, H. *J. Chem. Soc., Chem. Commun.* **2000**, 557−558.

(7) Jemmis, E. V.; Sastry, G. N.; Mehta, G. *J. Chem. Soc., Perkin Trans. 2* **1994**, 437−441.

(8) Misumi, S. *Pure Appl. Chem.* **1987**, *59*, 1627−1636.

(9) Hopf, H.; Wituslki, B.; Jones, P. G.; Schomberg, D. *Liebigs Ann.* **1995**, 609−612.

(10) (a) Murad, A. F.; Kleinschroth, J.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 389−390. (b) Matsumoto, K.; Toda, M.; Kakehi, A. *Hetereocycles* **1995**, *41*, 471−476.

(11) The heats of formation for (**2b** + propane) and (**2c** + ethane) were calculated using the Chem3D package of software (MOPAC, AM1, closed shell). The 15.0 kcal/mol difference between the calculated heats of formation of these two systems was taken to be the difference in the strain energy between **2b** and **2c**.

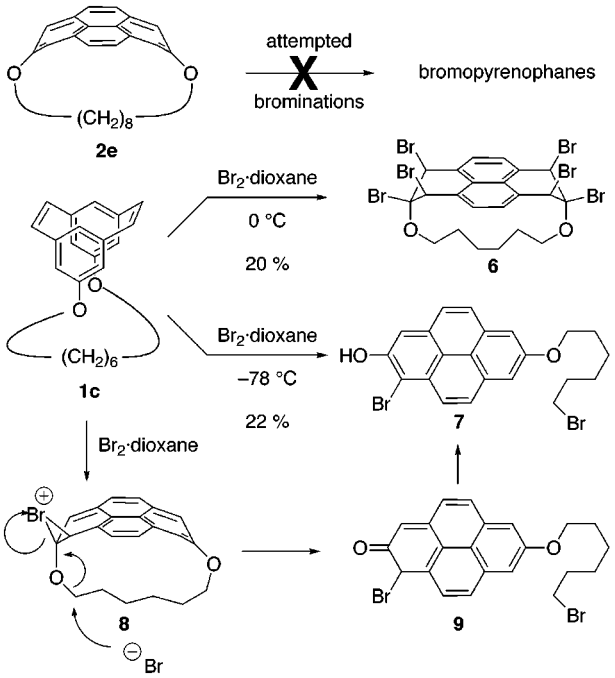
(12) Full details of the synthesis and crystal structures of a series of higher homologues of **2** are contained in a manuscript soon to be submitted.

(13) (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1995. (b) *Modern Cross-Coupling Reactions*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1997.

(14) (a) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1957**, *79*, 4348−4353. (b) Smith, B. H. Ph.D. Thesis, Cornell University, Ithaca, New York, 1960; cited in Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: New York, 1964; p. 211. (c) Parham, W. E.; Johnson, D. R.; Hughes, C. T.; Meilahn, M. K.; Rinehart, J. K. *J. Org. Chem.* **1970**, *35*, 4048−4552.

(15) (a) Tobe, Y.; Ueda, K.-I.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron* **1986**, *62*, 1851−1858. (b) Liebe, J.; Tochterman, W. *Tetrahedron Lett.* **1983**, *24*, 2549−2552.

Scheme 2

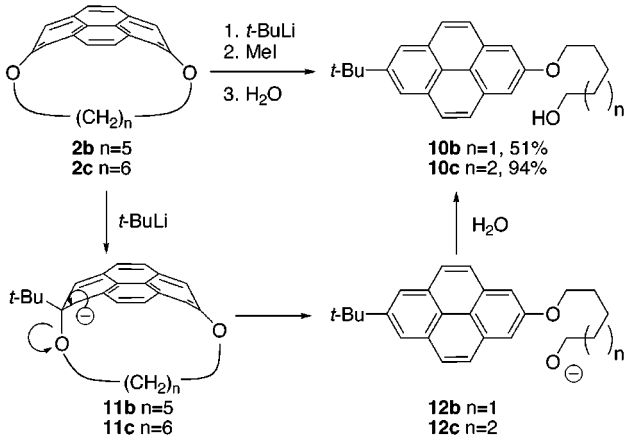


all led to the formation of only baseline material (TLC analysis). No products were isolated from these reactions.

Since tether cleavage was likely occurring in these reactions, no attempt was made to brominate the more strained **2b** and **2c**. The alternative strategy of brominating the precursor cyclophanedienes was pursued instead (Scheme 2). Cyclophanediene **1c** reacted readily with 2 equiv of Br_2 in CH_2Cl_2 at room temperature to give a dark, sparingly soluble ($CDCl_3$) precipitate, from which no compound could be isolated or identified. Treatment of **1c** with Br_2·dioxane in CH_2Cl_2 at 0 °C also led to formation of a poorly soluble precipitate (grey), but TLC analysis of the supernatant revealed the presence of a number of mobile spots. The least polar of these was isolated by column chromatography. Structural assignment of this product was complicated by the absence of a molecular ion in its mass spectrum and its propensity to decompose to a brown, tarry substance in the solid state, thus precluding elemental analysis. The ^{1}H and ^{13}C NMR spectra are consistent with structure **6**, which is tentatively assigned to the product. The carbon signal at δ 98.9, which is in accord with the bridgehead carbon (an α-bromo ether),[18] rules out a number of other possible di-, tetra-, and hexabromides with the same number of proton and carbon signals. This product does not react with DDQ in toluene at reflux and its reaction with *t*-BuOK immediately affords baseline material (TLC analysis).

If structure **6** is correct, then it would appear that Br_2·dioxane brings about intraannular bond formation in **1c** more quickly than addition of Br_2 to the unsaturated

Scheme 3



bridges. An analogous ring closure is known to occur in [2.2]metacyclophanes to give tetrahydropyrenes.[19] To determine whether this process could be selectively suppressed, the reaction was repeated at −78 °C. In this case, isolation of the least polar spot afforded a brown solid that blackened upon standing. The ^{1}H NMR and mass spectra point toward structure **7**. The formation of this product can be accounted for by conversion of **1c** to **2c** and subsequent formation of the bromonium ion **8**, which undergoes nucleophilic attack by bromide ion to give ketone **9**, a less favorable tautomer of **7**.

In light of the disappointing results using mild bromination reactions, the Friedel−Crafts acylations that had been initially planned were not carried out. Instead, attention was turned to the possibility of performing a directed orthometalation,[20] which does not appear to have any precedent in any [*n*]cyclophane, but which Hopf has shown to be compatible with the [2.2]paracyclophane system.[21] Treatment of a −78 °C solution of **2b** or **2c** with *t*-BuLi (Scheme 3) resulted in the formation of a deep red-orange color. The color was not bleached upon the addition of excess CH_3I but did fade somewhat upon warming of the reaction mixture to room temperature. Subsequent addition of water fully bleached the color. Isolated from these reactions were the pyrene derivatives **10b** (51%) and **10c** (94%). Higher homologues of **2**[12] were unreactive under the same conditions, indicating that, as expected, strain relief is a driving force in these reactions. These products presumably arise through an addition−elimination mechanism that goes through the Meisenheimer-like intermediates **11**. That the presumed lithium alkoxides **12** are not alkylated by CH_3I to any appreciable extent before the aqueous quench is not surprising.[22]

The initial decision to include oxygen atoms in the bridges of pyrenophanes **2b** and **2c** was made in order to keep their syntheses as simple as possible, but it was soon realized that their presence would provide a convenient means for the tether removal in step 3 of our

(16) (a) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; J. Wiley & Sons: New York, 1967; pp 333−334. (b) Buehler, C. A.; Pearson, D. E. *Survey of Organic Syntheses*; Wiley-Interscience: New York, 1971; p 360.

(17) Husstedt, U.; Schafer, H. J. *Tetrahedron Lett.* **1981**, *22*, 623−624.

(18) (a) Kalinowski, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; J. Wiley and Sons: New York, 1988. (b) The calculated chemical shift of this carbon atom in **6** (Chem NMR in the ChemOffice Ultra package of software) is δ 101.6. The remaining calculated ^{13}C NMR resonances for **6** have shifts very similar to those observed.

