1 H), 5.4-5.5 (m, 1 H), 6.8-6.9 (m, 1 H), 7.0-7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.5, 32.5, 33.5, 102.5, 119.9, 126.3, 128.2, 128.7, 138.1, 141.8, 150.6; IR (film) 694, 745, 870, 1447, 1493, 1598, 2960, 3035 cm^{-1}. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.49; H, 8.35.

2a: 78% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.6-1.8 (m, 4 H), 2.2-2.4 (m, 2 H), 2.4-2.6 (m, 2 H), 4.6-4.8 (m, 1 H), 4.9-5.0 (m, 1 H), 6.5-6.6 (m, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.8, 27.3, 30.2, 35.9, 109.2, 123.7, 126.8, 128.5, 129.8, 138.3, 143.2, 151.6; IR (film) 658, 750, 865, 1430, 1480, 1615, 2830, 2920, 3005, 3060 cm^{-1}; UV (cyclohexane) λ_{max} 260 (ε 630); maleic anhydride adduct mp 137-138 °C (lit.[7] mp 139 °C).

3a: 79% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.5-1.7 (m, 6 H), 2.3-2.4 (m, 2 H), 2.5-2.6 (m, 2 H), 4.7-4.8 (m, 1 H), 5.4-5.5 (m, 1 H), 6.6-6.7 (m, 1 H), 7.1-7.4 (m, 5 H); IR (film) 690, 747, 875, 1435, 1590, 2840, 2905, 3010, 3070 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H. 9.15. Found: C, 90.53; H, 8.96.

4a: 44% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.4-1.8 (m, 8 H), 2.3-2.4 (m, 2 H), 2.5-2.6 (m, 2 H), 4.8-4.9 (m, 1 H), 5.1-5.2 (m, 1 H), 6.6-6.7 (m, 1 H), 7.1-7.5 (m, 5 H); IR (film) 696, 749, 894, 1444, 1491, 1597, 2920, 3030, 3085 cm^{-1}. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.54; H, 9.33.

5a: 73% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92, (d, J = 6.3 Hz, 3 H), 1.24 (dq, J = 4.4, 12.2 Hz, 1 H), 1.5-1.7 (m, 1 H), 1.8-1.9 (m, 2 H), 2.2-2.3 (m, 1 H), 2.46 (dt, J = 3.9, 13.7 Hz, 1 H), 2.8-2.9 (m, 1 H), 4.6-4.7 (m, 1 H), 4.9-5.1 (m, 1 H), 6.5-6.6 (m, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.0, 32.4, 34.4, 34.9, 37.9, 108.7, 123.2, 126.2, 128.0, 129.3, 137.7, 142.1, 150.6; IR (film) 690, 730, 857, 886, 1151, 1435, 1620, 2910, 2940, 3010, 3070 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 9.06.

6a (Wittig reaction using ethyltriphenylphosphonium iodide): 49% yield (as a mixture of isomers); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.5-1.8 (m with doublets at 1.68 and 1.78, total of 7 H), 2.2-2.4 (m, 2 H), 2.4-2.6 (m, 2 H), 5.3-5.7 (quartets, 1 H), 6.2-6.5 (multiplets, 1 H), 7.1-7.4 (m, 5 H); IR (film) 688, 751, 810, 909, 985, 1436, 1590, 2830, 2910, 3010 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.65; H, 9.47.

7a: 74% yield; colorless oil; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.5-1.9 (m, 4 H), 2.2-2.7 (m with s at 2.33, 7 H), 4.6-4.8 (m, 1 H), 4.9-5.0 (m, 1 H), 6.4-6.6 (m, 1 H), 7.0-7.2 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 26.7, 27.3, 30.2, 35.8, 108.9, 123.5, 129.1, 129.7, 135.4, 136.4, 142.5, 151.7; IR (film) 800, 880, 1430, 1500, 1610, 2850, 2920, 3010, 3070 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.75; H, 8.91.

8a: 66% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.4-1.8 (m, 4 H), 2.2-2.5 (m, 4 H), 4.8 (m, 1 H), 5.1 (m, 1 H), 7.0 (m, 1 H), 7.2-7.6 (m, 4 H), 7.6-7.9 (m, 2 H), 7.9-8.1 (m, 1 H); IR (film) 770, 880, 1385, 1430, 1620, 2840, 2920, 3045 cm^{-1}. Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 91.81; H, 7.64.

