Synthesis of Cuppedophanes and Cappedophanes. Two New Classes of Cyclophanes with Molecular Cavities

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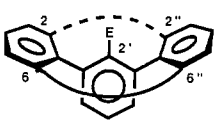
Short routes to cuppedophanes **1** and cappedophanes **2** are described. Key tetrabromide intermediate **8** is synthesized in two steps and 50% overall yield from 2,6-dichloroiodobenzene, **3** (Scheme I). Treatment of **8** with 2 equiv of a dinucleophile such as *o*-, *m*- or *p*-xylylenedithiol results in bridging across the *m*-terphenyl moiety to give cuppedophanes **23**, **17**, and **22**, respectively. Conversely **8** could be converted to tetrathiol **11** (two steps, 46%), which functioned as a tetranucleophile with dihalides to form cuppedophanes (i.e., **31** and **33**). Preparation of cuppedophane **34**, containing an intracavity substituent, is described, via precursor **15** (Scheme II). Treatment of **8** with 1 equiv of tetranucleophile **35** gave cappedophanes **36** (16%) and **37** (1.9%). Sulfur atoms in the linking arms of cuppedophanes and cappedophanes were extruded by oxidation to tetrasulfones followed by flash vacuum pyrolysis, leading to hydrocarbons **39**, **40**, **41**, and **43** as well as tilted cappedophane disulfone **44**. Certain aromatic protons in cappedophanes are highly shielded; the highest field aryl proton observed thus far appears in **44** at δ 3.31.

Macrocycles constitute a major class of selective complexing agents.[1] We describe here the synthesis, generally in just a few steps and in good yield, of two new classes of macrocycles represented by general formulas **1** and **2** that should have considerable potential as molecular hosts.[2] Because of their shape and cyclophane nature we refer to **1** and **2** as cuppedophanes and cappedophanes, respectively.[3]



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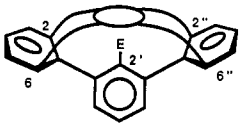


2

Structures **1** and **2** are based on a *m*-terphenyl framework in which the outer rings are orthogonal to the central ring. Links between the 2,2″- and 6,6″-positions in **1** create a molecular bowl or cup whose depth and host capacity will depend upon the nature of the linking units.[4] As a consequence of our synthetic route to *m*-terphenyls,[5] various groups E can be readily incorporated at C2′.

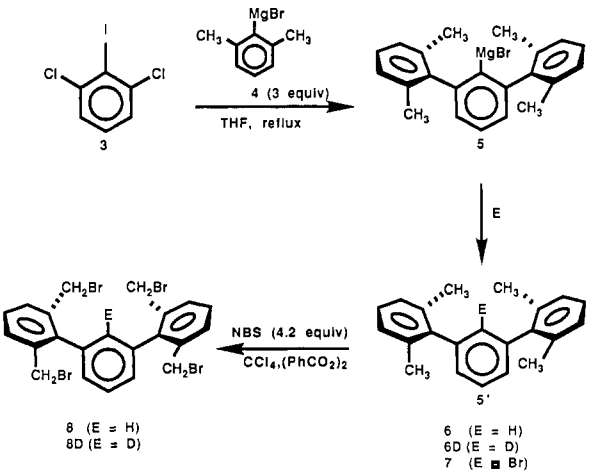
In **2**, four tethers connect a capping unit to positions 2,2″, 6,6″.[4] Depending on the length of the tethers, a group E may be accommodated within the cavity thus created, enabling one to study functional group chemistry in a specialized microenvironment.

In this paper we present a detailed account of our first results in this area.

Results and Discussion

Synthesis and Functionalization of the *m*-Terphenyl Framework. The key intermediate sought for constructing the molecular base of **1** and **2** was tetrakis(bromomethyl)-*m*-terphenyl, **8**, from which the bromines at the benzylic sites could be displaced to attach the linking chains.

Scheme I



Addition of 2,6-dichloroiodobenzene (**3**)[6] to 3 equiv of (2,6-dimethylphenyl)magnesium bromide (**4**) in refluxing tetrahydrofuran (THF) gave, via a tandem aryne formation–nucleophilic capture sequence,[5] the *m*-terphenyl Grignard **5** (Scheme I). Quenching with H_2O or D_2O gave respectively **6** or **6D**, mp 37–39 °C, in 70% overall yield. The methyl protons in **6** appeared as a singlet at δ 2.15, the 5′ aromatic proton in the central ring appeared as a triplet (J = 7.6 Hz) at δ 7.52, and the remaining aromatic protons were a complex multiplet. This spectrum was unchanged in **6D** except that the area of the multiplet was reduced by one proton.

In this synthesis of **6**, only 2 of the 3 equiv of Grignard reagent **4** appear in the product. One equivalent is used for the first step in the reaction sequence, i.e. Grignard exchange to convert **3** to (2,6-dichlorophenyl)magnesium bromide (**9**), the required aryne precursor. In view of the rather high cost of **4**,[7] one can use a less expensive Grignard reagent for this exchange. Treatment of **3** with 1 equiv of vinylmagnesium bromide[8] generates **9**, which is then

(1) *Synthesis of Macrocycles*; Izatt, R. M.; Christensen, J. J., Eds.; John Wiley and Sons: New York, 1987.

(2) For inspiring reviews, see: Pederson, C. J. *J. Inclusion Phenom.* **1988**, *6*, 337–350. Lehn, J.-M. *J. Inclusion Phenom.* **1988**, *6*, 351–396. Cram, D. J. *J. Inclusion Phenom.* **1988**, *6*, 397–413.

(3) For a preliminary account of this work, see: Vinod, T. K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 6574–6575.

(4) Other modes of linking the outer terphenyl rings are, of course, also possible (i.e. 3,3″,5,5″, etc.), including molecules with a single link or with more than two links (in the case of **2**, various numbers of links to the cap). These possibilities remain for further development.

(5) Du, C.-J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162–3165. Du, C.-J. F.; Hart, H. *J. Org. Chem.* **1987**, *52*, 4311–4314. Hart, H.; Ghosh, T. *Tetrahedron Lett.* **1988**, *29*, 881–884. Vinod, T. K.; Hart, H. *Tetrahedron Lett.* **1988**, *29*, 885–888.

(6) Bolton, R.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1977**, 278–280.

(7) 2-Bromo-*m*-xylene from which **4** is prepared currently costs $44.80/25 g from Aldrich Chemical Co.

(8) Vinylmagnesium bromide is preferable to methylmagnesium bromide since the other product of exchange (vinyl iodide) is not susceptible to displacement by the Grignard; methyl iodide is, and gives some methylated arene byproducts.

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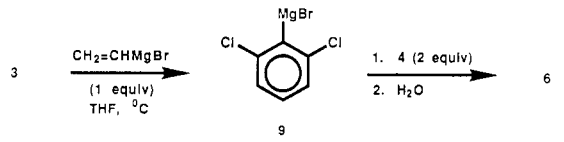
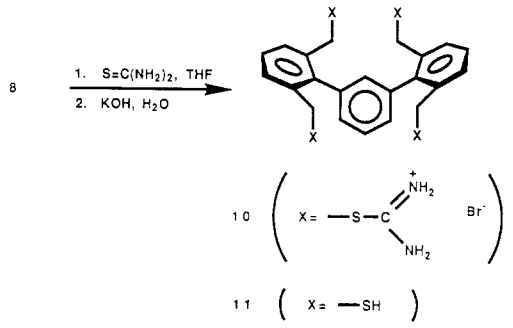
added to 2 equiv of **4** to give after aqueous quench, **6** in 66% yield.



Quenching **5** with bromine prior to aqueous workup gave the bromo-*m*-terphenyl, **7**, mp 130 °C, in 62% yield. However, attempts to prepare the corresponding aldehyde or acid by quenching **5** with *N*-formylpiperidine or CO_2, respectively, gave **6** as the only isolable product.

Bromination of **6** or **6D** with 4.2 equiv of *N*-bromosuccinimide (NBS) in refluxing CCl_4 gave the desired **8** or **8D**, mp 136 °C, in nearly 70% yield. To minimize the formation of more highly brominated products it was important to use freshly crystallized NBS and to add this reagent to the hydrocarbon in portions. The structure of **8** was clear from its spectra. As a consequence of restricted rotation, the methylene protons in the ^1H NMR spectrum of **8** appeared as closely spaced AB quartets (J = 10.2 Hz) at δ 4.30 and 4.35.

Another useful synthon desired for construction of **1** and **2** is the tetrathiol **11**, which was prepared from **8** in two steps. Treatment of **8** with thiourea (4 equiv) in refluxing THF gave a quantitative yield of the isothiouronium salt **10**, which, on alkaline hydrolysis, gave tetrathiol **11**, mp 88–90 °C, in 46% yield. In its ^1H NMR spectrum the SH protons appeared as a triplet at δ 1.64 (J = 7.4 Hz) and the benzylic methylenes gave a complex multiplet centered at δ 3.55.

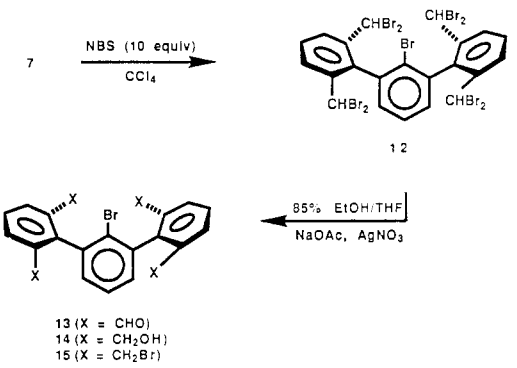


The analogue of **8** with a bromine at C2′ (i.e., **15**), would be a useful synthon for constructing cupped- and cappedophanes with functionality on the central arene ring. Unfortunately, NBS bromination of **7** with 4.2 equiv of NBS (as in the preparation of **8** from **6**) gave **15** mixed with more highly brominated contaminants, and it was not possible to obtain **15** pure from the product mixture. Therefore an alternate route to **15** was sought.

Treatment of **7** with excess (10 equiv) of NBS in refluxing CCl_4 gave nonabromide **12**, mp 220 °C, in 85% yield, uncontaminated by other polybromoterphenyls (Scheme II). The methine protons in the ^1H NMR spectrum of **12** appeared as a singlet at δ 6.23. The four aromatic protons ortho to the $CHBr_2$ groups were deshielded from the remaining aromatic protons and appeared as a doublet at δ 8.12 (J = 8.0 Hz).