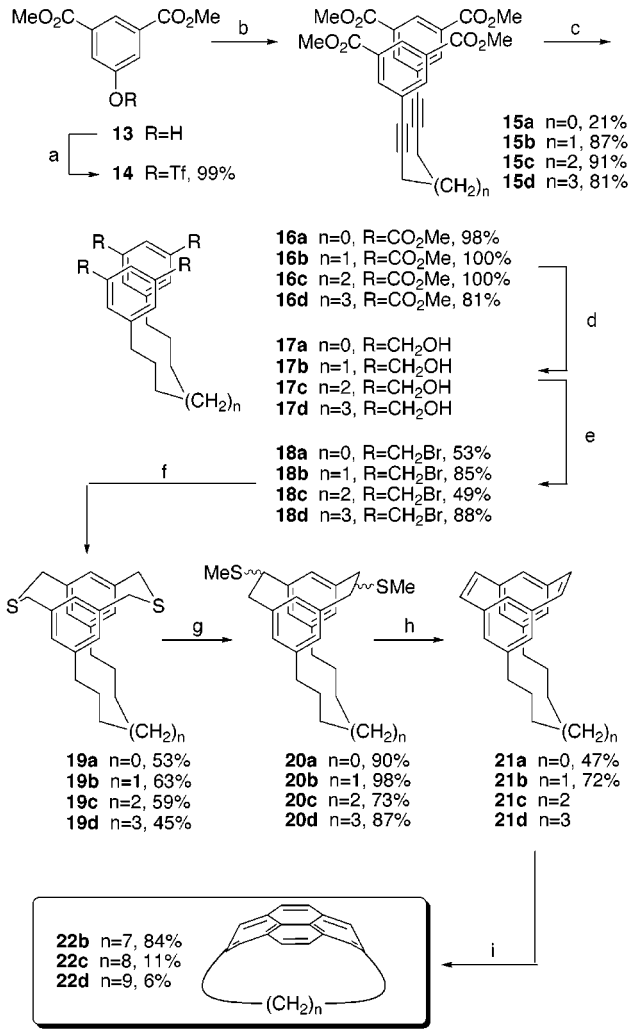
(19) Umemoto, T.; Satani, S.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1975**, 3159−3162. Mitchell, R. H., Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514−1532.

(20) (a) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879−933. (b) Snieckus, V. *Pure Appl. Chem.* **1990**, *62*, 2047−2056.

(21) (a) Pamperin, D.; Schulz, C.; Hopf, H.; Syldatk, C.; Pietzsch, M. *Eur. J. Org. Chem.* **1998**, *63*, 1441−1445. (b) Hopf, H.; Barrett, D. G. *Liebigs Ann.* **1995**, 449−451.

(22) Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1976**, *41*, 1373−1379. (b) Guibe, F.; Bram, G. *Bull. Soc. Chim. Fr.* **1975**, 933−948.

Scheme 4[a]



[a] (a) Tf_2O, pyridine, 0 °C, CH_2Cl_2; (b) 1,5-hexadiyne−1,8-nonadiyne, $Pd(PPh_3)_2Cl_2$, CuI, DBU, rt, benzene; (c) H_2, Pd(OH)/C, rt, ethyl acetate; (d) $LiAlH_4$, reflux, THF; (e) HBr/acetic acid, reflux, yields are from **16**; (f) Na_2S/Al_2O_3, rt, 10% ethanol (abs)/CH_2Cl_2; (g) i. $(MeO)_2CHBF_4$, rt, CH_2Cl_2; ii. *t*-BuOK, rt, THF; (h) i. $(MeO)_2CHBF_4$, rt, CH_2Cl_2; ii. *t*-BuOK, rt, *t*-BuOH/THF yield for **21a**−**b** are from **19a**−**b**; (i) DDQ, reflux, benzene; yields for **22c**−**d** are from **20**.

strategy. Thus it was disappointing that the aryl alkyl ethers cleaved readily during attempted functionalization of the pyrene moiety. Even if milder aromatic substitution reactions could be applied successfully, the bridge would still need to survive subsequent reactions leading to the formation of a more complex polycyclic aromatic system. With the prospects for this looking bleak, work on the substitution of **2b** and **2c** was abandoned in favor of preparing and investigating the analogous systems that lack the oxygen atoms in the bridge. Although the absence of functionality in the bridges of such systems was seen as a potential source of problems in step 3 of the strategy, the inertness of a purely aliphatic tether was expected to at least permit study of the substitution chemistry of the pyrene unit.

Synthesis and Reactions of [*n*](2,7)Pyrenophanes 22. The synthesis of the targeted pyrenophanes **22** (Scheme 4) commenced with the triflation of dimethyl 5-hydroxyisophthalate **13**[23] to give **14** (99%). Coupling of **14** with a series of diynes (1,5-hexadiyne through 1,8-nonadiyne) under Sonogashira conditions[13,24] afforded the diynetetraesters **15a**−**d**. The yields for this reaction were consistently over 80%, except for the one leading to the product with the six-carbon tether **15a** (21%). The volatility of the 1,5-hexadiyne may be responsible for this anomoly. Catalytic hydrogenation of **15a**−**d** afforded tetraesters **16a**−**d** (81−100%) and these were reacted with $LiAlH_4$ to give tetraalcohols **17a**−**d**. Unlike their 1,*n*-dioxa counterparts,[5] they could be isolated in reasonably pure form by extraction into hot ethyl acetate. However, they were sparingly soluble at room temperature and difficult to purify, so they were used without further purification in the next step.

Initial attempts to brominate tetraalcohols **17a**−**d** with 48% aqueous HBr resulted in very low yields of the desired tetrabromides **18a**−**d**, presumably due to insolubility of partially brominated products in the aqueous medium. The use of HBr/HOAc proved to be more effective, giving acceptable yields (53−88%) of **18a**−**d**. Treatment of these with Na_2S/Al_2O_3[25] afforded the dithiacyclophanes **19a**−**d** (45−59%) in slightly lower yield than for their 1,*n*-dioxa analogues.[5,12] Ring contraction was accomplished by an *S*-methylation/Stevens rearrangement protocol that gave isomer mixtures **20a**−**d** (73−98%). The crude products were then *S*-methylated and treated with *t*-BuOK. For **20a** and **20b**, cyclophanedienes **21a** (42% from **19a**) and **21b** (72% from **19b**), were obtained. For **20c** and **20d**, mixtures of products were obtained, one component of which were the pyrenophanes **22c** and **22d** according to both TLC analysis and the ^1H NMR spectrum of the crude product. Treatment of these mixtures with a slight excess of DDQ in reluxing benzene afforded the pyrenophanes **22c** (5% overall from **19c**) and **22d** (2% overall from **19d**). The majority of the losses were suffered during the methylation/Hofmann elimination sequence.[26] We continue to find the yields of this transformation very erratic, but more often than not on the low side.[5,12,25b] Reaction of cyclophanediene **21b** with DDQ led to the formation of pyrenophane **22b** in 84% yield.

As in the case of its 1,*n*-dioxa analogue **1a**,[5] attempted conversion of cyclophanediene **21a** to pyrenophane **22a** led to the return of the starting material almost quantitatively after column chromatography. To more closely monitor this reaction for the formation of traces of **22a**, a small scale run was performed in an NMR tube in C_6D_6. After heating at 75−80 °C for 20 h, some small new signals had appeared, clearly not those of pyrenophane **22a**. Column chromatography of the reaction mixture afforded ca. 1 mg of a product, the ^1H NMR spectrum of which indicated that it was the major product of two similar, possibly isomeric, new products observed in the crude reaction mixture. Traces of what may have been the minor product were obtained, but not enough to allow measurement of its ^1H NMR spectrum. The level of complexity of the ^1H NMR spectrum of the major product

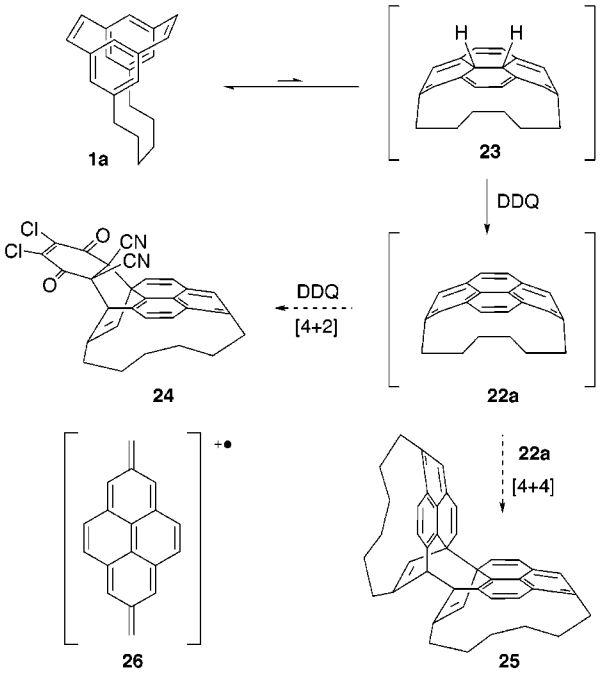
(23) Although this is a commercially available compound, we prepared it from the corresponding diacid. See ref 5.

(24) (a) Ritter, K. *Synthesis* **1993**, 735−762. (b) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379−2411. (c) Ensley, H. E.; Mahadevan, S.; Mague, J. *Tetrahedron Lett.* **1996**, *37*, 6255−6258.

(25) (a) Bodwell, G. J.; Houghton, T. J.; Koury, H. E.; Yarlagadda, B. *Synlett* **1995**, 751−752. See also ref 5 and (b) Bodwell, G. J.; Houghton, T. J.; Kennedy, J. W. J.; Mannion, M. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2121−2123.

(26) Mitchell, R. H. *Heterocycles* **1978**, *11*, 563−568.