Photocyclization of Dienes. General Procedure. A solution of 1 mmol of diene in 200 mL of benzene in an open quartz beaker was placed approximately 15 cm from a 450-W medium-pressure mercury vapor lamp in a water-cooled quartz immersion apparatus and irradiated for 3-6 h. After the irradiation the solvent was evaporated and the product was purified by flash chromatography (petroleum ether eluent). All photoproducts except **7b** were known compounds and were identified by comparison of melting points and/or spectroscopic data with literature values.

1b: 57% yield; mp 94-95 °C (lit.[8] mp 94 °C).

2b: 57% yield; mp 98-99 °C (lit.[6,9] mp 92-94 °C, 103-105 °C).

3b: 74% yield; mp 103-105 °C (lit.[6] mp 104-105 °C).

4b: 58% yield; colorless oil (lit.[10] mp 54-55 °C).

5b: 45% yield; 70-72 °C (lit.[11] mp 69-74 °C).

6b: 56% yield; colorless oil.[12]

7b: 61% yield; white crystals; mp 72-73 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.8-2.0 (m, 4 H), 2.46 (s, 3 H), 2.9-3.1 (m, 4 H), 7.2-7.3 (m, 1 H), 7.4-7.7 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 21.8, 23.2, 23.5, 29.7, 125.7, 126.2, 126.5, 127.0, 127.3, 130.5, 132.4, 134.3, 135.2, 136.2; IR (Nujol) 797, 876, 922, 1501 cm^{-1}. Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.68; H, 8.24.

8b: 48% yield; mp 89-90 °C (lit.[13] mp 89-90 °C).

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Registry No. 1, 1921-90-0; **1a**, 130954-49-3; **1b**, 1624-26-6; **2**, 1467-15-8; **2a**, 130954-50-6; **2a** (maleic anhydride adduct), 130954-57-3; **2b**, 2141-42-6; **3**, 88356-04-1; **3a**, 130954-51-7; **3b**, 7092-91-3; **4**, 69202-72-8; **4a**, 130954-52-8; **4b**, 16271-28-6; **5**, 75910-68-8; **5a**, 130954-53-9; **5b**, 85268-79-7; (*E*)-**6a**, 130954-54-0; (*Z*)-**6a**, 130954-55-1; **6b**, 101111-40-4; **7**, 130954-47-1; **7a**, 130954-56-2; **7b**, 89155-69-1; **8**, 130954-48-2; **8a**, 122214-17-9; **8b**, 67064-62-4; methyltriphenylphosphonium iodide, 2065-66-9; methyltriphenylphosphonium bromide, 1779-49-3; ethyltriphenylphosphonium iodide, 4736-60-1.

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Reduction of DMAD-Anthracene Adducts. Synthesis and Conformations of Substituted Cyclodecadienes

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A general method for reducing DMAD-anthracene adducts to the corresponding enediols is described. Thus, the ester groups of **1** were reduced without C=C reduction using the DIBAH-*n*BuLi "ate" complex to give previously unknown **2** in high yield. Analogous enediols **5-7** were similarly prepared. Base treatment of dibromide **3** and dithiol **9**, both prepared from **2** by standard methods, gave conformationally rigid dithiacyclodecadiene **10**. With *o*-, *m*-, and *p*-xylylenedithiols, dibromide **3** gave respectively the conformationally labile cyclophanes **12** and **13** and the rigid cyclophane **14**. Tetrabromide **16** and dithiol **9** gave cuppedophane **17**, but tetrabromide **18** and **9** formed bis-*m*-cyclophane **19** instead.

It is surprising that although the dimethyl acetylenedicarboxylate (DMAD) adduct of anthracene (**1**) has been known since 1931,[1] the enediol **2** that might be derived from it by reduction is as yet unreported. Attempts to

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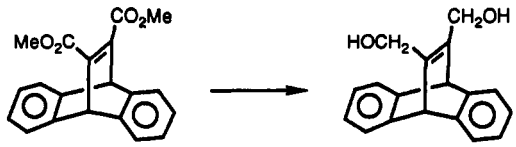


1 2

prepare 2 directly by cycloaddition of 2-butyne-1,4-diol to anthracene failed,[2] as did attempts to reduce 1 to 2 with lithium aluminum hydride.[2] Even inverse addition led to C=C reduction, the trans saturated diol being obtained in low (15%) yield.[2]