Hydrolysis of **12** gave tetraaldehyde **13**, mp 243–246 °C, in 63% yield. The aldehyde protons in **13** appeared as a singlet at δ 9.91, and the aromatic protons ortho to the formyl groups were deshielded at δ 8.30 (doublet, J = 7.7 Hz). Reduction of **13** with sodium borohydride afforded tetraol **14** (83%), which was converted with PBr_3 to the desired tetrakis(bromomethyl) compound **15**, mp 232–234 °C, in 70% yield. The methylene protons in the ^1H NMR

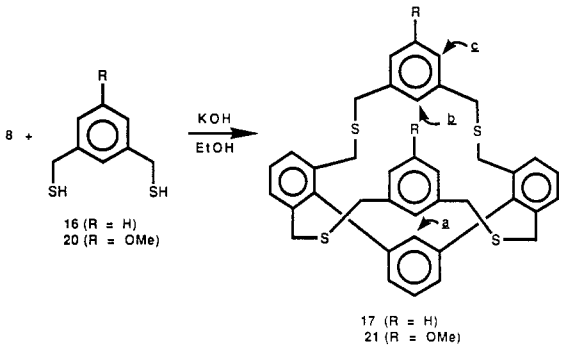
Scheme II



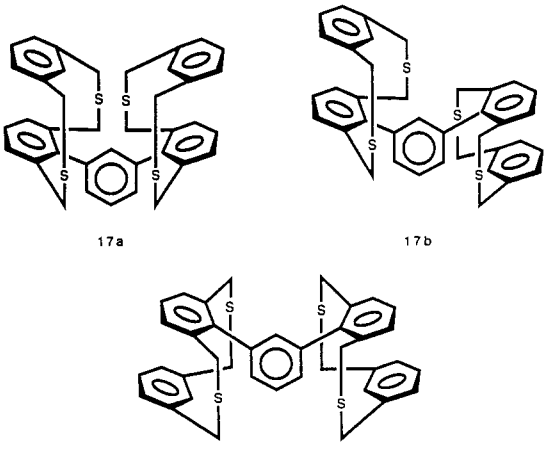
spectrum of **15** appeared as two doublets at δ 4.21 and 4.37 (J = 10.3 Hz).

Synthesis of Macrocycles via Thiolate Coupling. (a) Cuppedophanes from 8. A widely used and often high-yield method for constructing cyclophanes is the high-dilution coupling of thiols with reactive (usually benzylic) bromides.[9] Xylylenedithiols were selected as the first choice for linking units in **1** because they were expected to confer rigidity to the "cups" and deepen the molecular cavity by building up its walls.

Addition of a benzene solution of **8** and *m*-xylylenedithiol (**16**)[10] to ethanolic KOH under high dilution conditions gave the tetrathiacyclophane **17**, mp 154 °C, in 70%

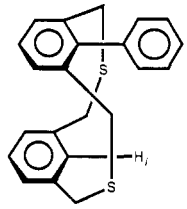


yield. The ^1H NMR spectrum of **17** was decisive in establishing the mode of linking as drawn, and in ruling out alternative possibilities such as **17a–c**. A reasonable model for **17a–c** is the phenyl-[3.3]-*m*-cyclophane, **18**,[11] which is



(9) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 1–86.
(10) Autenrieth, W.; Beuttel, F. *Chem. Ber.* **1909**, *42*, 4357–4361.

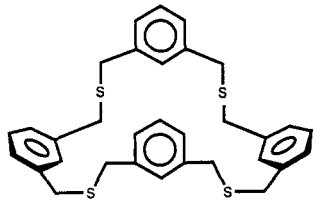
known (X-ray)[12] to have the syn conformation shown (anti conformations for **17a–c** appear unduly strained and unlikely). The internal aromatic proton H_i in **18** appears at



18

δ 5.47 (20 °C).[12] Hence we would expect to see a two-proton signal for that type of proton in **17a** and **17c**, and two similar one-proton signals for **17b**, with approximately that chemical shift. Instead, **17** shows as its highest field aromatic signal a broad one-proton singlet at δ 6.39, assigned to H_a, the isolated proton on the central ring of the *m*-terphenyl moiety. This proton is shielded by the two cofacially arranged *m*-xylylene units. This assignment was confirmed by deuterium replacement; reacting **8D** with **16** gave **17D** in which the δ 6.39 peak was absent. Also consistent with structure **17** is a two-proton broadened singlet at δ 6.74, assigned to the isolated protons (H_b) on the two *m*-xylylene linking units. These protons are in the shielding zone of the central ring of the *m*-terphenyl unit.

Compound **19**, which contains the internal macrocyclic ring of **17** but lacks the central ring of the *m*-terphenyl unit, has been prepared.[13] Its internal hydrogens (comparable to H_b in **17**) appeared at lower field than those of **17** (δ 7.03 vis-a-vis δ 6.74), supporting the suggestion that in **17** these protons are shielded by the central ring.



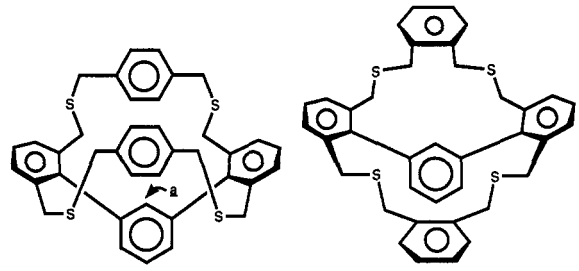
19

The remaining 15 aryl protons in **17** appeared as a multiplet at lower field (δ 6.81–7.43).

The dimethoxy analogue **21** was synthesized in a similar manner, and its ^{1}H NMR spectrum was only consistent with the type of linking proposed for **17**. Proton H_a gave a broad singlet at δ 6.35, protons H_b gave a singlet at δ 6.33, and the four protons ortho to the methoxyl substituents appeared as a narrow doublet at δ 6.60 (J = 1.2 Hz). All the remaining aryl protons were at lower field.

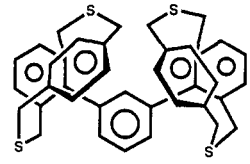
Finally, removal of the sulfurs from **17** gave hydrocarbon **39** whose X-ray structure confirmed the assignment (vide infra).

Tetrathiacyclophanes **22** and **23** were prepared from **8** in a manner analogous to **17**, but using the *p*- and *o*-xylylenethiols, respectively. In **22** the internal proton H_a appears at δ 6.26 (confirmed by synthesis of **22D** from **8D**), shielded by the bridging *p*-xylylene rings. Rotation of these rings is restricted. At room temperature their aromatic protons appeared as two broadened singlets (δ 6.83, 7.20), which coalesced at 342 K and gave a sharp singlet



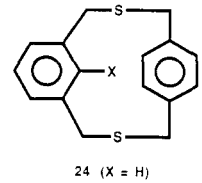
22 23

at 378 K ($\Delta G^{\ddagger}$ = 17.0 kcal mol^{-1}). We believe these data safely exclude structure **22a**, for which CPK models show



22a

a crowded structure in which the *p*-xylylene rings lie over and in contact with the outer *m*-terphenyl rings and also nearly touch at the center of the molecule. If this structure were correct we would expect aryl protons in all four "outer" rings to be highly shielded. Although **24**,[14] a possible model for **22a**, is mobile at room temperature, that mobility should be severely restricted in **22a**, and if that were the structure, we would not have expected the observed rotation of the *p*-xylylene rings. Unfortunately **24** (X = Ph), which would be a better model for **22a**, is not known.



24 (X = H)

Structures in which one or both of the *p*-xylylene rings are "below" the outer rings of the terphenyl unit (analogous to **17b** or **17c**) appear even more strained since they encounter interference with the central terphenyl ring.

All of the aromatic protons in **23** appear in the region δ 7.09–7.50. The *o*-xylylene rings are not cofacial (as in **17** and **22**), but are probably tilted outwards as drawn. The flattened structure of orthocyclophanes (in contrast with meta or para isomers) has been noted previously.[15] As with **22**, CPK models of isomers of **23** in which each *o*-xylylene bridge is connected across a single outer ring of the *m*-terphenyl unit appear to have much greater strain than **23**, which is quite flexible. Nevertheless, the absence of any diagnostic aromatic proton signals in the ^{1}H NMR spectrum of **23** prompted us to synthesize model compounds **25** and **26** for comparison. The required dibromide precursor **29** was synthesized as outlined in Scheme III. Cross-coupling of (dimethylphenyl)magnesium bromide **4** with 3-chlorobromobenzene using 1,3-bis(diphenylphosphino)propanenickel(II) chloride as catalyst[16] gave chlorobiphenyl **27** in 41% yield. Addition of

(11) Vögtle, F.; Grütze, J.; Nätscher, R.; Wieder, W.; Weber, E.; Grün, G. *Chem. Ber.* **1975**, *108*, 1694–1711. Böckmann, K.; Vögtle, F. *Chem. Ber.* **1981**, *114*, 1065–1073.

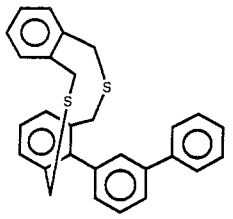
(12) Anker, W.; Beveridge, K. A.; Bushnell, G. W.; Mitchell, R. H. *Can. J. Chem.* **1984**, *62*, 661–666.

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

(14) Boekelheide, V.; Anderson, P. H.; Hylton, T. A. *J. Am. Chem. Soc.* **1974**, *96*, 1558–1564. Vögtle, F. *Chem. Ber.* **1969**, *102*, 3077–3081.

(15) Mataka, S.; Takahashi, K.; Mimura, T.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M.; Imada, K.; Kuniyoshi, M. *J. Org. Chem.* **1987**, *52*, 2653–2656. Lai, Y.-H.; Nakamura, M. *J. Org. Chem.* **1988**, *53*, 2360–2362.

(16) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969.



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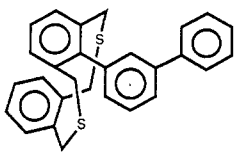
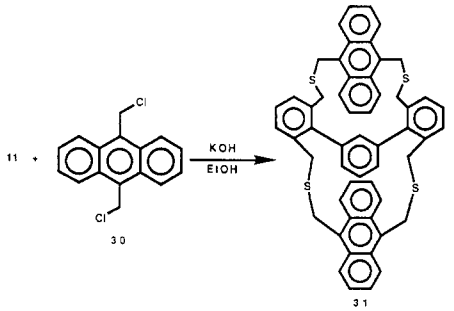


26

(2-chlorophenyl)magnesium bromide (prepared from 2-iodochlorobenzene and vinylmagnesium bromide at −20 °C) to the Grignard derived from **27** in refluxing THF gave **28** (50%) via nucleophilic capture of benzyne. NBS bromination gave **29** (52%), which was then coupled with *o*-xylylenedithiol to give (46%) an inseparable mixture of **25** and **26**. These compounds are rotamers, prevented from interconversion by restricted rotation about the bond to the diphenyl moiety.