Scheme 5



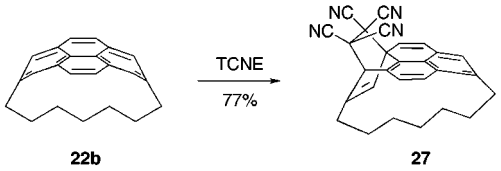
was reminiscent of those of the TCNE adducts **4b** and **27** (vide infra). This might be indicative of a 1:1 DDQ adduct, e.g., **24**, although the absence of signals above 0 ppm tends not to support this. A 2:1 adduct analogous to **5** would not be expected to exhibit signals above 0 ppm but would be expected to exhibit a less complex spectrum than the one observed.

The mass spectrum contains a small peak at $m/z = 568$ (1% relative intensity), double the mass of pyrenophane **22a**. The base peak is observed at $m/z = 284$, which is the correct mass for **22a**. The peak at $m/z = 568$ may be that of a dimer, which, given the complexity of the ^{1}H NMR spectrum, would have to be a symmetrical dimer such as **25**. However, by analogy to **4b** and **27**, such a compound would also be expected to exhibit signals above 0 ppm in its ^{1}H NMR spectrum. Compound **25** could arise by a [4 + 4] cycloaddition between two molecules of **22a** (Scheme 5). Intramolecular [4 + 4] cycloadditions have been reported in strained cyclophanes,[27] but we are unaware of any reports of intermolecular reactions. The strong peak at $m/z = 284$ suggests that, whatever the nature of the isolated compound, it reacts in the mass spectrometer (e.g., retro Diels−Alder for **24**, retro [4 + 4] for **25**) to generate **22a**. That this peak is actually the molecular ion of **22a** is supported by the presence of a strong peak at $m/z = 228$ (90% relative intensity), which is the base peak in the mass spectra of each of the pyrenophanes **22b**−**d**. This corresponds to the quinodimethide ion **26**. Other strong peaks common to **22b**−**d** were also present.

The observation of a minor product, presumably an isomer, is consistent with both **24** and **25**. In the case of **24**, *endo* and *exo* modes of addition are possible, as is cycloaddition at the chlorine-substituted double bond of DDQ. Dimer **25**, which is a *meso* compound, has a (±) diastereoisomer.

The results of the reaction of **21a** with DDQ suggest that its valence isomerization to give dihydropyrene **23** does occur to a small extent and that **23** can be deydrogenated by DDQ to give **22a**, which then undergoes some sort of follow-up reaction. However, not enough evidence is yet available to confidently assign the structure of the end product and its minor isomer. Obtaining such evidence is the subject of current investigations.

Scheme 6



Having successfully prepared pyrenophanes **22b**−**d**, the possibility of functionalizing them was investigated. Analogous to **2b**, **22b** reacted with TCNE (Scheme 6) to give a 1:1 adduct **27** (77%), the structure of which was confirmed crystallographically. With no ether linkages in the bridge to pose a threat of cleavage, Friedel−Crafts acylation (CH_3COCl, $AlCl_3$) of **22b** was attempted. The starting material was consumed rapidly, giving rise to a complex mixture of products. Bearing in mind that even the minimally strained [10]paracyclophane undergoes rearrangement under milder conditions,[28] it is likely that migration, rather than cleavage, of the tether is occurring. In fact Lewis acid catalyzed rearrangements of small cyclophanes to give less strained products are quite common.[29] In the hopes of intentionally generating a less strained pyrenophane (e.g., a (1,8)pyrenophane) **22b** was treated with $AlCl_3$ alone. Unfortunately, another complex mixture was produced. However, the mass spectrum of the crude product mixture contained a cluster of peaks around $m/z = 596$, double that of the molecular ion of **22b** ($m/z = 298$). This suggests that a telomerization, akin to that observed for [6](1,4)naphthalenophane[30a] and [6](1,4)anthracenophane,[30b] took place.

Hopes that bromination would provide the first real progress toward the accomplishment of step 2 were dashed when the reaction of **22b** with Br_2 in CH_2Cl_2 afforded another complex mixture of products. The ^{1}H NMR spectrum of the crude product mixture contained some signals at higher field than δ 0, which suggested that bridge cleavage was at least partially averted. However, no inferences regarding the relative amounts of substitution (if any), addition and bridge migration products could be drawn. Hopf and Noble's observation[31] that [8]paracyclophane, which is not particularly strained, does not undergo substitution when reacted with Br_2/Fe, but rather gives bridge cleavage and bridge migration products serves only to further blacken the outlook for the efficient aromatic substitution of the pyrenophanes.

The lack of success to date in preparing functionalized pyrenophanes, while disappointing, does not mean that

(27) (a) Inoue, T.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1974**, 2969−2972. (b) Tsuji, T.; Ohkita, M.; Konno, T.; Nishida, S. *J. Am. Chem. Soc.* **1997**, *119*, 8425−8431.

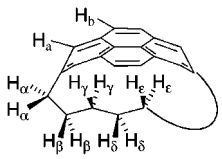
(28) (a) Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: New York, 1964; p 220. (b) Smith, B. H. Ph.D. Thesis, Cornell University, Ithaca, New York, 1960. (c) Stahl, R. E. Ph.D. Thesis, Cornell University, Ithaca, New York, 1954. See also (d) Blomquist, A. T.; Stahl, R. E.; Meinwald, Y. C.; Smith, B. H. *J. Org. Chem.* **1961**, *26*, 1687−1691.

(29) Examples can be found in (a) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983; Vols. 1−2. (b) Vögtle, F. *Cyclophan-Chemie*; Teubner: Stuttgart, 1990. (c) Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: New York, 1964.

(30) (a) Tobe, Y.; Jimbo, M.; Kobiro, K.; Kakiuchi, K. *J. Org. Chem.* **1991**, *56*, 5241−5243. (b) Tobe, Y.; Jimbo, M.; Takahashi, T.; Kobiro, K.; Kakiuchi, K. *J. Am. Chem. Soc.* **1992**, *114*, 3479−3491.

(31) Noble, K.-L.; Hopf, H.; Ernst, L. *Chem. Ber.* **1984**, *117*, 455−473.

Table 1. ^{1}H NMR Chemical Shifts (δ) of Pyrenophanes 22b−d



compound	H_a	H_b	H_α	H_β	H_γ	H_δ	H_ϵ
22b	7.34	7.67	2.30	0.45	−1.38	−1.38	
22c	7.59	7.84	2.59	0.88	−0.69	−1.45	
22d	7.75	7.91	2.84	1.10	0.05	−0.94	−2.08
2b[a]	7.22	7.72		3.31	−0.04	−2.10	
2c[b]	7.44	7.84		3.59	0.10	−1.46	

[a] Reference 5a. [b] Reference 5b.

proposed strategy for the synthesis of Buckybowls can be pronounced a failure. It merely suggests that alternative pathways, such as the introduction of appropriate substituents at an earlier stage in the synthesis, will have to be developed. Work aimed at achieving this goal has been initiated.

NMR Properties of the Pyrenophanes. Assignment of the ^{1}H NMR spectra of the pyrenophanes **22b−d** were made on the basis of NOED and ^{1}H−^{1}H COSY experiments. The results are given in Table 1. Unmistakeable trends as the tether length shortens and the degree of bend in the pyrene unit increases are the movements to higher field of both of the aromatic protons (H_a and H_b), the benzylic protons (H_α), the homobenzylic protons (H_β) and the bis(homo)benzylic protons (H_γ). Regarding the bridge protons H_α, H_β and H_γ, it would appear from simple inspection of models as though they move out of the deshielding zone and/or further into the shieding zone of the pyrene system as the length of the tether decreases. As for the trend in the aromatic protons, the situation is less clear. The notion that diminishing ring current in the increasingly nonplanar aromatic is responsible for the upfield trend in their chemical shift[32] would seem to be at odds with the presence of tether signals at very high field for all of the pyrenophanes prepared to date. The pyrene nucleus clearly still exerts a strong magnetic anisotropic effect, even when it is in a far from planar conformation.

Another interesting observation comes from the comparison of the ^{1}H NMR spectra of **22b** and **22c** with their 1,*n*-dioxa analogues **2b**[5a] and **2c**.[5b] It can be seen that the chemical shifts of the bridge protons H_β and H_γ of any given cyclophane are considerably more different from those of its counterpart than would be expected from just a change in the nature of the benzylic atom. This suggests that a small change in the position of a nucleus in the region of space underneath a bent pyrene, whether it be a consequence of changes in the conformation of the tether or the degree of bend of the pyrene system (vide infra), results in a substantial change in its chemical shift. In other words, this appears to be a region of high magnetic flux.