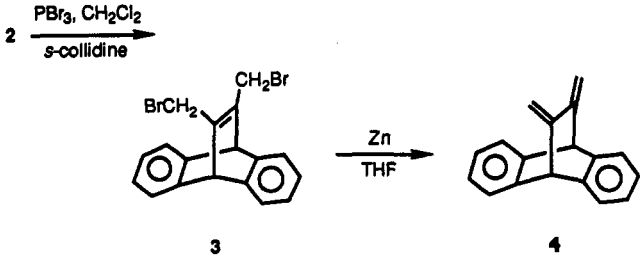
In view of the synthetic potential of 2, its dihalides and the corresponding dithiol for ring construction (vide infra), we reexamined the reduction of 1 and analogous adducts. The "ate" complex from diisobutylaluminum hydride (DIBAH) and *n*-butyllithium was reported to reduce esters containing conjugated (i.e., methyl cinnamate) or nonconjugated (i.e., methyl 10-undecenoate) double bonds cleanly and quantitatively to the corresponding unsaturated alcohols,[3] and hence seemed a likely candidate for the successful reduction of 1 to 2. We report here the preparation of 2, its conversion to the corresponding dibromide and dithiol, and their use in the construction of rings, including cyclophanes, flanked by aryl groups that project above and below the mean ring plane. We also describe the conformations of such rings.

Results and Discussion

Reduction of DMAD Adducts to Enediols. Reduction of 1 with the DIBAH–BuLi "ate" complex at −78 °C followed by warming to room temperature gave the enediol 2 in 87–92% yield. Reduction with DIBAH alone at −78 °C gave a mixture containing about 80–85% of 2 together with 15–20% of overreduction product (saturated diol); it was difficult or impossible to obtain pure 2 from this mixture. Therefore use of the "ate" complex is necessary.

The structure of 2, mp 193–194 °C, was clear from its spectra and subsequent reactions. In particular, its ^{1}H NMR spectrum showed sharp singlets at δ 4.30 (4 H) and 5.18 (2 H) for the methylene and bridgehead protons, as well as a broad singlet at δ 1.57 (2 H, exchangeable with D_2O) for the hydroxyl protons and an aromatic AA'BB' multiplet (8 H).

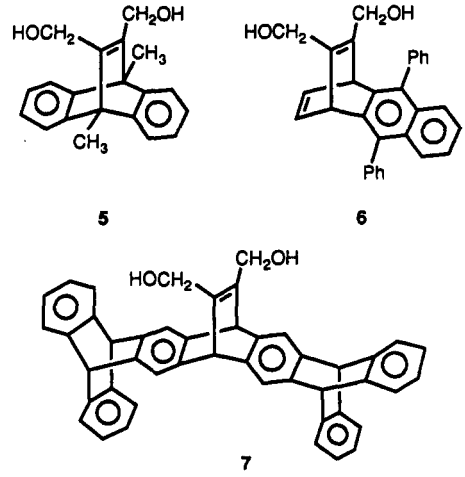
Diol 2, when treated at −20 °C to room temperature with PBr_3 and *s*-collidine, gave dibromide 3 (63–68%), which in turn with zinc dust gave the known[2,4-6] diene 4 in 93% yield. This route to 4 compares favorably with literature



3 4

routes, especially since the cycloaddition of 1,4-dichloro-2-butene to anthracene, the first step in the shorter routes,[5,6] involves a sealed tube reaction that is sometimes erratic and difficult to scale up.

Reduction of DMAD–anthracene adducts to the corresponding enediol with the "ate" complex is general. Thus, diols 5–7 were similarly prepared. The 9,10-dimethyl-



5 6 7

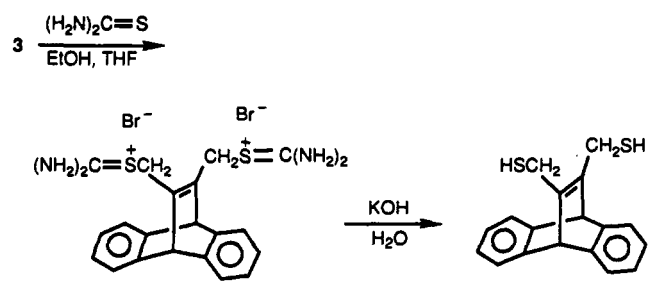
anthracene–DMAD adduct gave 5, mp 215 °C, in 88% yield. The structure was clear from its ^{1}H and ^{13}C NMR spectra (see the Experimental Section).