The aromatic proton region of the ^{1}H NMR spectrum of **25** and **26** was complex and not very useful, but the methylene proton region was very different from that of **23**. It appeared as 14 (of a possible 16) sharp signals between δ 3.00 and 3.95, presumably arising from the four AB quartets expected for the conformationally rigid **25** and **26**.[17] In the more flexible and relatively strain free **23**, the methylene protons appeared as an AB quartet (δ 3.49 and 3.77, 8 H) and a broad singlet (δ 3.63, 8 H). Although not unequivocal, this result strongly supports bridging as drawn in **23**.

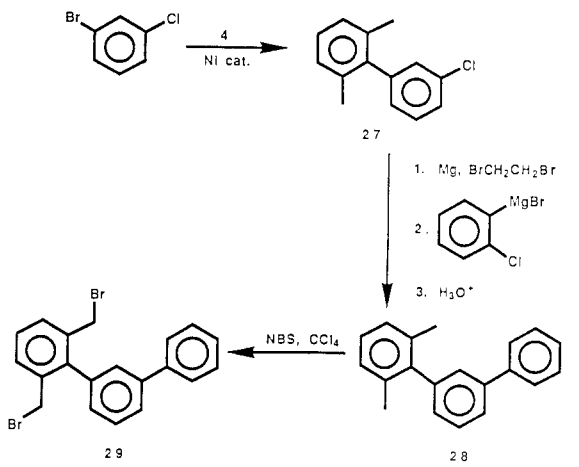
(b) Cuppedophanes from 11. The utility of **11** as a synthon is illustrated by its reaction with 9,10-bis(chloromethyl)anthracene, **30**.[18] Addition of a toluene solution of **11** and **30** (2 equiv) to ethanolic KOH afforded **31**, mp



30 31

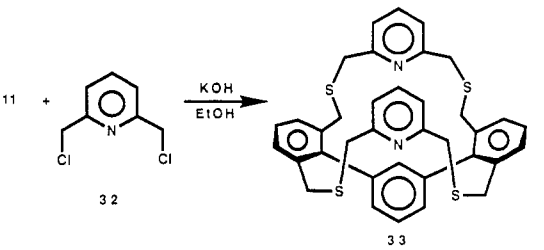
264 °C, in 33% yield. Structures of the type **22a** are impossible for this product because of steric hindrance. The cofacial arrangement of the anthracene units in **31** was evident from its ^{1}H NMR spectrum. The isolated proton on the central *m*-terphenyl ring was highly shielded and appeared as a broad singlet at δ 5.03. The other aryl protons on this ring appeared as a triplet at δ 5.61 (1 H, J = 7.7 Hz) and a doublet of doublets at δ 6.41 (2 H, J = 7.7 and 1.8 Hz). The anthracene protons fell into four AA′BB′ 4-proton multiplets. Those at low field (δ 8.33, 8.18) are assigned to the "top" anthracene ring protons, well above the central cavity. Those at higher field (δ 7.58, 7.31) are assigned to the "bottom" anthracene ring protons, presumably somewhat shielded by the central *m*-terphenyl ring. The methylene protons occur as four sets of geminally coupled doublets at δ 5.51, 4.42, 2.85, and 1.61, the latter set highly shielded by nearby aryl rings.

Scheme III



27 29 28

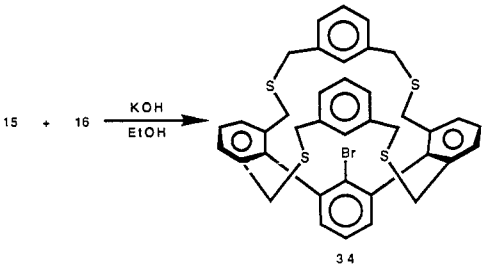
In a similar manner, **11** was coupled with 2,6-bis(chloromethyl)pyridine (**32**)[19] to give the heterocuppedophane **33**, mp 225–228 °C, in 74% yield. The isolated aryl proton on the central *m*-terphenyl ring was the highest field aromatic proton, at δ 6.54 (cf. δ 6.39 in **17**), shielded by the pyridine rings.



32 33

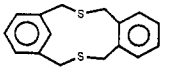
(c) Cuppedophanes with an Intracavity Substituent. Presence of functionality at the center of the cup (i.e., replacement of the isolated proton on the central *m*-terphenyl ring) might have interesting consequences. Bromine was selected for initial study since it could presumably be converted, via metalation, to a variety of other functional groups.

Treatment of pentabromide **15** with *m*-xylylenedithiol **16** and base proceeded smoothly to give **34**, mp 197 °C, in 67% yield. Its ^{1}H NMR spectrum is similar to that of **17** except that the peak due to the isolated proton on the central *m*-terphenyl ring (δ 6.39) was absent; the highest field aryl protons were the isolated hydrogens on the *m*-xylylene links, which appeared as a broad singlet at δ 6.71 (cf. 6.74 in **17**).



34

(17) In contrast i, the analogue of **25** and **26** that lacks the biphenyl substituent on the meta-ring of the cyclophane, is conformationally mobile even at −60 °C; its methylene protons appear as two sharp singlets. Vögtle, F. *Tetrahedron* **1969**, *25*, 3231–3242.



i

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(19) Baker, W.; Briggle, K. M.; McOmie, J. F. W.; Watkins, D. A. M. *J. Chem. Soc.* **1958**, 3594–3603.

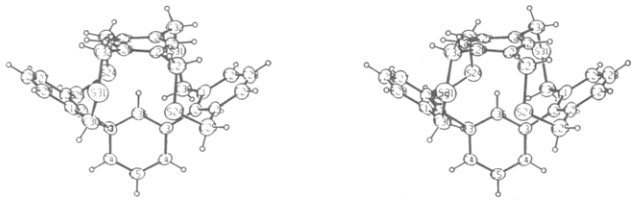
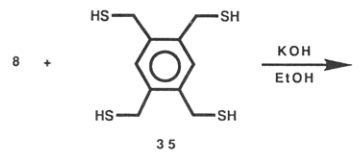


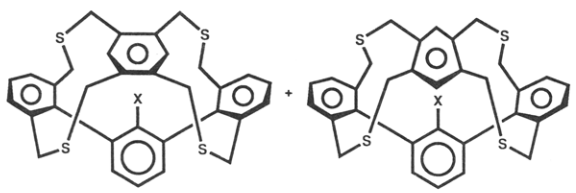
Figure 1. Stereoview of **36** showing nonplanarity of the cap and twisting of the linking arms.

The structure of **34** was proved by conversion, through halogen–metal exchange with butyllithium followed by aqueous quench, to **17**.

(d) Cappedophanes. Reaction of **8** with 1,2,4,5-tetrakis(mercaptomethyl)benzene, **35** (prepared from the known corresponding tetrabromide[20]), gave two cappedophanes, **36** and **37**, in 16 and 1.9% yields, respectively (the remaining product was polymeric). The low yields may be a reflection of the difficulty in bridging across each external *m*-terphenyl ring.



35



36 (X = H)
36D (X = D)

37 (X = H)
37D (X = D)

The two isomers were readily distinguished by their ^1H NMR spectra. The two aryl protons of the capping ring appeared as singlets at δ 4.75 in **36** and at δ 8.30 in **37**. In **36**, these protons lie directly over the outer rings of the *m*-terphenyl unit and are hence highly shielded. In **37**, these are the lowest field protons in the spectrum, though the reason for their deshielding is not obvious.

The internal aryl proton X in both compounds is highly shielded (at δ 3.97 in **36** and δ 4.23 in **37**) as a consequence of its location directly under the capping ring. As a reference, the equivalent proton in tetrathiol **11** appears at δ 7.23. The observed upfield shift of 3.26 ppm in **36** corresponds, using the Johnson and Bovey table,[21] to a distance from the internal proton to the center of the capping ring of 2.36 Å, but in actuality, the observed distance was even smaller. The assignment of these signals to the internal hydrogens was confirmed by absence of their signals in **36D** and **37D**, prepared from **8D**.

An X-ray structure determination on a single crystal of **36** verified the overall cappedophane structure and exhibited some interesting features. Although one might have expected that **36** would have C_{2v} symmetry from its structural formula, distortion of the capping ring and connecting arms reduced the observed symmetry to C_2 (Figure 1). The capping ring is not planar, but adopts a pseudoboat conformation. Two opposite methylene carbons attached to this ring (C32, at the front left and rear

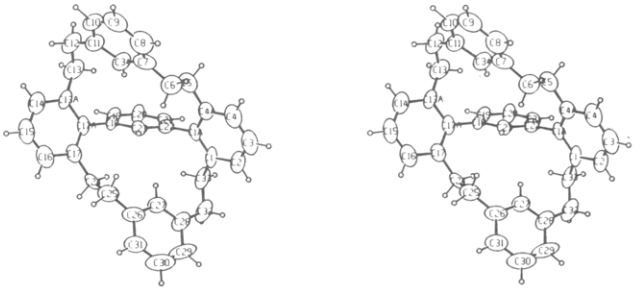
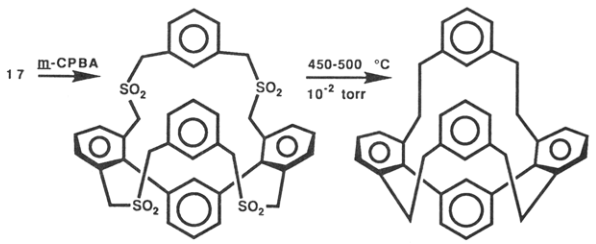


Figure 2. Stereoview of **39** showing the face-to-face arrangement of the *m*-xylylene bridges.

right in Figure 1) lie above its mean plane, and the other two methylene carbons (C23, front right and rear left in Figure 1) lie below that plane. The two CH_2–S–CH_2 dihedral angles in the two types of arms are consequently quite different from one another, being −46.79° for C30–S31–C32–C20 and 92.65° for C25–S24–C23–C22. The internal aryl proton that gives rise to the δ 3.97 NMR peak is estimated to be only 2.16 Å from the mean molecular plane of the capping ring.

Extrusion of Sulfur. Hydrocarbon Cuppedophanes and Cappedophanes. Several methods to remove the sulfur atoms from tetrasulfides **17**, **22**, and **23** were tried. Carbanionic rearrangements such as the Wittig,[22] Stevens,[23] or benzyne-Stevens[24] gave only unidentifiable tars, perhaps because the requirement for 4-fold success is too demanding. Oxidation to tetrasulfones followed by pyrolytic elimination of sulfur dioxide[25] proved to be more successful.

Oxidation of **17** with *m*-chloroperbenzoic acid (*m*-CPBA) in HOAc–CH_2Cl_2 at room temperature gave a nearly quantitative yield of tetrasulfone **38**, mp >370 °C dec. The isolated aromatic proton on the central *m*-terphenyl ring of **38** appeared at δ 6.10 (confirmed by synthesis of **38D** from **17D**), even more shielded than the corresponding proton in **17** (δ 6.39).