Pyrenophane Structures. A noteworthy feature of **22b−d** is their high solubility, even in cold pentane, which contrasts that of many pyrene derivatives. This is most likely a consequence of the nonplanarity of the pyrene moieties of the pyrenophanes. This made it difficult to grow crystals for X-ray structure determination and suitable crystals could ultimately only be obtained for **22c** (Figure 1). Nevertheless, this provided the first opportunity to examine the effect of changing atom types in the tether on the degree of bend on the pyrene moiety. The end-to-end bend[5] of **22c** is 80.8°, a full 7.0° smaller than that of its 1,8-dioxa analogue **2c** (87.8°).[5a]

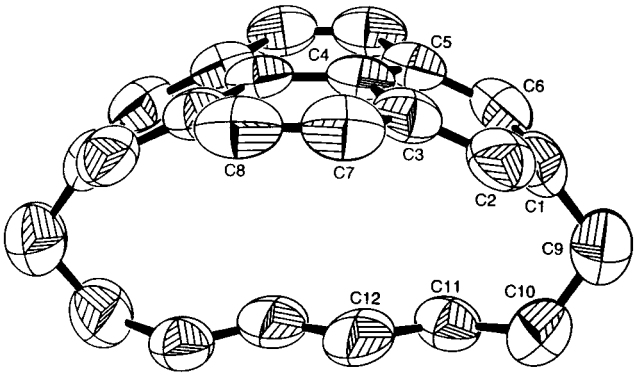


Figure 1. ORTEP drawing of **22c** in the crystal. Carbon eleven was modeled as two disordered carbons, C(11) and C(11a), with occupancies of 0.75 and 0.25, respectively. The angle between the C(1)−C(2)−C(6) plane and its symmetry-related counterpart in the same molecule is 80.8°.

Since C−C bonds are longer than analogous C−O bonds,[33] the effective length of the tether of **22c** would be expected to be slightly greater than that of **2c**. Therefore, it came as no surprise that the pyrene unit of **22c** was less bent than that of **2c**, although the magnitude of the difference was perhaps a little greater than anticipated. The difference in the bond angles about the benzylic O vs C atoms is also a potential contributor to the overall bend of the pyrene system. However, the measured angles at these positions in **2c** (C−O−C = 110.6°) and **22c** (C−C−C = 109.2°) are not substantially different. Thus it would seem that differences in bond lengths exert a more pronounced effect on the degree of bend in the pyrene moiety. This being the case, the judicious incorporation of heteroatoms in the tethers of [*n*](2,7)pyrenophanes should provide a means for fine-tuning the bend of the pyrene unit, much like Bickelhaupt has done for the fine-tuning of the [5]metacyclophane system.[34]

Structures for **22a−d** and their 1,*n*-dioxa analogues **2a−d** were calculated at the AM1 level of theory (MOPAC−Chem3D). The calculated and experimentally determined end-to-end bend angles are presented in Table 2. As in the case of semiempirical (MNDO) calculations on [*n*]metacyclophanes,[35] these AM1 calculations consistently overestimate the degree of bend of the aromatic system. Nevertheless, the pyrenophanes **22** are consistently calculated to be less bent than the corresponding dioxa compounds **2**. In the case of the [8]pyrenophanes

(32) (a) Allinger, N. L.; Freiberg, L. A.; Herman, R. B. Miller, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 1171−1176. See also (b) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100−5104.

(33) For bond length data, see March, J. *Advanced Organic Chemistry*, 4th ed.; J. Wiley and Sons: New York, 1992; p 21.

(34) (a) Bickelhaupt, F.; de Wolf, W. H. *J. Phys. Org. Chem.* **1998**, *11*, 362−376. (b) van Eis, M. J.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1998**, *120*, 3371−3375. (c) Kane, V. V.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1994**, *50*, 4575−4622.

(35) Jenneskens, L. W.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. *J. Comput. Chem.* **1987**, *8*, 1154−1169.

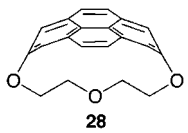
Table 2. Calculated and Experimental Bend Angles (deg) for Pyrenophanes 2a−d and 22a−d

	1,*n*-dioxa series (**2**)		parent series (**22**)	
atoms in tether (series member)	X-ray	calcd	X-ray	calcd
6 (a)	*a*	132.1	*a*	122.9
7 (b)	109.2	113.3	*a*	104.5
8 (c)	87.8	94.9	80.8	87.0
9 (d)	72.9[b]	77.8	*a*	70.3

[a] Crystal structure has not been determined. [b] Reference 12.

2c and **22c**, the only pair for which experimental data for both pyrenophanes is available, the difference between the bend angles of the calculated structures (7.9°) is pleasingly close to that between the observed angles (7.0°). In examining the calculated bend angles, it is evident that the bend angle for each member of the parent series **22** lies approximately halfway between that of its 1,*n*-dioxa analogue and the next higher 1,*n*-dioxa homolog, e.g., the calculated angle for **22b** lies about halfway between those of **2b** and **2c**. Thus, according to calculations, combination of the two pyenophane series provides a means of increasing the bend of the magnitude of pyrene skeleton in consistent increments of about 8−9°.

The structural data may help to put some earlier results in perspective. For a start, the H_β/H_γ chemical shift discrepancy between **22b**−**c** and **2b**−**c** would appear to be a consequence of a significant difference in the degree of bend in the pyrene unit and not of changes in the conformation in the tether. Neither the calculated nor the experimentally determined structure point to major conformational changes. Second, cyclophanediene **1a** showed no signs of conversion to **2a**[5] (calculated bend angle = 132.1°), even when more forcing conditions were employed, whereas there is evidence (vide supra) that **21a** did react under standard conditions to give traces of the less distorted **22a** (calculated bend angle = 122.9°). The next less bent pyrene unit is found in **2b** (calculated bend angle = 113.3°), which is an isolable compound (measured bend angle = 109.2°). Pyrenophane **2b** is also the current record holder for the largest bend angle. If this record is to be broken, then further fine-tuning of the tether will have to be carried out. One possibility is to incorporate another oxygen atom into the tether, giving 1,4,7-trioxa[7](2,7)pyrenophane **28** as a target. The calculated bend angle of this stucture is 117.2°, which is 3.9° greater than that calculated for **2b** and 5.7° less than that calculated for **22a**. Work aimed at the synthesis of **28** has been initiated.



28

Conclusion

A new three step strategy for the synthesis of Buckybowls has been proposed. Step 1 has been successfully completed, but efforts toward accomplishing step 2 have so far been thwarted by tether cleaveage, bridge migration and addition reactions. Effective methods for functionalizing the pyrenophanes or their synthetic precursors will need to be found if step 2 is to be accomplished. Work aimed at achieving these goals is underway.

That subtle changes in the tether have a significant effect on the degree of bend in the pyrene moiety was ascertained from comparisons of calculated and crystallographically derived structural data for **2a**−**d** and **22a**−**d**. On the basis of these comparisons, 1,4,7-trioxa[7](2,7)-pyrenophane **28** was identified as a target that will have a pyrene moiety more bent than that of the current record holder, **2b**.

Experimental Section

General. Reactions were performed under air unless otherwise indicated. THF was distilled from sodium/benzophenone ketyl under N_2 immediately prior to use. Spectroscopic grade benzene was degassed under reduced pressure prior to use. All other solvents and chemicals were used as received. Chromatographic purification was accomplished with 230−400 mesh silica gel. Tlc plates were visualized using a short wave (254 nm) UV lamp. Melting points are uncorrected. Reported multiplicities of ^{1}H NMR signals are apparent. Combustion analyses were performed by the Microanalytical Services Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta.

Reaction of Pyrenophane 2b with PTAD To Give 2:1 Adduct 5b. To a stirred, room-temperature solution of pyrenophane **2b** (0.026 g, 0.085 mmol) in benzene (5 mL) was added PTAD (0.033 g, 0.19 mmol). After stirring for 1 h, the mixture was suction filtrered and the precipitate was rinsed with pentane and dried under high vacuum, leaving **5b** as a fine white powder (0.050 g, 88%): mp >250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.34 (m, 12H), 7.21 (s, 2H), 5.57 (d, J = 2.1 Hz, 2H), 5.08 (d, J = 2.3 Hz, 2H), 4.00−3.85 (m, 4H), 1.43−1.27 (m, 2H), 1.20−1.11 (m, 2H), 0.67−0.53 (m, 1H), 0.17−0.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (some quaternary signals not observed) 171.3, 136.5, 129.1, 128.3, 127.6, 125.6, 121.8, 101.8, 68.6, 59.8, 34.4, 30.0; MS (EI) m/z M^+ not observed, 119 (100).

Reaction of Pyrenophane 2c with PTAD To Give 2:1 Adduct 5c. To a stirred, room-temperature solution of pyrenophane **2c** (0.029 g, 0.092 mmol) in benzene (5 mL) was added PTAD (0.043 g, 0.25 mmol). After stirring for 3 h, the red color of the dienophile had stopped fading and no mobile spots were observed by TLC analysis. Stirring was continued for 21 h, over which no observable change occurred. The mixture was suction filtered and the precipitate was rinsed with pentane and dried under high vacuum, leaving **5c** as a fine white powder (0.062 g, 85%): mp >250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.43, (m, 6H), 7.39−7.35, (m, 6H), 7.25 (s, 2H), 5.65 (d, J = 2.0 Hz, 2H), 5.31 (d, J = 2.0 Hz, 2H), 3.97−3.88 (m, 2H), 3.83−3.74 (m, 2H), 1.33−1.16 (m, 2H), 0.95−0.76 (m, 6H).