9,10-Diphenylanthracene cycloadds DMAD across the 1,4-positions.[7] Reduction of that adduct with DIBAH–BuLi proceeded without affecting either the conjugated or the isolated C=C bond, to give 6 in 80% yield. The ^{1}H NMR spectrum of 6 showed two AB quartets for the methylene protons (δ 4.13 and 4.23), mutually coupled bridgehead and vinyl protons at δ 4.75 and 6.79, respectively, two exchangeable hydroxyl protons at δ 1.8 and a multiplet at δ 7.23–7.58 for the 14 aromatic protons. The ^{13}C NMR spectrum also supported the assigned structure (see the Experimental Section).

Diol 7 was obtained in 87% yield by reducing the DMAD adduct of the known[6,8] pentiptycene precursor 5,18:9,14-di-*o*-benzeno-5,9,14,18-tetrahydroheptacene. Its symmetric structure was clear from its ^{1}H NMR spectrum, particularly a singlet at δ 4.15 for the methylene protons, and singlets at δ 5.23 and 4.98 (4 H and 2 H, respectively) for the outer and inner bridgehead protons.

It is clear from these examples that "ate" complexes can be used generally to reduce DMAD cycloadducts to enediols.

Ring Constructions. It was thought that doubly allylic dibromide 3 and the corresponding dithiol 9 would be useful synthons for ring construction. Dithiol 9 was readily prepared from 3 vis the bisisothiouronium salt 8 in 67% overall yield. The salt 8 was obtained analytically pure,



8 (100%) 9 (67%)

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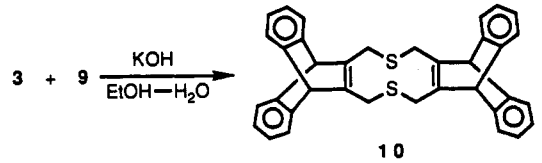
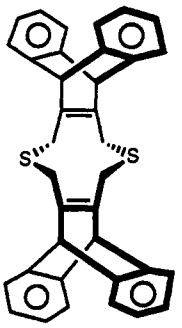
but **9**, mp 152 °C, was rather air-sensitive. Nevertheless its ^1H and ^{13}C NMR spectra were consistent with the structure. For example, the SH protons appeared as a triplet (δ 1.3, J = 7.2 Hz), coupled with the methylene protons at δ 3.42, and the bridgehead protons appeared as a sharp singlet at δ 5.14.

Slow addition of an equimolar mixture of **3** and **9** to aqueous alcoholic KOH gave the cyclization product **10** in 44% yield. The symmetric structure of **10** was clear from



10

its ^1H NMR spectrum, which showed a singlet at δ 5.20 (4 H) for the bridgehead protons. However, the signal for the methylene protons was not a singlet. Instead, they appeared as two geminally coupled doublets at δ 2.28 and 2.55 (4 H each, J = 14.2 Hz). Therefore the structure is rigid at room temperature, most likely in the anti conformation **10a** (anti refers to the relationship between the



10a

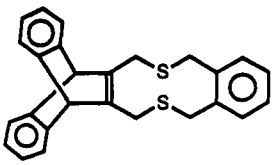
double bonds) in which the bridgehead protons are equivalent, but the methylene protons fall into two sets. Two of the aromatic rings are directed over the 10-membered ring, whereas the other two lie well away from that ring; the aromatic proton signals and ^{13}C spectrum were consistent with this arrangement. Heating **10** to 130 °C caused no change in the methylene spectrum.

The parent ring system 4,9-dithia-1,6-cyclodecadiene **11**, in contrast to **10**, is conformationally mobile at room temperature, the methylene and vinyl protons being singlets at δ 3.08 and 5.38, respectively.[9] However, at −57 °C the methylene protons of **11** resolve to an AA′BB′ quartet as a consequence of 'freezing out' into the anti conformations **11a** and **11a′**. The barrier for anti–anti

11a **11s** **11a′**

interconversion is 12.1 kcal mol^{-1} (T_c = −24 °C),[9] and the presumed intermediate is the syn conformer **11s**.[10] With **10**, the syn conformation is impossible due to collision of two of the aryl rings. Hence, in contrast with **11**, **10** is conformationally rigid.

Coupling of dibromide **3** with *o*-, *m*-, and *p*-xylylenedithiols (KOH, EtOH–benzene) under high dilution gave disulfides **12–14** in 58–78% yield.