38 39

An X-ray structure of **39** verified the structure and shows (Figure 2) that the linking *m*-xylylene rings are in a face-to-face conformation. This structure rationalizes the substantial shielding of the internal hydrogen, which appeared at δ 5.70 (this peak is absent in the spectrum of **39D**).

In a similar manner, **22** and **23** were converted, via the corresponding tetrasulfones, to hydrocarbons **40** and **41**, respectively. The para-linked hydrocarbon **40**, mp 243 °C, has a rigid structure with the "top" and "bottom" aryl protons of the linking rings distinguishable from one another. They appeared as narrowly spaced doublets (J =

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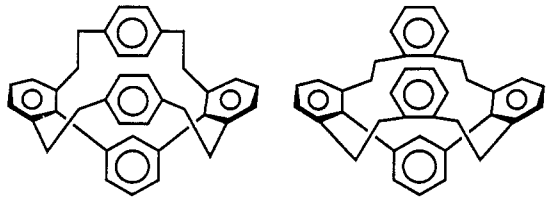
(22) Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 219–222.
(23) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547–1557.
(24) Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 3881–3884.
(25) For a review, see: Vögtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 515–529.

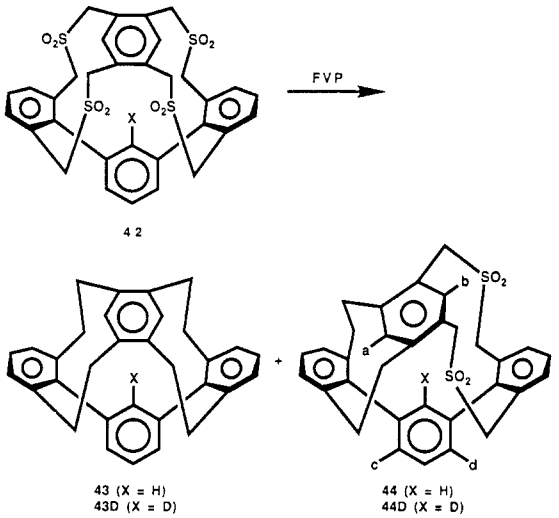
1.0 Hz) at δ 6.43 and 6.27. The isolated central proton was somewhat shielded, but not nearly as much as in **39** (it appears as a broadened singlet at δ 6.59, absent in the spectrum of **40D**.



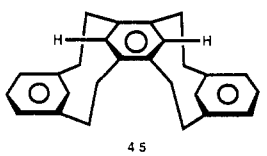
40 41

The ortho-linked hydrocarbon **41**, mp 198 °C, has no uniquely shielded aromatic protons, all of them appearing between δ 7.05–7.60. It seems likely that the linking aryl rings are tilted outward from the central cavity, as in its precursor **23**. Unfortunately we were unable to prepare crystals of **40** or **41** that were satisfactory for X-ray study.

Cappedophane **36** was oxidized to the tetrasulfone **42** mp 310 °C dec, in 76% yield. Flash vacuum pyrolysis of **42** gave the desired hydrocarbon **43**, mp 265–266 °C, in 24% yield, but also gave a disulfone in 32% yield, assigned the tilted capped structure **44**. The structure assignments are based primarily on NMR spectra.



The simpler case to establish is hydrocarbon **43**. The internal proton X appeared as a triplet at δ 3.77 (J = 1.7 Hz), weakly coupled with the two meta hydrogens on the same ring. This peak was absent in the spectrum of **43D**. There was another high-field aryl proton peak, a sharp two-proton singlet at δ 3.67, which is assigned to the two isolated aromatic protons of the capping ring. These protons lie directly over the two outside aryl rings of the m-terphenyl moiety. The planes of these rings are tilted toward these aryl protons, accounting for the substantially larger shielding than was observed previously[26] for the corresponding protons in **45**, where the indicated protons in the central ring appear at δ 5.03. In **45** the aryl rings lie in parallel planes.



45

(26) Umemoto, T.; Otsubo, T.; Misumi, S. *Tetrahedron Lett.* **1974**, 1573–1576.

Table I. Chemical Shifts of the Internal[a] Aromatic Proton in Selected Cuppedophanes and Cappedophanes

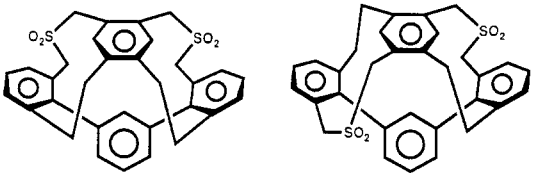
cuppedophanes		cappedophanes	
compd	δ (ppm)	compd	δ (ppm)
6[b]	6.97	36	3.97
17	6.39	37	4.23
39	5.70	43	3.77
22	6.26	44	3.31
40	6.59		
31	5.03		
33	6.54		

[a] Isolated proton on the central ring of the m-terphenyl moiety. [b] Acyclic reference terphenyl.

The three remaining aryl protons on the central ring of the m-terphenyl unit in **43** are also readily apparent as a one-proton triplet at δ 7.11 (J = 7.6 Hz) for the proton para to X, and a two-proton doublet of doublets at δ 6.69 (J = 7.6, 1.7 Hz) for the meta protons in that ring.

It seems curious that the central proton in **43** appears at only slightly higher field (δ 3.77) than the corresponding proton in tetrasulfide **36** (δ 3.97). We expected this proton to be much closer to the capping ring, and hence substantially more shielded (it is quite impossible to construct a CPK model of **43** that includes this hydrogen, which is clearly "jammed" into the capping ring). The molecule must distort to accommodate the strain. Unfortunately we have thus far been unable to get a suitable crystal of **43** for X-ray study.

Disulfone **44** must be distinguished from the other two possible structures, **44A** and **44B**. This is easily done,



44A 44B

because the two aryl protons in the capping ring of **44** appeared as two singlets, at δ 3.45 and 5.16. The symmetry of **44A** and **44B** is such that these protons should be magnetically equivalent. As a consequence of tilting, one aryl cap proton in **44** is much more shielded than the other by the outer aryl rings of the m-terphenyl unit; indeed H_a in **44** is more shielded than the capping ring protons in **43** (δ 3.45 vis-a-vis δ3.67), and H_b in **44** has nearly the same chemical shift (δ 5.16 vis-a-vis δ 5.03) as the central ring protons in **45**, consistent with a near-parallel arrangement of the capping ring with one of the outer m-terphenyl rings.

Tilting of the cap in **44** is also evident from the aryl protons in the central ring of the m-terphenyl moiety. Protons H_c and H_d are not equivalent (unlike those protons in **43**; vide supra) and appear as two one-proton multiplets at δ 6.78 and 6.87.

The internal aryl proton in **44** appears at δ 3.31 (absent in the spectrum of **44D**) and is the most shielded internal proton in any of the cappedophanes described here. It may be that because of tilting, the capping ring in **44** remains planar and hence generates the maximum ring current; the capping ring in **36** is nonplanar (X-ray) and that ring in **43** is almost certainly nonplanar, and this probably decreases the ring current.

Chemical shifts of the internal protons of selected cuppedophanes and cappedophanes are summarized in Table I. All chemical shifts appear at higher field than the acyclic reference compound **6**. The most shielded internal cuppedophane proton is in the anthracene **31**, where the extra ~1 ppm shielding is caused by the additional arene

rings. Capping causes a 2.5–3 ppm upfield shift relative to the cuppedophanes.

In conclusion, we have developed short synthetic routes to two new general classes of host molecules, cuppedophanes **1** and cappedophanes **2**. In the latter, isolated aryl protons on the central *m*-terphenyl ring are highly shielded by the aryl cap, and aryl protons on the capping ring are highly shielded by the outer rings of the *m*-terphenyl moiety.

So far the linking units in **1** and **2** have been relatively nonpolar. Work is in progress on units with heteroatoms that should function well in binding guest molecules to these potential hosts. Compounds **1** and **2** also provide the opportunity to study the chemistry of functional groups (i.e., E) in a unique and well-defined microenvironment. Toward this end, cuppedophanes with deeper cavities and cappedophanes with larger enclosures are being developed and will be reported in due course.

Experimental Section

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-250 MHz spectrometer in $CDCl_3$ with CH_2Cl_2 (δ 5.30) as the internal reference, unless otherwise stated. Chemical shifts are reported in δ, and coupling constants in hertz. IR spectra were determined on a Nicolet Model IR/42 FT spectrometer. Mass spectra were measured at either 70 or 25 eV with a Finnigan 4000 spectrometer equipped with the INCOS data system. High-resolution or FAB mass spectra were obtained at the Michigan State University mass spectrometry facility, supported in part by a grant (DRR-00480) from the Biotechnology Resources Branch, National Institutes of Health. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Anhydrous $MgSO_4$ was the drying agent throughout, and the silica gel for chromatography was 60–200 mesh. Elemental analyses were performed by either Spang Microanalytical Laboratory, Eagle Harbor, MI, or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

2,6,2″,6″-Tetramethyl-1,1′:3′,1″-terphenyl (6). To a solution of (2,6-dimethylphenyl)magnesium bromide [prepared from 2,6-dimethylbromobenzene (20.4 g, 110 mmol) and magnesium (2.95 g, 126.0 mmol) in 300 mL of anhydrous THF] heated at reflux under Ar was added dropwise a solution of 2,6-dichloroiodobenzene[6] (10 g, 36.7 mmol) in 30–40 mL of anhydrous THF. The resulting solution was heated at reflux for an additional 3 h, cooled, quenched with 40 mL of cold 10% HCl, extracted with ether (2 × 100 mL), and dried. The crude product obtained after removal of the ether (rotavap) was vacuum distilled to remove the byproduct 2,6-dimethyliodobenzene, and the residue was chromatographed over silica gel using petroleum ether (30–60 °C) as eluent to give 7.4 g (70%) of **6**: mp 37–38 °C (recrystallized from hexanes); ^{1}H NMR δ 7.52 (t, J = 7.6, 1 H), 7.26–6.97 (m, 9 H), 2.15 (s, 12 H); mass spectrum, m/e (relative intensity) 286 (100), 271 (30), 181 (15), 165 (20). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.82.

2,6,2″,6″-Tetramethyl-1,1′:3′,1″-terphenyl-2′-*d* (6D). The procedure for **6** was followed, but the reaction was quenched with 5 mL of D_2O to give **6D**: ^{1}H NMR δ 7.52 (t, J = 7.6, 1 H), 7.26–7.14 (m, 8 H), 2.15 (s, 12 H); mass spectrum, m/e (relative intensity) 287 (100), 272 (29), 182 (12), 167 (10), 166 (18).