Reaction of Cyclophanediene 1c with Br_2·Dioxane at 0 °C To Give 6. To a stirred 0 °C solution of cyclophanediene **1c** (0.150 g, 0.47 mmol) in CH_2Cl_2 (20 mL) was added Br_2·dioxane (0.250 g, 1.03 mmol). A gray precipitate formed immediately and this was removed by suction filtration. Concentration of the filtrate afforded a sticky brown solid. Column chromatography of this mixture (hexanes) afforded a colorless solid (0.060 g), tentatively assigned as **6** (20%), that became brown upon standing: mp 190 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 4H), 5.48 (s, 4H), 3.39−3.37 (m, 4H), 1.10−1.06 (m, 4H), −0.02 to −0.06 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 128.5, 125.9, 98.9, 65.6, 51.0, 29.2, 24.4; MS (EI) m/z M^+ not observed, 80 (100).

Reaction of Cyclophanediene 1c with Br_2·Dioxane at −78 °C To Give 7. To a stirred −78 °C solution of cyclophanediene **1c** (0.059 g, 0.19 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of Br_2·dioxane (0.046 g, 0.19 mmol) in CH_2Cl_2 (10 mL). After the starting material had been consumed (TLC analysis), aqueous 5% $Na_2S_2O_3$ solution (10 mL) was added and the mixture was allowed to warm to room temperature. The organic layer was separarted and washed with

saturated NaCl solution (20 mL), dried ($MgSO_4$) and solvents were removed under reduced pressure. Column chromatography of the residue (40% CH_2Cl_2/hexanes) afforded a brown solid (20 mg), tentatively assigned as **7** (22%), that darkened upon standing: mp 92−94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, J = 9.2 Hz, 1H), 8.08 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.80 (s, 1H), 7.72 (s, 2H), 6.05 (s, 1H), 4.25 (t, J = 6.4 Hz, 2H), 3.46 (t, J = 6.8 Hz, 2H), 1.99−1.91 (m, 4H), 1.62−1.56 (m, 4H); MS (EI) m/z 478 (43), 476 (84, M^+ $^{81}Br^{79}Br$), 474 (40), 314 (98), 312 (100).

7-*tert*-Butyl-2-(5-hydroxypentoxy)pyrene (10b). To a −78 °C solution of pyrenophane **2b** (0.025 g, 0.083 mmol) in THF (20 mL) under N_2 was added *t*-BuLi (1.0 M in pentane, 0.2 mL, 0.2 mmol) and the reaction was stirred at −78 °C for 1 h. Dry CH_3I (1 mL) was added and the mixture was allowed to warm to room temperature. The reaction was quenched with water (ca.1 mL) and then poured into a separatory funnel containing water (25 mL) and CH_2Cl_2 (25 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (25 mL). The combined organic layers were washed with saturated NaCl solution (25 mL), dried ($MgSO_4$) and the solvents were removed under reduced pressure. Column chromatography (CH_2Cl_2) afforded **10b** (0.015 g, 51%) as an off-white solid: mp 108−112 °C; IR ($CHCl_3$) 3620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 2H), 8.02 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 9.0 Hz, 2H), 7.67 (s, 2H), 4.25 (t, J = 6.2 Hz, 2H), 3.73−3.69 (m, 2H), 1.98−1.93 (m, 2H), 1.73−1.65 (m, 4H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 147.9, 132.4, 130.0, 128.2, 126.7, 122.9, 122.4, 120.0, 110.7, 68.2, 62.9, 35.1, 32.5, 31.9, 29.2, 22.5; MS (EI) m/z 360 (93, M^+), 259 (100).

7-*tert*-Butyl-2-(6-hydroxyhexoxy)pyrene (10c). Using the procedure described for **10b** above, pyrenophane **2c** (0.040 g, 0.17 mmol) and *t*-BuLi (1.0 M, 0.2 mL, 0.2 mmol) afforded **10c** (0.055 mg, 94%) as a pale brown solid: mp 95−97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 2H), 8.02 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 9.0 Hz, 2H), 7.67 (s, 2H), 4.25 (t, J = 6.5 Hz, 2H), 3.71−3.67 (m, 2H), 1.95−1.91 (m, 2H), 1.67−1.50 (m, 6H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 147.9, 132.4, 130.0, 128.1, 126.7, 122.9, 122.4, 120.0, 110.7, 68.3, 63.0, 35.1, 32.7, 32.0, 29.7, 26.0, 25.6; MS (EI) m/z 374 (100, M^+). Anal. Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.07; H, 8.08.

3,5-Bis(methoxycarbonyl)phenyl Triflate (14). To a 0 °C solution of dimethyl 5-hydroxyisophthalate **13** (21.39 g, 101.8 mmol) and pyridine (12.0 mL, 148 mmol) in CH_2Cl_2 (450 mL) under N_2 was added by syringe trifluoromethanesulfonic anhydride (18.0 mL, 105 mmol). The mixture was stirred for 20 min and then quenched with 5% HCl solution (100 mL). The layers were separated and the organic layer was washed with 1 M HCl solution (200 mL), saturated $NaHCO_3$ solution (200 mL), saturated NaCl solution (200 mL), dried ($MgSO_4$) and the solvents were removed under reduced pressure. The residue was taken up in CH_2Cl_2 and passed through a ca. 10 cm plug of silica. Removal of the solvent under reduced pressure afforded **14** (34.45 g, 99%) as a white solid: mp 68.5−69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.13 (s, 2H), 4.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 149.2, 133.0, 130.3, 126.5, 118.6 (q, J_{C-F} = 320 Hz), 52.8; MS (EI) m/z 342 (52, M^+), 311 (100). Anal. Calcd for $C_{11}H_9F_3O_7S$: C, 38.60; H, 2.65. Found: C, 38.55; H, 2.49.

General Procedure for the Preparation of Diynetetraesters 15a−d. To a degassed solution of triflate **14**, the appropriate diyne and DBU in benzene under N_2 was added $Pd(PPh_3)Cl_2$ and CuI and the reaction was stirred at room temperature for 24 h. The mixture was washed with 1 M HCl solution (2 × ca. 100 mL), brine (ca.100 mL), dried ($MgSO_4$) and the solvents were removed under reduced pressure. The residue was then chromatographed (CH_2Cl_2). Samples for analysis were obtained by recrystallization.

1,6-Bis(3,5-bis(methoxycarbonyl)phenyl)-1,5-hexadiyne (15a). Triflate **14** (6.85 g, 20.0 mmol), 1,5-hexadiyne (0.80 g, 10 mmol), DBU (3.60 g, 23.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.30 g, 0.43 mmol) and CuI (0.50 g, 2.63 mmol) in benzene (60 mL) afforded **15a** (0.99 g, 21%) as a colorless solid: mp 133−135 °C (cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 2H), 8.25 (s, 4H), 3.94 (s, 12H), 2.77 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 136.9, 130.8, 129.7, 124.5, 90.2, 80.0, 52.4, 19.5; MS (EI) m/z 462 (6, M^+), 231 (100). Anal. Calcd for $C_{26}H_{22}O_8$: C, 67.53; H, 4.79. Found: C, 67.49; H, 4.80.

1,7-Bis(3,5-bis(methoxycarbonyl)phenyl)-1,6-heptadiyne (15b). Triflate **14** (31.29 g, 91.42 mmol), 1,6-heptadiyne (4.01 g, 43.4 mmol), DBU (17.5 g, 115 mmol), $Pd(PPh_3)_2Cl_2$ (0.86 g, 1.20 mmol) and CuI (0.86 g, 4.52 mmol) in benzene (400 mL) afforded **15b** (19.00 g, 87%) as a colorless solid: mp 105−107 °C (ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 2H), 8.24 (s, 4H), 3.95 (s, 12H), 2.64 (t, J = 7.0 Hz, 4H), 1.94 (quintet, J = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 136.6, 130.7, 129.6, 124.8, 91.2, 79.6, 52.5, 27.4, 18.6; MS (EI) m/z 476 (68, M^+), 411 (100). Anal. Calcd for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 67.61; H, 4.81.

1,8-Bis(3,5-bis(methoxycarbonyl)phenyl)-1,7-octadiyne (15c). Triflate **14** (33.19 g, 96.98 mmol), 1,7-octadiyne (5.15 g, 48.5 mmol), DBU (18.3 g, 120 mmol), $Pd(PPh_3)_2Cl_2$ (0.90 g, 1.28 mmol) and CuI (0.90 g, 4.73 mmol) in benzene (400 mL) afforded **15c** (20.48 g, 91%) as a colorless solid: mp 105−107 °C (2:3 toluene/cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 2H), 8.23 (s, 4H), 3.94 (s, 12H), 2.53−2.50 (m, 4H), 1.84−1.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 136.5, 130.7, 129.5, 124.9, 91.9, 79.2, 52.5, 27.6, 19.0; MS (EI) m/z 490 (100, M^+). Anal. Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 69.03; H, 5.22.