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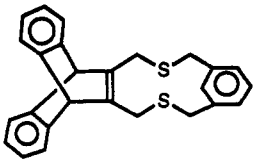

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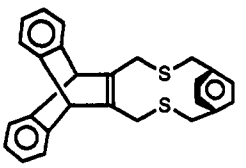
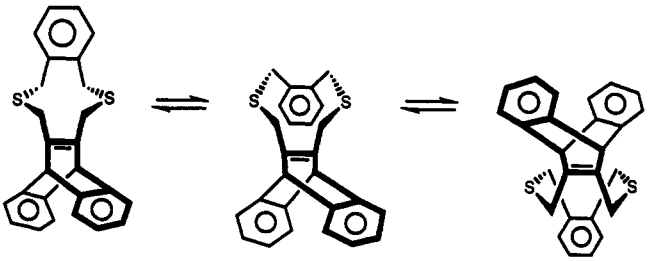


14

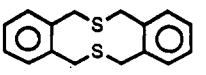
Unlike **10**, disulfide **12** was conformationally mobile. At room temperature in toluene-d_8 the eight methylene protons appeared as a broad multiplet at δ 2.6–3.2. On cooling to −20 °C this multiplet resolved into two sets of doublets, one at δ 2.38 and 2.84 (J = 14.5 Hz) and the other at δ 2.49 and 2.59 (J = 15.0 Hz). These two sets fused to two 4-proton singlets at high temperature (100 °C), at δ 2.69 and 2.63, respectively. The aromatic protons showed similar behavior. At room temperature they appeared as a multiplet at δ 6.7–7.4, but at −20 °C they resolved to four 2-proton AA′BB′ multiplets at δ 6.80–6.83, 6.85–6.88, 6.89–6.92, and 7.04–7.07, and a 4-proton multiplet at δ 7.36–7.40. Throughout the entire temperature range, the peak for the bridgehead protons remained a sharp singlet at δ 5.20. A VT NMR study in toluene-d_8 gave a $\Delta G^{\ddagger}$ of 15.0 kcal mol^{-1} for the dynamic process.

These data suggest that at low temperature **12** exists in the anti conformation **12a**, and that the interconversion **12a** ⇌ **12a′** proceeds via the syn conformer **12s**. The



12a **12s** **12a′**

symmetry plane (C_s symmetry) maintained throughout this process ensures that the peak due to the bridgehead protons remains a sharp singlet. Unlike the situation with **10**, conformation **12s** is possible although there is an unfavorable steric interaction between the *o*-xylyl ring and one of the other aryl rings. For this reason, the barrier is higher than the 11.0 kcal mol^{-1} measured[11] for the related 2,11-dithia[3.3]orthocyclophane **15**[12] (or the 12.1 kcal mol^{-1} reported for **11**).[9]



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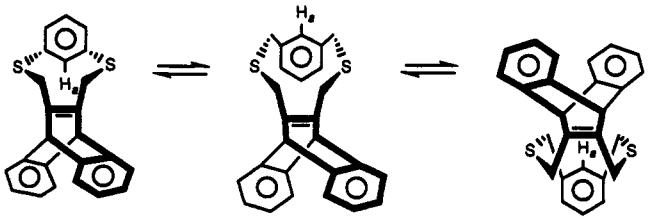
Metacyclophane **13** was also conformationally mobile.[13] In its room temperature spectrum ($CDCl_3$), the methylene protons appeared as two broad 4-proton singlets centered at δ 2.73 and 3.49. At −40 °C, these signals were split into two sets of 2-proton doublets, one at δ 2.64 and 2.80 (J = 14.5 Hz) and one at δ 3.38 and 3.57 (J = 12.2 Hz). The bridgehead protons appeared as a sharp 2-proton singlet (δ 5.43 at room temperature, δ 5.47 at −40 °C). One aromatic proton was highly shielded and appeared as a slightly broadened singlet at δ 5.66 (room temperature) or δ 5.55 (−40 °C); the remaining 11 aryl protons appeared as a complex multiplet in the range δ 6.9–7.4. VT NMR studies using each methylene proton set gave $\Delta G^{\ddagger}$ of 13.5 and 13.4 kcal mol^{-1} for the dynamic process.