Alternative Preparation of 6 Using Vinylmagnesium Bromide. Vinylmagnesium bromide (1.46 g, 11.1 mmol as a 1.0 M solution in THF) was added to a stirred solution of 2,6-dichloroiodobenzene (3 g, 11.0 mmol) in THF (40 mL) under Ar maintained at −18 °C. After the mixture was stirred at that temperature for 2 h, it was added over 20 min under Ar to a refluxing solution of (2,6-dimethylphenyl)magnesium bromide (prepared from 4.13 g, 22.2 mmol of 2,6-dimethylbromobenzene and 0.55 g, 22.6 mmol of magnesium in 80 mL of anhydrous THF). The resulting mixture was stirred at reflux for an additional 3 h. Workup as before provided 2.1 g (66%) of **6** identical in all respects with product prepared as above.

2′-Bromo-2,6,2″,6″-tetramethyl-1,1′:3′,1″-terphenyl (7). The procedure for **6** was followed except that prior to aqueous quench bromine (6 g in 20 mL of CCl_4) was added, and the mixture was stirred for an additional 30 min before quench. Workup as above except for washing with sodium bisulfite to remove the excess bromine gave 8.4 g (62%) of **7** as a white solid: mp 129 °C (hexanes); ^{1}H NMR δ 7.47 (t, J = 7.5, 1 H), 7.26–7.13 (m, 8 H), 2.07 (s, 12 H); mass spectrum, m/e (relative intensity) 366 (80), 364 (87), 285 (59), 270 (100), 255 (67), 253 (44). Anal. Calcd for $C_{22}H_{21}Br$: C, 72.33; H, 5.79. Found: C, 72.16; H, 5.77.

2,6,2″,6″-Tetrakis(bromomethyl)-1,1′:3′,1″-terphenyl (8). Freshly recrystallized *N*-bromosuccinimide (NBS) (32.7 g, 184 mmol) was added in 5–6 equal portions 6 h apart to a solution of **6** (12.5 g, 44 mmol) in 350 mL of CCl_4 heated at reflux; each addition was immediately followed by adding a few milligrams of benzoyl peroxide. After 40-h total reaction time at reflux, the mixture was cooled and the precipitated succinimide was removed by filtration. The solvent was removed (rotavap), and the residue was chromatographed over silica gel using CH_2Cl_2–hexanes (1:10 v/v) as eluent. Fractions rich in **8** were combined, and the remaining fractions that contained some **8** were rechromatographed. The resulting **8** was recrystallized from CH_2Cl_2–hexanes (1:4 v/v) to give 18.3 g (70%) of **8** as white needles: mp 136 °C; ^{1}H NMR δ 7.65–7.25 (m, 10 H), 4.35 and 4.29 (AB q, J = 10.2, 8 H); mass spectrum, m/e (relative intensity) 602 (1), 515 (3), 360 (38), 359 (100), 280 (54), 265 (57). Anal. Calcd for $C_{22}H_{18}Br_4$: C, 43.89; H, 3.01. Found: C, 43.81; H, 3.02.

2,6,2″,6″-Tetrakis(bromomethyl)-1,1′:3′,1″-terphenyl-2′-*d* (8D). The same procedure as for **8** was followed, starting from **6D**: ^{1}H NMR δ 7.69–7.26 (m, 9 H), 4.34 and 4.30 (AB q, J = 9.8, 8 H); mass spectrum at 12 eV, m/e (relative intensity) 605 (0.3), 603 (0.3), 523 (0.6), 522 (0.9), 521 (1.4), 444 (9), 443 (12), 441 (32), 440 (48), 439 (36), 438 (22), 362 (93), 361 (84), 360 (100), 359 (73), 358 (16).

2,6,2″,6″-Tetrakis(mercaptomethyl)-1,1′:3′,1″-terphenyl (11). A stirred solution of tetrabromide **8** (5.0 g, 8.3 mmol) and thiourea (2.54 g, 33.4 mmol) in THF (150 mL) was heated at reflux for 12 h. After cooling, the precipitated tetrakisisothiouronium salt **10** was collected and dried under vacuum to give 7.5 g (100%) as a white powder. This salt was heated under reflux with a deoxygenated solution of KOH (7.5 g, 134 mmol) in water (300 mL) under Ar for 12 h. The mixture was cooled (ice bath), and 100 mL of 1:1 concentrated sulfuric acid–water was added dropwise. The mixture was extracted with CH_2Cl_2 (3 × 150 mL), and the combined organic layers were dried. Solvent was removed (rotavap), and the residue was chromatographed over silica gel using CH_2Cl_2–hexanes (2:1 v/v) as eluent to give 1.6 g (46%) of **11**: mp 88–90 °C; ^{1}H NMR δ 7.58 (t, J = 7.6, 1 H), 7.40–7.23 (m, 9 H), 3.55 (m, 8 H), 1.64 (t, J = 7.4, 4 H); mass spectrum at 25 eV, m/e (relative intensity) 414 (1), 380 (5), 346 (13), 314 (12), 313 (40), 312 (25), 311 (24), 281 (100). Anal. Calcd for $C_{22}H_{22}S_4$: C, 63.72; H, 5.35. Found: C, 63.54; H, 5.33.

2′-Bromo-2,6,2″,6″-tetrakis(dibromomethyl)-1,1′:3′,1″-terphenyl (12). *N*-Bromosuccinimide (9.75 g, 54.8 mmol) was added in two equal portions 6 h apart to a solution of **7** (2 g, 5.48 mmol) in 200 mL of CCl_4 heated at reflux; each addition was followed by adding a few milligrams of benzoyl peroxide. After a total time at reflux of 36 h the mixture was cooled, and the succinimide was removed by filtration. The filtrate was evaporated to yield 4.7 g (85%) of **12** as a white solid: mp 220 °C; ^{1}H NMR δ 8.12 (d, J = 8.0, 4 H, H_3, H_5, $H_{3''}$, $H_{5''}$), 7.75–7.66 (m, 3 H), 7.51 (d, J = 7.4, 2 H, $H_{4'}$ and $H_{6'}$), 6.23 (s, 4 H, $CHBr_2$). This compound was not further characterized, but was used directly to prepare **13**.

2′-Bromo-2,6,2″,6″-tetraformyl-1,1′:3′,1″-terphenyl (13). A mixture of nonabromide **12** (4.0 g, 4.0 mmol), sodium acetate (2.7 g, 37.5 mmol), and silver nitrate (5.45 g, 32.2 mmol) in 240 mL of a solvent mixture of 80% EtOH–THF (5:1 v/v) was heated at reflux for 24 h. The solid that separated was filtered, and the filtrate was evaporated to yield crude product containing **13** and its diethyl acetal. This crude product was dissolved in CH_2Cl_2 (100 mL), 10% hydrochloric acid (5 mL) was added, and the mixture was stirred at room temperature overnight. The organic layer was washed with water (2 × 50 mL), dried, and evaporated to yield 1.1 g (65%) of **13**: mp 243–246 °C (recrystallized from diethyl ether–hexane); ^{1}H NMR δ 9.91 (s, 4 H, CHO), 8.30 (d, J = 7.7, 4 H, H_3, H_5, $H_{3''}$, $H_{5''}$), 7.79 (t, J = 7.7, 2 H, H_4, $H_{4''}$), 7.65 (t, J = 7.6, 1 H, $H_{5'}$), 7.48 (d, J = 7.6, 2 H, $H_{4'}$, $H_{6'}$); mass spectrum at 25 eV, m/e (relative intensity) 341 (100, M^+ − Br), 295 (11), 267 (29), 255 (13), 239 (35), 226 (36); IR (KBr) 1691 cm^{-1}. Anal.

Calcd for $C_{22}H_{13}BrO_4$: C, 62.73; H, 3.11. Found: C, 61.33; H, 2.81;[27] high-resolution mass spectrum calcd 421.0045, found 421.0048.

2′-Bromo-2,6,2″,6″-tetrakis(hydroxymethyl)-1,1′:3′,1″-terphenyl (14). A solution of tetraaldehyde **13** (1 g, 2.4 mmol) in hot methanol (30 mL) was added dropwise to a slurry of $NaBH_4$ (0.12 g, 3.2 mmol) in 30 mL of THF at room temperature. After 6 h the mixture was acidified with a minimum of 1:1 concentrated hydrochloric acid–water. The solvent was removed (rotavap), and the crude product was extracted (soxhlet) with chloroform to yield 0.85 g (83%) of **14**: ^{1}H NMR (DMSO-d_6) δ 7.52–7.18 (m, 9 H), 4.12 (s, 8 H); mass spectrum at 25 eV, *m/e* (relative intensity) 330 (12, $M^+ - Br - H_2O$), 312 (100, $M^+ - Br - 2H_2O$), 294 (97, $M^+ - Br - 3H_2O$), 266 (25); IR (KBr) 3286, 2860, 2360, 1045 cm^{-1}. Anal. Calcd for $C_{22}H_{21}BrO_4$: C, 61.55; H, 4.93. Found: C, 61.04; H, 4.84.

2′-Bromo-2,6,2″,6″-tetrakis(bromomethyl)-1,1′:3′,1″-terphenyl (15). A solution of PBr_3 (0.4 g, 1.48 mmol) in anhydrous benzene (10 mL) was added slowly to a vigorously stirred solution of tetraalcohol **14** (0.9 g, 2.1 mmol) in 40 mL of benzene containing 2–3 drops of pyridine. The mixture was stirred for 16 h, washed successively with water, aqueous sodium bicarbonate, and water, and dried. Evaporation of the solvent gave 1.0 g (70%) of **15** as a white solid: mp 232–234 °C (recrystallized from 1:1 CH_2Cl_2–hexanes); ^{1}H NMR δ 7.64–7.43 (m, 9 H), 4.37 (d, J = 10.3, 4 H), 4.21 (d, J = 10.3, 4 H); mass spectrum, *m/e* (relative intensity) 681 (0.15), 679 (0.15), 521 (0.16), 520 (0.16), 519 (0.16), 443 (4.5), 442 (19), 441 (29), 440 (30), 439 (35), 362 (24), 361 (88), 360 (26), 359 (76), 282 (14), 281 (51), 280 (50), 279 (42), 265 (100). Anal. Calcd for $C_{22}H_{17}Br_5$: C, 38.81; H, 2.52. Found: C, 38.53; H, 2.35.

General Procedure for Tetrathiacuppedophanes 17, 21, 22, and 23. A solution of tetrakis(bromomethyl) compound **8** (1 g, 1.7 mmol) and the required bis(mercaptomethyl)benzene (3.4 mmol) in Ar-degassed benzene (250 mL) was added dropwise over 10–12 h with vigorous stirring under Ar to a solution of KOH (0.5 g, 8.9 mmol) in 500 mL of 95% ethanol. After addition was complete, the mixture was stirred for an additional 2 h and then evaporated to dryness. The crude product was chromatographed over silica gel using CH_2Cl_2–hexanes (2:1 v/v) as eluent to obtain pure products with the properties listed below.