1,9-Bis(3,5-bis(methoxycarbonyl)phenyl)-1,8-nonadiyne (15d). Triflate **14** (7.49 g, 21.9 mmol), 1,8-nonadiyne (1.31 g, 10.9 mmol), DBU (4.12 g, 27.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.30 g, 0.43 mmol) and CuI (0.40 g, 2.1 mmol) in benzene (100 mL) afforded **15d** (4.45 g, 81%) as a waxy, pale yellow solid: mp 80−85 °C (1:1 toluene/cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (s, 2H), 8.20 (s, 4H), 3.94 (s, 12H), 2.48−2.44 (m, 4H), 1.69−1.66 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 136.5, 130.6, 129.3, 124.6, 92.3, 79.0, 52.4, 28.0, 27.9, 19.2; MS (EI) m/z 504 (100, M^+). Anal. Calcd for $C_{29}H_{28}O_8$: C, 69.04; H, 5.59. Found: C, 69.04; H, 5.64.

General Procedure for the Preparation of Tetraesters 16a−d. Pd(OH)/C (Pearlman's catalyst) was added to a solution of diynetetraester **15** in ethyl acetate and the mixture was stirred under an atmosphere of hydrogen for 20 min. The flask was subjected to reduced pressure and let down to nitrogen several times before being filtered through a plug of Celite. Removal of the solvent afford tetraesters **16a−d**, which were sufficiently pure for use in the following step. Samples for analysis were obtained by recrystallization.

1,6-Bis(3,5-bis(methoxycarbonyl)phenyl)hexane (16a). Diynetetraester **15a** (0.90 g, 1.9 mmol) and Pearlman's catalyst (0.50 g) in ethyl acetate (200 mL) afforded tetraester **16a** (0.90 g, 98%) as a colorless solid: mp 119−121.5 °C (1:1 ether/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.04 (s, 4H), 3.94 (s, 12H), 2.67 (t, J = 7.5 Hz, 4H), 1.65−1.61 (m, 4H), 1.39−1.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 143.4, 133.6, 130.3, 128.0, 52.1, 35.3, 31.0, 29.3; MS (EI) m/z 470 (6, M^+), 438 (100). Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.37; H, 6.43. Found: C, 65.95; H, 6.44.

1,7-Bis(3,5-bis(methoxycarbonyl)phenyl)heptane (16b). Diynetetraester **15b** (9.55 g, 20.0 mmol) and Pearlman's catalyst (1.40 g) in ethyl acetate (250 mL) afforded tetraester **16b** (9.67 g, 100%) as a colorless solid: mp 89−91 °C (ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.04 (s, 4H), 3.94 (s, 12H), 2.70 (t, J = 7.6 Hz, 4H), 1.67−1.63 (m, 6H), 1.35 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 143.5, 133.7, 130.4, 128.1, 52.2, 35.4, 31.1, 29.1, 28.9; MS (EI) m/z 484 (7, M^+), 189 (100). Anal. Calcd for $C_{27}H_{32}O_8$: C, 66.93; H, 6.66. Found: C, 66.76; H, 6.74.

1,8-Bis(3,5-bis(methoxycarbonyl)phenyl)octane (16c). Diynetetraester **15c** (9.00 g, 18.3 mmol) and Pearlman's catalyst (1.20 g) in ethyl acetate (250 mL) afforded tetraester **16c** (9.14 g, 100%) as a colorless solid: mp 80.5−83 °C (1:1 toluene/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.05 (s, 4H), 3.94 (s, 12H), 2.70 (t, J = 8.0 Hz, 4H), 1.64−1.60 (m, 4H), 1.31 (br s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9,

143.6, 133.3, 130.1, 127.8, 51.8, 35.1, 30.8, 28.9, 28.8; MS (EI) *m*/*z* 498 (2, M^+), 189 (100). Anal. Calcd for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87. Found: C, 67.58; H, 7.01.

1,9-Bis(3,5-bis(methoxycarbonyl)phenyl)nonane (16d). Diynetetraester **15d** (4.35 g, 8.62 mmol) and Pearlman's catalyst (0.50 g) in ethyl acetate (300 mL) afforded tetraester **16d** (3.60 g, 81%) as a colorless solid: mp 62.5−64 °C (cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.05 (s, 4H), 3.94 (s, 12H), 2.70 (t, J = 7.1 Hz, 4H), 1.67−1.61 (m, 4H), 1.30 (br s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 143.7, 133.8, 130.5, 128.2, 52.3, 35.5, 31.2, 29.7, 29.3, 29.1; MS (EI) *m*/*z* 512 (2, M^+), 448 (100). Anal. Calcd for $C_{29}H_{36}O_8$: C, 67.95; H, 7.08. Found: C, 67.95; H, 7.30.

General Procedure for the Preparation of Tetrabromides 18a−d. To a stirred 0 °C suspension of $LiAlH_4$ in THF (100 mL) was added dropwise a solution of the tetraester **16** in THF (100 mL) under nitrogen. The reaction was held at reflux for 15 h and then cooled to 0 °C. The reaction was quenched by the slow addition of ethyl acetate (300 mL) and then 1 M HCl solution (100 mL). After stirring for 1 h, the layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with saturated NaCl solution (100 mL), dried ($MgSO_4$) and concentrated to afford the tetraalcohol **17**, which was used immediately in the following step.

The tetraalcohol **17** thus obtained was suspended in glacial acetic acid (50 mL). To this was added 30% HBr in acetic acid and the mixture was heated at reflux for 12−16 h. After cooling to room temperature, water (50 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water (50 mL), saturated $NaHCO_3$ solution (50 mL), saturated NaCl solution (50 mL), dried ($MgSO_4$) and the solvents were removed under reduced pressure. Chromatographic separation (40% CH_2Cl_2/hexanes) of the resulting brown oil afforded the tetrabromide **18**.

1,6-Bis(3,5-bis(bromomethyl)phenyl)hexane (18a). $LiAlH_4$ (1.87 g, 49.3 mmol) and tetraester **16a** (1.90 g, 4.04 mmol) gave tetraalcohol **17a** (1.20 g, 83%) as a light gray solid. Reaction of **17a** (1.14 g, 3.18 mmol) with 30% HBr/HOAc (5.0 mL, 25 mmol) afforded tetrabromide **18a** (1.24 g, 53% from **16a**) as a colorless solid: mp 73−74 °C (ether/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 2H), 7.13 (s, 4H), 4.44 (s, 8H), 2.58 (t, J = 7.4 Hz, 4H), 1.61−1.57 (m, 4H), 1.38−1.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.2, 129.1, 126.9, 35.5, 33.1, 31.0, 29.0; MS (EI) *m*/*z* M^+ not observed, 197 (100). Anal. Calcd for $C_{22}H_{26}Br_4$: C, 43.31; H, 4.30. Found: C, 43.49; H, 4.31.

1,7-Bis(3,5-bis(bromomethyl)phenyl)heptane (18b). $LiAlH_4$ (8.40 g, 221 mmol) and tetraester **16b** (9.07 g, 18.7 mmol) gave tetraalcohol **17b** (8.62 g, >100%) as a light gray solid. Reaction of **17b** (6.97 g) with 30% HBr/HOAc (25 mL, 125 mmol) afforded tetrabromide **18b** (9.90 g, 85% from **16b**) as a colorless solid: mp 59−64 °C (heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 2H), 7.12 (s, 4H), 4.42 (s, 8H), 2.57 (t, J = 7.5 Hz, 4H), 1.61−1.57 (m, 4H), 1.32 (br s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.1, 129.1, 126.8, 35.4, 33.1, 31.0, 29.1, 29.0; MS (EI) *m*/*z* 660 (3), 658 (11), 656 (16, M^+ ^{81}Br^{81}Br^{79}Br-^{79}Br), 654 (11), 652 (3). Anal. Calcd for $C_{23}H_{28}Br_4$: C, 44.26; H, 4.52. Found: C, 44.33; H, 4.51.

1,8-Bis(3,5-bis(bromomethyl)phenyl)octane (18c). $LiAlH_4$ (8.42 g, 222 mmol) and tetraester **16c** (8.70 g, 17.4 mmol) gave tetraalcohol **17c** (6.69 g, 99%) as a light gray solid. Reaction of **17c** (3.44 g) with 30% HBr/HOAc (6.0 mL, 30 mmol) afforded tetrabromide **18c** (2.78 g, 49% from **16c**) as a colorless solid: mp 85−86 °C (heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 2H), 7.14 (s, 4H), 4.46 (s, 8H), 2.59 (t, J = 7.5 Hz, 4H), 1.63−1.57 (m, 4H), 1.32 (br s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 138.2, 129.2, 126.9, 35.6, 33.1, 31.1, 29.3, 29.2; MS (EI) *m*/*z* M^+ not observed, 199 (100). Anal. Calcd for $C_{24}H_{30}Br_4$: C, 45.17; H, 4.74. Found: C, 45.43; H, 4.69.