13*H*,15*H*-1,19-(Methanothiomethano[1,3]benzenomethanothiomethano)-8,12:20,24-dimetheno-5*H*,7*H*-dibenzo[*k*,*r*][1,9]dithiacycloeicosin (17): yield 70%, mp 154 °C; ^{1}H NMR δ 7.43–6.81 (m, 15 H), 6.74 (br s, 2 H, H_b), 6.39 (br s, 1 H, H_a), 3.63 and 3.51 (AB q, J = 14.1, 8 H), 3.36 (d, J = 11.1, 4 H), 3.04 (d, J = 11.1, 4 H); ^{13}C NMR δ 33.2, 37.2 (bridging methylenes), 127.4, 127.6, 127.7, 128.0, 128.4, 128.5, 128.6, 128.9, 135.3, 137.1, 138.0 (aromatic carbons, one overlapped); mass spectrum, *m/e* (relative intensity) 618 (M^+, 20), 481 (15), 449 (10), 448 (12), 447 (10), 313 (24), 312 (29), 311 (100), 281 (48); high-resolution mass spectrum, calcd for $C_{38}H_{34}S_4$ 618.1543, found 618.1522. Anal. Calcd: C, 73.74; H, 5.54. Found: C, 72.97; H, 5.42. The deuterio analogue **17D** (**17**-*25-d*) was prepared similarly from **8D** (58% yield) and had the same ^{1}H NMR spectrum except that the br s at δ 6.39 was absent: mass spectrum, *m/e* (relative intensity) 619 (M^+, 57), 482 (32), 481 (10), 451 (11), 450 (22), 449 (31), 448 (21), 447 (13), 314 (18), 313 (35), 312 (52), 311 (100), 310 (34).

10,33-Dimethoxy-13*H*,15*H*-1,19-(methanothiomethano[1,3]benzenomethanothiomethano)-8,12:20,24-dimetheno-5*H*,7*H*-dibenzo[*k*,*r*][1,9]dithiacycloeicosin (21): yield 73%, mp 194 °C; ^{1}H NMR δ 7.42–7.23 (m, 6 H), 6.97–6.87 (m, 3 H), 6.60 (d, J = 1.2, 4 H, protons adjacent to the methoxyls), 6.35 (br s, 1 H, H_a), 6.33 (br s, 2 H, H_b), 3.81 (s, 6 H, methoxyls), 3.54 and 3.48 (AB q, J = 14.3, 8 H), 3.37 (d, J = 11.0, 4 H), 2.96 (d, J = 11.0, 4 H); ^{13}C NMR δ 33.1, 37.2 (bridging methylenes), 55.1 (methoxyl), 113.1, 121.4, 127.0, 127.7, 128.1, 128.5, 135.3, 137.3, 139.4, 141.1, 160.0 (aromatic carbons); mass spectrum, *m/e* (relative intensity) 678 (M^+, 13), 644 (2), 543 (14), 511 (15), 477 (11), 343 (20), 313 (27), 312 (41), 311 (100), 310 (62), 309 (33), 308 (17); high-resolution mass spectrum calcd for $C_{40}H_{39}O_2S_4$ (MH^+) 679.1833, found 679.1898. Anal. Calcd for $C_{40}H_{38}O_2S_4$: C, 70.76; H, 5.64. Found: C, 70.56; H, 5.62.

7,12-Dihydro-14*H*-8,11-etheno-1,18-(methanothiomethano[1,4]benzenomethanothiomethano)-19,23-metheno-5*H*-dibenzo[*j*,*g*][1,8]dithiacyclononadecin (22): yield 64%, mp 260 °C dec; ^{1}H NMR δ 7.52–7.23 (m, 9 H), 7.20 (s, 4 H, "top" aryl protons on bridging rings), 6.83 (s, 4 H, "bottom" aryl protons on bridging rings), 6.26 (br s, 1 H, H_a), 3.73 and 3.63 (AB q, J = 13.4, 8 H), 3.04 (d, J = 10.8, 4 H), 2.39 (d, J = 10.8, 4 H); ^{13}C NMR δ 33.4, 37.0 (bridging methylenes), 127.1, 127.6, 128.1, 129.1, 129.5, 135.3, 136.3, 137.4, 141.2 (aromatic carbons, one overlapped); mass spectrum, *m/e* (relative intensity) 618 (M^+, 64), 481 (17), 313 (47), 312 (39), 311 (100), 310 (53), 281 (59), 280 (67), 279 (45); high-resolution mass spectrum calcd for $C_{38}H_{34}S_4$ 618.1543, found 618.1522. Anal. Calcd: C, 73.74; H, 5.54. Found: C, 73.52; H, 5.38. The deuterio analogue **22D** was prepared similarly from **8D** (68% yield) and had the same ^{1}H NMR spectrum except that the br s at δ 6.26 was absent: mass spectrum at 25 eV, *m/e* (relative intensity) 619 (M^+, 37), 314 (67), 313 (60), 312 (58), 311 (100), 310 (54), 282 (58), 281 (99), 234 (57).

5,15,20,30-Tetrahydro-13*H*,28*H*-31,32-[1′,3′]benzeno-8,12:23,27-dimetheno-7*H*,22*H*-dibenzo[*c*,*p*][1,6,14,19]tetrathiacyclohexacosin (23): yield 54%, mp 110 °C; ^{1}H NMR δ 7.50–7.09 (m, 18 H), 3.77 and 3.49 (AB q, J = 11.8, 8 H), 3.63 (s, 8 H); ^{13}C NMR δ 34.6, 36.0 (bridging methylenes), 127.4, 127.7, 128.0, 128.4, 128.7, 130.0, 130.6, 135.7, 135.9, 138.6, 141.6 (aromatics); mass spectrum, *m/e* (relative intensity) 618 (M^+, 0.8), 311 (0.5), 280 (2), 279 (1), 135 (100); high-resolution mass spectrum calcd for $C_{38}H_{34}S_4$ 618.1543, found 618.1583. Anal. Calcd: C, 73.74; H, 5.54. Found: C, 73.36; H, 5.55.

2,6-Dimethyl-3′-chlorobiphenyl (27). In a 250-mL three-necked flask equipped with a pressure-equalizing dropping funnel, a reflux condenser attached to an Ar source, and a magnetic stirring bar was placed 100 mg (0.18 mmol) of [Ni(DPPP)Cl_2], 4 g (20.9 mmol) of 3-chlorobromobenzene, and 80 mL of dry THF. To this mixture was added dropwise a THF solution of (2,6-dimethylphenyl)magnesium bromide **4** (prepared from 3.87 g, 20.9 mmol of 2,6-dimethylbromobenzene and 0.58 g, 23.9 mmol, of Mg turnings in 60 mL of dry THF) at room temperature with stirring over a period of 30 min. The mixture was heated at reflux for an additional 24 h, cooled, quenched with dilute HCl, extracted with ether (3 × 100 mL), and dried. The crude product obtained after removal of the solvent (rotavap) was chromatographed over silica gel using hexane as the eluent to give 1.85 g (41%) of **27** as a colorless oil: ^{1}H NMR δ 7.42–7.05 (m, 7 H), 2.07 (s, 6 H); mass spectrum, *m/e* (relative intensity) 218 (32), 216 (100), 181 (76), 166 (44); high-resolution mass spectrum calcd for $C_{14}H_{13}Cl$ 216.0726, found 216.0716.

2,6-Dimethyl-1,1′:3′,1″-terphenyl (28). Vinylmagnesium bromide (1.22 g, 9.3 mmol, as a 1.0 M solution in THF) was added to a stirred solution of 2-iodochlorobenzene (2.21 g, 9.3 mmol) in THF (30 mL) under Ar maintained at −18 °C. After the mixture was stirred at that temperature for 2 h, it was added over 20 min under Ar to a refluxing solution of 2,6-dimethyl-3′-(chloromagnesio)biphenyl (prepared from 2 g, 9.3 mmol of **27** by the molar entrainment method, using 0.49 g, 20.1 mmol of Mg and 1.74 g, 9.3 mmol of 1,2-dibromoethane in 40 mL of dry THF). The resulting mixture was stirred at reflux for an additional 4 h, cooled to room temperature, quenched slowly with dilute HCl, extracted with ether (2 × 100 mL), and dried. The crude product obtained after removal of the solvent (rotavap) was chromatographed over silica gel using hexane as the eluent to give 1.19 g (50%) of **28** as a colorless gum: ^{1}H NMR δ 7.72–7.18 (m, 12 H), 2.17 (s, 6 H); mass spectrum, *m/e* (relative intensity) 258 (M^+, 100), 243 (46), 165 (20), 152 (6), 77 (10).

2,6-Bis(bromomethyl)-1,1′:3′,1″-terphenyl (29). Freshly recrystallized NBS (1.13 g, 6.34 mmol) was added in two equal portions 4 h apart to a refluxing solution of **28** (0.78 g, 3.02 mmol) in 80 mL of CCl_4. Each addition was followed by a few milligrams of benzoyl peroxide. After 24 h at reflux the mixture was cooled, and the precipitated succinimide was removed by filtration. The solvent was removed (rotavap), and the residue was chromatographed over silica gel using CH_2Cl_2–hexanes (1:10) as eluent to give 0.65 g (52%) of **29** as a colorless gum: ^{1}H NMR δ 7.74–7.36 (m, 12 H), 4.29 (s, 4 H); mass spectrum, *m/e* (relative intensity) 416 (2), 362 (8), 361 (12), 360 (17), 317 (20), 275 (36), 256 (23),

(27) It was not possible to obtain an accurate elemental analysis, probably due to some oxidation to acid between purification and subjection to analysis. However an accurate analysis of **14**, prepared from **13**, was obtained, as well as a high-resolution mass spectrum of **13**.

255 (100), 253 (25), 127 (41). Anal. Calcd for $C_{20}H_{16}Br_2$: C, 57.77; H, 3.88. Found: C, 57.56; H, 3.92.

Dithiacyclophanes 25 and 26. A solution of **29** (0.283 g, 0.68 mmol) and 1,2-bis(mercaptomethyl)benzene (0.115 g, 0.68 mmol) in Ar-degassed benzene (40 mL) was added dropwise over 4–5 h under Ar to a stirred solution of KOH (0.115 mg, 2.70 mmol) in 200 mL of 95% ethanol. After an additional 2 h of stirring the solvent was removed under a vacuum, and the crude product was chromatographed over silica gel using CH_2Cl_2–hexanes (3:7) as eluent to give 0.130 g (46%) of an inseparable mixture of rotamers **25** and **26**: ^{1}H NMR δ 7.62–6.73 (m, 16 H), 3.95–3.00 (14 lines out of a required 16 for 4 AB q, 8 H); mass spectrum, *m/e* (relative intensity) 424 (M^+, 1.3), 255 (18), 241 (24), 135 (100); high-resolution mass spectrum calcd for $C_{28}H_{24}S_2$ 424.1320, found 424.1342.

6,16,23,33-Tetrahydro-14*H*,31*H*-41,48-[1′,3′]benzeno-5,34-[1′,2′]:17,22[1″,2″]-dibenzeno-9,13:26,30-dimetheno-8*H*,25*H*-dibenzo[*d*,*s*][1,8,16,23]tetrathiacyclotriacontin (31). A solution of tetrakis(mercaptomethyl) compound **11** (0.5 g, 1.21 mmol) and 9,10-bis(chloromethyl)anthracene[18] (0.66 g, 2.4 mmol) in Ar-degassed toluene (400 mL) was added dropwise over 10–12 h with vigorous stirring under Ar to a solution of KOH (0.5 g, 8.9 mmol) in 500 mL of 95% ethanol. After addition was complete, the mixture was stirred for an additional 2 h and then evaporated, and the crude product was chromatographed over silica gel using CH_2Cl_2–hexanes (3:1 v/v) to yield 0.33 g (33%) of **31** as a yellow solid: mp 264 °C dec; ^{1}H NMR δ 8.33 (m, 4 H), 8.18 (m, 4 H), 7.58 (m, 4 H), 7.31 (m, 4 H), 7.28–7.13 (m, 6 H), 6.41 (dd, J = 7.7, 1.8, 2 H), 5.61 (t, J = 7.7, 1 H), 5.51 (d, J = 13.7, 4 H), 5.03 (br s, 1 H), 4.42 (d, J = 13.7, 4 H), 2.85 (d, J = 10.9, 4 H), 1.61 (d, J = 10.9, 4 H) (for assignments, see text); ^{13}C NMR (DMSO-d_6) δ 27.1, 31.8 (bridging methylenes), 124.7, 125.0, 125.1, 125.3, 125.4, 125.8, 127.0, 127.2, 128.4, 128.7, 128.8, 128.9, 134.6, 134.9, 140.3 (aromatic); mass spectrum 818 (M^+, 0.6), 646 (0.8), 614 (4), 582 (1), 532 (0.5), 501 (0.8), 311 (6), 286 (5), 252 (5), 221 (10), 204 (100); high-resolution mass spectrum calcd for $C_{54}H_{42}S_4$ 818.2163, found 818.2169.

30,38-Diaza-17 (33). A solution of **11** (0.5 g, 1.21 mmol) and 2,6-bis(chloromethyl)pyridine[19] (0.42 g, 2.42 mmol) in Ar-degassed benzene (100 mL) was added dropwise over 5–6 h under Ar to a solution of KOH (0.41 g, 7.25 mmol) in 300 mL of 95% ethanol. After addition was complete, the mixture was stirred for an additional 2 h. Workup as for **17** gave 0.57 g (74%) of **28** as a white solid: mp 225–230 °C (recrystallized from $CHCl_3$–methanol). ^{1}H NMR δ 7.57 (t, J = 7.7, 2 H, protons para to the nitrogens in the pyridine rings), 7.41–7.26 (m, 6 H), 7.11 (d, J = 7.7, 4 H, protons meta to the nitrogens in the pyridine rings), 6.95 (m, 2 H, protons in the central ring of the *m*-terphenyl unit), 6.79 (m, 1 H, proton in the central ring of the *m*-terphenyl unit), 6.54 (t, J = 1.6, internal H on the central *m*-terphenyl ring), 3.72 and 3.67 (AB q, J = 13.9, 8 H), 3.58 (d, J = 10.6, 4 H), 3.09 (d, J = 10.6, 4 H); ^{13}C NMR δ 34.2, 39.2 (bridging methylenes), 121.4, 126.8, 127.4, 127.8, 128.3, 128.9, 129.4, 135.2, 137.4, 157.8 (aromatic carbons, one overlapped); mass spectrum, *m/e* (relative intensity) 620 (M^+, 100), 588 (10), 587 (22), 515 (8), 514 (10), 482 (7), 450 (7), 416 (7), 343 (6), 312 (14), 311 (26), 310 (33), 296 (15), 277 (17), 139 (18), 138 (19), 107 (45); high-resolution mass spectrum calcd for $C_{36}H_{33}N_2S_4$ (MH^+) 621.1527, found 621.1526. Anal. Calcd for $C_{36}H_{32}N_2S_4$: C, 69.64; H, 5.19. Found: C, 69.38; H, 5.12.

25-Bromo-13*H*,15*H*-1,19-(methanothiomethano[1,3]benzenomethanothiomethano)-8,12:20,24-dimetheno-5*H*,7*H*-dibenzo[*k*,*r*][1,9]dithiacycloeicosin (34). The general procedure for **17** was followed, using pentabromide **15** in place of **8**, with bisthiol **16**: yield 67%, mp 197 °C; ^{1}H NMR δ 7.43–7.21 (m, 9 H), 7.11 (d, J = 8.2, 4 H), 6.95 (d, J = 7.7, 2 H), 6.71 (br s, 2 H, isolated protons on the bridging rings), 3.66 and 3.46 (AB q, J = 14.4, 8 H), 3.47 (d, J = 10.8, 4 H), 2.84 (d, J = 10.8, 4 H); ^{13}C NMR δ 33.2, 37.3 (bridging methylenes), 126.4, 126.8, 127.4, 128.2, 128.4, 128.9, 129.0, 129.1, 130.0, 135.3, 138.3, 140.1 (aromatics); mass spectrum at 25 eV, *m/e* (relative intensity) 696 (14), 694 (20), 615 (14), 480 (16), 479 (24), 446 (23), 313 (13), 311 (20), 310 (100); high-resolution mass spectrum, calcd for $C_{38}H_{34}BrS_4$ (MH^+) 697.0731, found 697.0727.

Conversion of 34 to 17. To a solution of **34** (0.1 g, 0.14 mmol) in 5 mL of dry THF was added 28 μL of *n*-butyllithium (3.0 equiv, 1.6 M in THF) at −78 °C under Ar. The mixture was stirred for 4 h at that temperature, quenched with dilute HCl, extracted with $CHCl_3$ (2 × 10 mL), and dried. The crude product obtained after solvent removal (rotavap) was chromatographed on a preparative silica gel plate using CH_2Cl_2–hexane (2:1) as eluent to give 55 mg (62%) of **17**, identical (melting point, NMR) with that prepared as above.

1,2,4,5-Tetrakis(mercaptomethyl)benzene (35). A stirred solution of 1,2,4,5-tetrakis(bromomethyl)benzene[20] [prepared from durene and NBS] (5.0 g, 11.1 mmol) and thiourea (3.63 g, 47.7 mmol) in THF (150 mL) was heated under reflux for 12 h. The mixture was cooled, and the precipitated isothiouronium salt was collected, suspended in aqueous KOH (5.0 g, 89.1 mmol of KOH in 200 mL of water), and heated at reflux under Ar for 6 h. The mixture was cooled in an ice bath, and 1:1 concentrated sulfuric acid–water (100 mL) was added dropwise. The tetrathiol was extracted with chloroform (3 × 150 mL). Combined organic layers were dried, and the solvent was evaporated. The residue was chromatographed over silica gel using CH_2Cl_2–hexanes (2:1 v/v) as eluent to give 1.48 g (51%) of **35**: mp 125–128 °C; ^{1}H NMR δ 7.21 (s, 2 H, arom), 3.83 (d, J = 7.1, 8 H, methylenes), 1.86 (t, J = 7.1, 4 H, thiol); mass spectrum, *m/e* (relative intensity) 262 (1), 228 (61), 194 (79), 193 (65), 192 (22), 163 (17), 162 (19), 161 (26), 149 (100). Anal. Calcd for $C_{10}H_{14}S_4$: C, 45.76; H, 5.38. Found: C, 45.41; H, 5.29.

Cappedophanes 36 (7,12-Dihydro-14*H*-1,9:10,18-bis(methanothiomethano)-19,23-metheno-5*H*-tribenzo[*c*,*h*,*o*][1,6]dithiacycloheptadecin) and 37. Coupling of **8** with **35** was carried out according to the general procedure for **17** except that the reagents were used in equimolar amounts. First to elute was the minor product **37** (1.9%, mp >260 °C, dec): ^{1}H NMR δ 8.30 (s, 2 H, aromatics on capping ring), 7.62–7.55 (m, 6 H, aromatic hydrogens in the "outer" *m*-terphenyl rings), 7.06 (t, J = 7.7, 1 H, H para to the isolated H in the central *m*-terphenyl ring), 6.50 (dd, J = 7.7, 1.8, 2 H, H's meta to the isolated H in the central *m*-terphenyl ring), 4.23 (br s, 1 H, isolated H in the central *m*-terphenyl ring), 3.61 and 3.51 (AB q, J = 12.0, 8 H), 3.07 and 2.85 (AB q, J = 16.1, 8 H); mass spectrum, *m/e* (relative intensity) 540 (M^+, 8), 311 (8), 297 (4), 281 (16), 265 (18), 195 (20), 194 (85), 193 (96), 192 (24), 191 (35), 44 (100); high-resolution mass spectrum calcd for $C_{32}H_{28}S_4$ 540.1074, found 540.1065. Next to elute was the major product **36** (16%, mp >270 °C, dec): ^{1}H NMR δ 7.59–7.51 (m, 6 H, aromatic hydrogens in the "outer" *m*-terphenyl rings), 7.27 (t, J = 7.5, 1 H, H para to the isolated H in the central *m*-terphenyl ring), 6.98 (dd, J = 7.5, 1.1, 2 H, H's meta to the isolated H in the central *m*-terphenyl ring), 4.75 (s, 2 H, aromatic H's in the capping ring), 3.97 (br s, 1 H, isolated proton in the central *m*-terphenyl ring), 3.77 and 3.69 (AB q, J = 13.1, 8 H), 3.52 and 3.30 (AB q, J = 14.0, 8 H); mass spectrum, *m/e* (relative intensity) 540 (14), 513 (7), 281 (27), 280 (38), 279 (23), 265 (37), 193 (40), 191 (36), 44 (100); high-resolution mass spectrum calcd for $C_{32}H_{28}S_4$ 540.1074, found 540.1065. Anal. Calcd: C, 71.07; H, 5.22. Found: C, 71.11; H, 5.20. The deuterio analogues **36D** and **37D** were similarly prepared from **8D**.