1,9-Bis(3,5-bis(bromomethyl)phenyl)nonane (18d). $LiAlH_4$ (1.94 g, 51.1 mmol) and tetraester **16d** (2.32 g, 4.53 mmol) gave tetraalcohol **17d** (1.53 g, 85%) as a light gray solid. Reaction of **17d** (1.50 g, 3.74 mmol) with 30% HBr/HOAc (7.0 mL, 35.0 mmol) afforded tetrabromide **18d** (2.14 g, 88% from **16d**) as a colorless solid: mp 69−71.5 °C (toluene/heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.12 (s, 4H), 4.41 (s, 8H), 2.56 (t, J = 8.0 Hz, 4H), 1.63−1.57 (m, 4H), 1.32 (br s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.0, 129.0, 126.8, 35.5, 33.1, 31.1, 31.0, 29.2, 29.1; MS (EI) *m*/*z* M^+ not observed, 197 (100). Anal. Calcd for $C_{25}H_{32}Br_4$: C, 46.04; H, 4.95. Found: C, 46.05; H, 4.82.

General Procedure for the Preparation of the Dithiacyclophanes 19a−d. To a solution of the tetrabromide **18** in 10% ethanol (abs)/CH_2Cl_2 was added Na_2S/Al_2O_3[25a] in four roughly equal portions over 1 h. After stirring at room teperature overnight, the reaction mixture was suction filtered and the solvents were removed under reduced pressure. Column chromatography (1:1 CH_2Cl_2/hexanes) of the residue afforded the thiacyclophane **19**, a small portion of which was recrystallized for analysis.

***syn*-14,23-Dithia[6.3.3](1,3,5)benzenophane (19a).** Tetrabromide **18a** (1.12 g, 1.84 mmol) and Na_2S/Al_2O_3 (2.50 g, 6.60 mmol) in 10% ethanol (abs)/CH_2Cl_2 (250 mL) afforded dithiacyclophane **19a** (0.35 g, 53%) as a colorless solid: mp 147−149 °C (1:1 ether/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 2H), 6.59 (s, 4H), 3.77 (d, J = 15.1 Hz, 4H), 3.70 (d, J = 15.0 Hz, 4H), 2.39−2.35 (m, 4H), 1.55−1.51 (m, 4H), 0.99−0.96 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 136.8, 128.4, 127.1, 38.8, 35.5, 28.7, 28.0; MS (EI) *m*/*z* 354 (100, M^+). Anal. Calcd for $C_{22}H_{26}S_2$: C, 74.53; H, 7.39. Found: C, 74.06; H, 7.52.

***syn*-15,24-Dithia[7.3.3](1,3,5)benzenophane (19b).** Tetrabromide **18b** (4.31 g, 6.91 mmol) and Na_2S/Al_2O_3 (11.0 g, 24.2 mmol) in 10% ethanol (abs)/CH_2Cl_2 (1500 mL) afforded dithiacyclophane **19b** (1.60 g, 63%) as a colorless solid: mp 145.5−146.5 °C (1:1 ether/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 6.65 (s, 4H), 3.83 (d, J = 15.3 Hz, 4H), 3.77 (d, J = 15.3 Hz, 4H), 2.37−2.33 (m, 4H), 1.56−1.52 (m, 4H), 1.16−1.08 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 137.0, 128.7, 127.1, 39.2, 34.1, 28.8, 26.5, 26.3; MS (EI) *m*/*z* 368 (100, M^+). Anal. Calcd for $C_{23}H_{28}S_2$: C, 74.95; H, 7.66. Found: C, 75.07; H, 7.86.

***syn*-16,25-Dithia[8.3.3](1,3,5)benzenophane (19c).** Tetrabromide **18c** (5.00 g, 7.84 mmol) and Na_2S/Al_2O_3 (9.87 g, 27.4 mmol) in 10% ethanol (abs)/CH_2Cl_2 (2000 mL) afforded dithiacyclophane **19c** (1.67 g, 56%) as a colorless solid: mp 119−121 °C (heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.66 (s, 4H), 3.84 (s, 8H), 2.42−2.38 (m, 4H), 1.44−1.28 (m, 8H), 1.03−0.98 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 138.6, 127.4, 120.3, 39.7, 35.5, 29.4, 26.0, 24.5; MS (EI) *m*/*z* 382 (100, M^+). Anal. Calcd for $C_{24}H_{30}S_2$: C, 75.34; H, 7.90. Found: C, 75.04; H, 8.08.

***syn*-17,26-Dithia[9.3.3](1,3,5)benzenophane (19d).** Tetrabromide **18d** (1.76 g, 2.70 mmol) and Na_2S/Al_2O_3 (3.14 g, 7.85 mmol) in 10% ethanol (abs)/CH_2Cl_2 (500 mL) afforded dithiacyclophane **19d** (0.48 g, 45%) as a colorless solid: mp 158−159 °C (1:1 toluene/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.64 (s, 4H), 3.83 (d, J = 14.9 Hz, 4H), 3.77 (d, J = 15.0 Hz, 4H), 2.39−2.35 (m, 4H), 1.58−1.49 (m, 4H), 1.31 (br s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 137.1, 128.7, 126.4, 39.1, 33.9, 27.4, 26.4, 25.4, 24.8; MS (EI) *m*/*z* 396 (80, M^+), 158 (100). Anal. Calcd for $C_{25}H_{32}S_2$: C, 75.70; H, 8.13. Found: C, 75.76; H, 8.37.

[6.2.2](1,3,5)Benzenophane-13,21-diene (21a). To a stirred solution of dithiacyclophane **19a** (0.32 g, 0.90 mmol) in CH_2Cl_2 (50 mL) under N_2 was added $(MeO)_2CHBF_4$ (0.3 mL, 0.3 mmol) and the mixture was stirred for 1 h. The solvent was removed under reduced pressure, ethyl acetate (10 mL) was added. The mixture was then stirred for a further 20 min and suction filtered. The solid was washed with cold ethyl acetate (5 mL) and dried under vacuum to yield a bis(sulfonium tetrafluoroborate) salt (0.51 g). This was slurried in THF (50 mL) under N_2 and *t*-BuOK (0.43 g, 3.8 mmol) was added. The mixture was stirred overnight and the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 (50 mL).and washed with 1 M HCl solution (50 mL), water (50 mL) and saturated NaCl solution (50 mL). The resulting solution was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was passed through a

short plug of silica (CH_2Cl_2) and concentration of the eluate afforded a mixture of bis(methylthio)cyclophane isomers **20a** (0.31 g, 90% from **19a**) as a foamy, colorless solid. This was dissolved in CH_2Cl_2 (20 mL) and $(MeO)_2CHBF_4$ (0.25 mL, 0.25 mmol) was added. The mixture was stirred under N_2 for 6 h and the solvent was under reduced pressure. The resulting oily brown residue was slurried in 1:1 *t*-BuOH/THF (50 mL) and to this mixture was added *t*-BuOK (0.40 g, 3.6 mmol). After stirring under N_2 overnight, the solvents were removed under reduced pressure and to the residue was added water (20 mL) and CH_2Cl_2 (50 mL). The organic layer was extracted with 1 M HCl solution (2 × 50 mL), water (50 mL), saturated NaCl solution (50 mL), dried ($MgSO_4$) and concentrated under reduced pressure to afford a yellow-brown oil. Column chromatography (35% CH_2Cl_2/hexanes) afforded cyclophanediene **21a** (0.11 g, 47% from isomer mixture **20a**) as a colorless solid: mp 60.5−65.5 °C (sublimed); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.12 (s, 4H), 6.36 (s, 4H), 2.37−2.33 (m, 4H), 1.48−1.42 (m, 4H), 0.72−0.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 136.8, 136.1, 133.8, 126.3, 35.5, 30.1, 28.7; MS (EI) *m*/*z* 286 (82, M^+), 215 (100). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 91.98; H, 7.74.

[7.2.2](1,3,5)Benzenophane-14,22-diene (21b). Using the procedure described above for **21a**, dithiacyclophane **19b** (4.40 g, 11.9 mmol) and $(MeO)_2CHBF_4$ (3.0 mL, 30 mmol) gave a bis(sulfonium tetrafluoroborate) salt (6.70 g) and treatment of this with *t*-BuOK (4.06 g, 36.2 mmol) afforded isomer mixture **20b** (4.53 g, 98% from **19b**) as a foamy, colorless solid. Reaction of this mixture with $(MeO)_2CHBF_4$ (3.1 mL, 29 mmol) and then *t*-BuOK (6.41 g, 57.1 mmol) afforded, after column chromatography (20% CH_2Cl_2/hexanes), cyclophanediene **21b** (2.46 g, 72% from isomer mixture **20b**) as a colorless solid: mp 82−84 °C (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.19 (s, 4H), 6.40 (s, 4H), 2.30−2.26 (m, 4H), 1.46−1.43 (m, 4H), 0.86−0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 136.9, 135.8, 132.8, 125.7, 34.7, 30.7, 27.8, 26.9; MS (EI) *m*/*z* 300 (47, M^+), 215 (100). Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.97; H, 8.08.

[7](2,7)Pyrenophane (22b). To a stirred, degassed solution of cyclophanediene **21b** (1.66 g, 5.52 mmol) in benzene (100 mL) under N_2 was added DDQ (1.61 g, 7.09 mmol) and the mixture was heated at reflux for 3 h. After cooling, the mixture was suction filtered, the solvent was removed under reduced pressure and the residue taken up in a mixture of CH_2Cl_2 (50 mL) and water (20 mL). The organic layer was washed with 1 M HCl solution (2 × 50 mL), 1 M NaOH solution (50 mL), saturated NaCl solution (50 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was subjected to column chromatography (5% CH_2Cl_2/hexanes) to provide pyrenophane **22b** (1.18 g, 71%) as a colorless solid: mp 151.5−153 °C (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.34 (s, 4H), 2.32−2.28 (m, 4H), 0.47−0.43 (m, 4H), −1.35 to −1.41 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 131.7, 130.3, 129.9, 126.4, 35.7, 33.2, 31.4, 23.5; MS (EI) *m*/*z* 298 (36, M^+), 241 (27), 229 (24), 228 (100), 215 (34). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.29; H, 7.59.

[8](2,7)Pyrenophane (22c). Using the procedure described above for **21a**, dithiacyclophane **19c** (11.75 g, 30.75 mmol) and $(MeO)_2CHBF_4$ (8.0 mL, 74 mmol) gave a bis(sulfonium tetrafluoroborate) salt (20.37 g) and treatment of this with *t*-BuOK (10.40 g, 92.7 mmol) afforded isomer mixture **20c** (9.24 g, 73% from **19c**) as a foamy, colorless solid. Reaction of this mixture with $(MeO)_2CHBF_4$ (6.1 mL, 56 mmol) and then *t*-BuOK (13.0 g, 116 mmol) afforded, after column chromatography (hexanes), a mixture of products (1.50 g). Reaction of this mixture with DDQ (1.30 g, 5.72 mmol) in benzene (100 mL) at reflux for 3 h followed by gravity filtration, concentration under reduced pressure and column chromatography (hexanes) of the residue afforded pyrenophane **22c** (0.78 g, 11% from isomer mixture **20c**) as a colorless solid: mp 175.5−176.5 °C (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 4H), 7.59 (s, 4H), 2.61−2.57 (m, 4H), 0.92−0.84 (m, 4H), −0.67 to −0.70 (m, 4H), −1.43 to −1.48 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 131.3, 128.9, 127.8, 126.6, 35.9, 31.7, 31.1, 23.5; MS (EI) *m*/*z* 312 (41, M^+), 229 (25), 228 (100), 215 (32). Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.80.

[9](2,7)Pyrenophane (22d). Using the procedure described above for **21a**, dithiacyclophane **19d** (0.43 g, 1.1 mmol) and $(MeO)_2CHBF_4$ (0.35 mL, 0.36 mmol) gave a bis(sulfonium tetrafluoroborate) salt (0.60 g) and treatment of this with *t*-BuOK (0.35 g, 3.1 mmol) afforded isomer mixture **20d** (0.40 g, 87% from **19d**) as a foamy, colorless solid. Reaction of this mixture with $(MeO)_2CHBF_4$ (0.3 mL, 0.3 mmol) and then *t*-BuOK (0.60 g, 5.4 mmol) afforded, after column chromatography (hexanes), a mixture of products. Reaction of this mixture with DDQ (0.60 g, 2.6 mmol) in benzene (20 mL) at reflux for 3 h followed by gravity filtration, concentration under reduced pressure and column chromatography (hexanes) of the residue afforded pyrenophane **22d** (0.020 g, 6% from isomer mixture **20d**) as a colorless solid: mp 213-215.5 °C (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, 4H), 7.75 (s, 4H), 2.86−2.82 (m, 4H), 1.14−1.06 (m, 4H), 0.29−0.20 (m, 4H), −0.90 to −0.97 (m, 2H), −2.03 to −2.14 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 131.3, 127.6, 126.7, 126.2, 36.3, 30.8, 29.7, 29.3, 25.2; MS (EI) *m*/*z* 327 (26), 326 (97, M^+), 240 (23), 229 (31), 228 (100), 215 (45). Anal. Calcd for $C_{25}H_{26}$: C, 91.96; H, 8.04. Found: C, 91.81; H, 8.11.

Reaction of Cyclophanediene 21a with DDQ. A solution of **21a** (0.025 g, 0.087 mmol) and DDQ (0.020 g, 0.088 mmol) in C_6D_6 (1 mL) was heated at 70−80 °C under nitrogen in an NMR tube for 20 h. The solvent was removed under reduced pressure and the residue was chromatographed (hexanes) to afford **21a** (0.023 g, 92% recovery) and then an off-white solid (ca. 1 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.22−7.10 (m, 6H), 6.75 (s, 1H), 6.29−6.25 (m, 3H), 5.14−5.10 (m, 1H), 2.56−2.49 (m, 1H), 2.16−1.97 (m, 2H), 1.80−1.69 (m, 1H), 1.60−1.50 (m, 1H), 1.27−1.15 (m, 1H), 1.05−0.97 (m, 1H), 0.87−0.78 (m, 1H), 0.30−0.15 (m, 2H); MS (EI) *m*/*z* 568 (1), 478 (7), 285 (29), 284 (100), 269 (20), 256 (19), 255 (68), 253 (20), 252 (19), 241 (54), 240 (39), 239 (61), 230 (26), 229 (38), 228 (90), 227 (24), 226 (34), 216 (55), 215 (86), 203 (21), 202 (36).

Reaction of [7](2,7)Pyrenophane 22b with TCNE To Give Adduct 27. A solution of pyrenophane **22b** (0.130 g, 0.436 mmol) and TCNE (0.056 g, 0.43 mmol) in benzene (20 mL) was stirred for 1 h. Cooling the mixture on a water bath resulted in the formation of colorless crystals, which were isolated by gravity filtration (0.041 g, 22%). Concentration of the filtrate afforded a second crop of crystals (0.10 g, 55%; total yield = 77%) of **27**: mp 110 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.5 Hz, 1H), 7.59 (s, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 9.9 Hz, 1H), 7.15 (s, 1H), 6.70 (d, J = 9.9 Hz, 1H), 5.99 (s, 1H), 4.43 (s, 1H), 3.11−3.04 (m, 1H), 2.39−2.33 (m, 2H), 1.94−1.72 (m, 2H), 1.09−0.80 (m, 3H), 0.42−0.28 (m, 1H), 0.20−0.00 (m, 1H), −0.29 to −0.36 (m, 1H), −0.48 to −0.62 (m, 1H), −0.86 to −0.96 (m, 1H), −1.37 to −1.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) (prominent peaks, some decomposition apparent) δ 153.3, 141.5, 135.1, 133.9, 130.3, 130.1, 128.0, 124.6, 122.8, 120.3, 111.8, 54.6, 53.7, 35.3, 34.8, 31.6, 30.6, 26.3, 24.5.

Crystal Data for 22c. Colorless irregular crystal (approximately 0.30 × 0.10 × 0.35 mm) from heptane, $C_{24}H_{24}$, M = 320.47, monoclinic, $C2/c$ (#15), Z = 4, a = 19.540 (2), b = 7.454 (1), c = 14.023 (2) Å, β = 120.372 (7)°, V = 1762.2 (4) Å^3, D_c = 1.178 g cm^{-3}, F(000) = 672, μ (Cu Kα) = 4.94 cm^{-1}. Data collection at 26 ± 1 °C with a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation (λ = 1.54178 Å), ω-2θ scan type with ω scan width = 1.57 + 0.14 tan θ, ω scan speed 4.0° min^{-1} (up to 10 rescans for weak reflections), 1484 reflections measured, 1434 unique (R_{int} = 0.009), empirical absorption correction (max., min. corrections = 1.00, 0.88) and secondary extinction correction (coefficient, 1.80917 × 10^{-6}), giving 994 with $I > 2\sigma(I)$. Solution and refinement by direct methods using the teXsan package of the Molecular Structure Corporation; all non-hydrogen atoms were refined anisotropically; full matrix least squares refinement with 119 variable parameters led to R = 0.066 and R_w = 0.056, GOF = 4.05. Carbon eleven, was modeled as two disordered carbons, C(11) and C(11a), with occupancies of 0.75 and 0.25, respec-

tively. Only C(11) was included in ORTEP drawing. Further details of the crystal structure may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (U.K.), on quoting the full journal citation.

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Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **5b**, **5c**, **6**, **7**, **10b**, **10c**, **14**, **15a**−**d**, **16a**−**d**, **18a**−**d**, **19a**−**d**, **21a**−**b**, **22b**−**d**, **27** and the product of the reaction of **21a** with DDQ. Copies of ^{13}C NMR spectra of compounds **5b**, **6**, **10b**, **10c**, **14**, **15a**−**d**, **16a**−**d**, **18a**−**d**, **19a**−**d**, **21a**−**b**, **22b**−**-d** and **27**. X-ray crystallographic data for **22c** and **27**. This material is available free of charge via the Internet at http://pubs.acs.org.

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