13*H*,15*H*-1,19-(Methanothiomethano[1,3]benzenomethanothiomethano)-8,12:20,24-dimetheno-5*H*,7*H*-dibenzo[*k*,*r*][1,9]dithiacycloeicosin 6,6,14,14,27,27,36,36-Octaoxide 38 (Typical Procedure for All Sulfones). To a solution of 198 mg (0.32 mmol) of **17** in CH_2Cl_2–glacial acetic acid (1:1, 30 mL), cooled in an ice bath and stirred magnetically, was added a solution of 0.85 g (3.95 mmol) of 85% *m*-chloroperbenzoic acid in 10 mL of glacial acetic acid. The mixture was allowed to slowly warm to room temperature and was stirred for 2 days. The precipitated tetrasulfone was filtered and washed several times with $CHCl_3$ to give 229 mg (96%) of **38**: mp 370 °C dec; ^{1}H NMR (DMSO-d_6) δ 7.55–7.25 (m, 14 H), 6.80–6.58 (m, 3 H, central *m*-terphenyl ring), 6.10 (s, 1 H, isolated proton on the central *m*-terphenyl ring), 4.48 (s, 8 H), 4.05 (d, J = 13.0, 4 H), 3.59 (d, J = 13.0, 4 H). The corresponding deuterio analogue **38D** was similarly prepared from **17D**. The sulfones were sufficiently pure for flash vacuum pyrolysis.

5,6,12,13-Tetrahydro-1,17-(ethano[1,3]benzenoethano)-7,11:18,22-dimethenodibenzo[*a*,*h*]cyclooctadecene (39) (Typical Procedure for Flash Vacuum Pyrolyses). Tetrasulfone **38** (201 mg, 0.27 mmol) was placed in a quartz boat inside a quartz tube and evacuated to 10^{-2} Torr. The tube was then heated to 450–500 °C. The product sublimed into colder zones

and was taken up in CH_2Cl_2. Crude product was chromatographed on a preparative silica gel plate (20 × 20 cm × 1 mm) using hexane as eluent to give 36 mg (27%) of pure **39**: mp 210 °C; ^1H NMR δ 7.41–7.23 (m, 7 H), 7.04 (dd, J = 7.6, 1.7, 2 H, H's meta to the isolated proton in the central *m*-terphenyl ring), 6.89 (t, J = 7.5, 2 H, para to the isolated proton in the bridging rings), 6.78 (br s, 2 H, isolated protons in the bridging rings), 6.63 (dd, J = 7.5, 1.8, 4 H, meta to the isolated proton in the bridging rings), 5.70 (br s, 1 H, isolated proton on the central *m*-terphenyl ring), 2.90–2.44 (m, 16 H, methylenes); mass spectrum, *m/e* (relative intensity) 490 (M^+, 100), 386 (20), 385 (70), 265 (24); high-resolution mass spectrum calcd for $C_{38}H_{34}$ 490.2653, found 490.2661. Anal. Calcd: C, 93.02; H, 6.98. Found: C, 92.84; H, 6.89. The deuterio analogue **39D** was similarly prepared from **38D**.

5,6,11,12-Tetrahydro-1,16-(ethano[1,4]benzenoethano)-7,10-etheno-21,17-metheno-17*H*-dibenzo[*a*,*h*]cyclo-heptadecene (40). Via the same procedure as for **38**, tetrasulfide **22** was converted to the corresponding tetrasulfone: yield 91%, mp 310 °C dec; ^1H NMR (DMSO-d_6) δ 7.45–7.26 (m, 17 H), 5.89 (s, 1 H, isolated H on the central *m*-terphenyl ring), 4.54 (br s, 8 H), 4.11 (d, J = 12.0, 4 H), 2.74 (d, J = 12.0, 4 H). The peak at δ 5.89 was absent from the ^1H NMR spectrum of the analogous tetrasulfone prepared from **22D**.

Flash vacuum pyrolysis of the tetrasulfone as in the preparation of **39** gave **40** in 21% yield: mp 243 °C; ^1H NMR δ 7.39–6.79 (m, 9 H), 6.59 (br s, 1 H, isolated aryl proton on the central *m*-terphenyl ring), 6.43 (d, J = 1.0, 4 H, "top" aryl protons in the bridging rings), 6.27 (d, J = 1.0, 4 H, "bottom" aryl protons in the bridging rings), 3.38–3.26 (m, 4 H), 3.14–3.05 (m, 4 H), 2.83–2.73 (m, 4 H), 2.61–2.53 (m, 4 H); the peak at δ 6.59 was absent from the NMR spectrum of **40D**, prepared analogously from **22D**; mass spectrum, *m/e* (relative intensity) 490 (M^+, 34), 386 (15), 385 (33), 281 (36), 280 (19), 279 (21), 267 (30), 266 (44), 119 (78), 105 (100); high-resolution mass spectrum calcd for $C_{38}H_{34}$ 490.2653, found 490.2657. Anal. Calcd: C, 93.02; H, 6.98. Found: C, 93.09; H, 6.89.

5,6,12,13,18,19,25,26-Octahydro-27,28-[1′,3′]benzeno-7,11:20,24-dimethenodibenzo[*a*,*l*]cyclodocosene (41). Via the same procedure as for **38**, tetrasulfide **23** was converted to the corresponding tetrasulfone: yield 87%, mp 360 °C dec; ^1H NMR (DMSO-d_6) δ 7.71–7.13 (m, 18 H), 4.65 and 4.11 (AB q, J = 13.8, 8 H), 4.44 (br s, 8 H).

Flash vacuum pyrolysis of the tetrasulfone as in the preparation of **39** gave **41** in 10% yield: mp 198 °C; ^1H NMR δ 7.60–7.05 (m, 18 H), 3.10–2.34 (m, 16 H); mass spectrum, *m/e* (relative intensity) 490 (M^+, 42), 386 (13), 385 (41), 371 (26), 281 (21), 279 (18), 267 (22), 119 (56), 117 (27), 105 (100); high-resolution mass spectrum calcd for $C_{38}H_{34}$ 490.2653, found 490.2641. Anal. Calcd: C, 93.02; H, 6.98. Found: C, 93.04; H, 6.93.

7,12-Dihydro-14*H*-1,9:10,18-bis(methanothiomethano)-19,23-metheno-5*H*-tribenzo[*c*,*h*,*o*][1,6]dithiacycloheptadecin 6,6,13,13,26,26,29,29-Octaoxide (42). By use of the same procedure as for the preparation of **38** from **17**, cappedophane **36** was oxidized to **42** in 76% yield: mp 310 °C dec; ^1H NMR (DMSO-d_6) δ 7.83–7.41 (m, 7 H), 6.79 (d, J = 7.6, 2 H, protons meta to X), 6.34 (s, 2 H, aryl protons on the capping ring), 5.07 (d, J = 14.8, 4 H), 4.70 (d, J = 14.8, 4 H), 4.19 (m, 9 H).

Pyrolysis of 42. Pyrolysis of **42** was carried out as in the preparation of **39** from **38**. The crude product was subjected to preparative TLC as with **39**. The front-running band gave **43** in 24% yield: mp 265–266 °C; ^1H NMR δ 7.41–7.24 (m, 6 H, aryl protons on the "outside" *m*-terphenyl rings), 7.11 (t, J = 7.6, 1 H, proton para to X), 6.69 (dd, J = 7.6, 1.7, 2 H, protons meta to X), 3.77 (t, J = 1.7, 1 H, H_x), 3.67 (s, 2 H, aryl protons on the capping ring), 3.25–3.17 (m, 4 H), 2.94–2.86 (m, 4 H), 2.36–2.25 (m, 4 H), 2.17–2.04 (m, 4 H); mass spectrum, *m/e* (relative intensity) 412 (M^+, 100), 387 (5), 293 (31), 283 (31), 280 (47), 279 (40), 265 (51); high-resolution mass spectrum, calcd for $C_{32}H_{28}$ 412.2213, found 412.1199. Anal. Calcd: C, 93.16; H, 6.84. Found: C, 93.32; H, 7.20.

The base-line band from TLC was extracted with CH_2Cl_2 to yield 32% of **44**: mp >340 °C dec; ^1H NMR δ 8.03 (d, J = 7.7, 2 H, aryl protons in "right outer" *m*-terphenyl ring), 7.67 (t, J = 7.7, 1 H, aryl proton in "right outer" *m*-terphenyl ring), 7.45–7.21 (m, 4 H, aryl protons in "left outer" *m*-terphenyl ring plus proton para to X), 6.87 and 6.78 (m, each 1 H, H_c and H_d), 5.16 (s, 1 H, H_b), 4.48–4.38 and 4.20–4.13 (m, each 4 H, methylenes adjacent to sulfone), 3.56–3.48, 3.15–3.07, 2.43–2.32, 2.16–2.05 (m, each 2 H, methylenes), 3.45 (s, 1 H, H_a), 3.31 (m, 1 H, H_x); ^{13}C NMR δ 35.4, 35.9, 39.5 (bridged methylenes, one overlapped), 125.6, 126.3, 126.5, 127.9, 128.2, 128.9, 129.1, 129.3, 129.4, 129.5, 134.2, 137.0, 137.6, 140.8, 140.9 (aromatics, three overlapped); IR (KBr) 2940, 2850, 1610, 1425, 1387, 1250 cm^{-1}; mass spectra, *m/e* (relative intensity) 540 (1.8), 412 (100), 397 (17), 293 (56), 280 (86), 279 (86), 265 (80). Anal. Calcd for $C_{32}H_{28}S_2O_4$: C, 71.08; H, 5.22. Found: C, 70.57; H, 5.22.

X-ray Data for 36. Recrystallization of **36** from CH_2Cl_2–hexane (2:1) gave a colorless rod crystal, $C_{32}H_{28}S_4$: tetragonal space group $I4_1cd$: a = b = 16.606 (4) and c = 18.751 (6) Å; Z = 8; M = 540.84; V = 5170.8 (28) Å^3; ρ = 1.389 g cm^{-3}. Preliminary examination and intensity data were measured by using Mo K_α radiation (λ = 0.710 73 Å) on a Nicolet P3F diffractometer ($2\theta_{max}$ = 45°), yielding a total of 1905 reflections of which 882 were unique and 633 were used in the refinement [$F_o^2 > 3.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-86). The final R value was 0.032.

X-ray Data for 39. Recrystallization of **39** from heptane gave a colorless crystal, $C_{38}H_{34}$: space group $P2_1/n$; a = 9.950 (1), b = 12.961 (2), and c = 21.051 (3) Å; β = 101.19 (1); Z = 4; M = 490.69; V = 2663.0 (6) Å^3; ρ = 1.224 cm^{-3}. Preliminary examination and intensity data were measured by using Mo Kα radiation (λ = 0.710 73 Å) on a Nicolet P3F diffractometer (2θ = 45°), yielding a total of 4957 reflections of which 4721 were unique and 1332 were used in the refinement [$F_o^2 > 3.0\sigma(F_3^2)$]. The structure was solved by direct methods (SHELXS-86). The final R value was 0.074.

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Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bond lengths, bond and torsion angles for **36** and **39** (18 pages). Ordering information is given on any current masthead page.