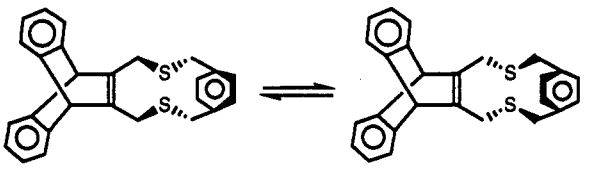
These data suggest that the preferred conformation of **13** is **13a**, in which the indicated proton on the *m*-xylylene bridge lies over and is shielded by one of the other two aryl rings (the "back" aryl ring in **13a**). This conformation also



13a **13s** **13a'**

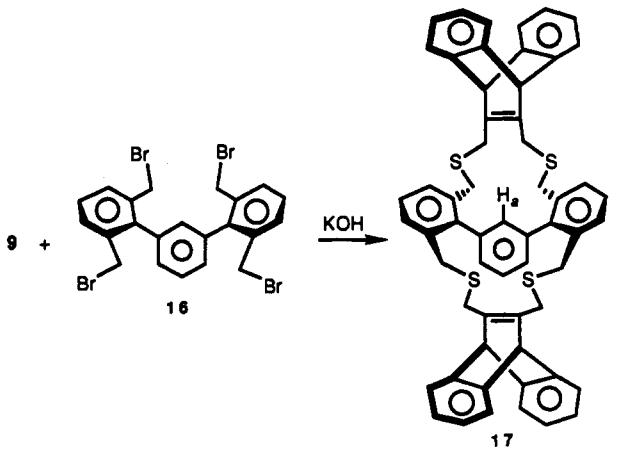
deshields one set of methylene protons (adjacent to the *m*-xylylene bridge). The dynamic process which equilibrates pairs of methylene protons involves interconversion of **13a** ⇌ **13a'** via the syn conformation **13s**. The σ-plane maintained throughout ensures that the bridgehead protons remain a sharp singlet.

In contrast to **12** and **13**, the *p*-xylylene isomer **14**, mp 245 °C, has a rigid symmetric structure (C_{2v}, **14**) or rapidly equilibrating tilted structures (C_s, **14a** ⇌ **14a'**) at room temperature, since the two sets of methylene protons, the bridgehead protons and the aromatic protons of the *p*-xylylene ring all appear as sharp singlets (δ 2.56, 2.70, 5.30, and 6.60, respectively). Cooling to −50 °C in toluene-d_8 caused only slight temperature broadening of the singlets, so if the structure is tilted, the interconversion barrier is low.



14a **14a'**

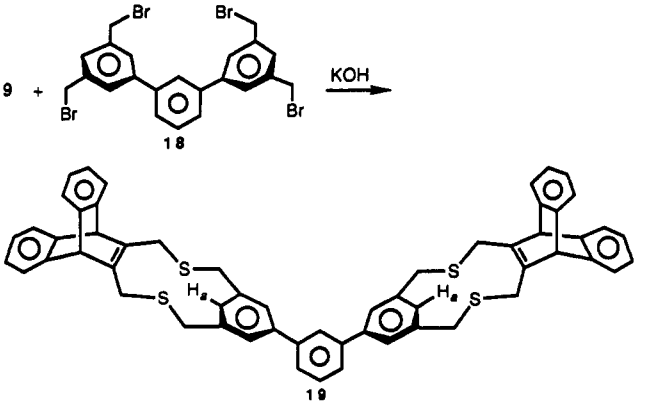
One reason to prepare dithiol **9** was for use as a bridging reagent in the synthesis of cuppedophanes.[14] Treatment of tetrabromide **16**[14] with dithiol **9** (2 equiv) and base afforded cuppedophane **17** in 41% yield. CPK models



16 **17**

show that two of the aryl rings in the bicyclic bridges (shown in boldface) form walls that tilt slightly in toward the center of the cuppedophane cavity. Consequently, H_a is shielded (δ 6.6, t, J = 1.8 Hz, weakly meta-coupled) relative to all the remaining aryl protons. This is in contrast to the analogous cuppedophane prepared from **16** and *o*-xylylenedithiol,[14] where all 18 aryl protons appear as a multiplet at δ 7.09–7.50.

Reaction of **9** (2 equiv) with the 3,5,3″,5″-tetrakis(bromomethyl)-*m*-terphenyl **18** and base gave, instead of the meta-linked analogue of **17**, the bis-*m*-cyclophane **19** (52%). The structure of **19** was based on the similarity



18 **19**

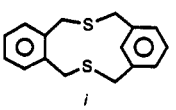
of its NMR spectra to that of *m*-cyclophane **13** (Table I). Apparently the S–S distance in **9** is too short to comfortably span the gap across the outer rings of **18**.

Table I. Comparison of the NMR Spectral Data of 13 and 19

signal	13, δ	19, δ
	^{1}H Spectrum, −40 °C	
CH_2	2.64, 2.80 (J = 14.5 Hz, 2 H each)	2.66, 2.82 (J = 15.1 Hz, 4 H each)
CH_2	3.38, 3.57 (J = 12.2 Hz, 2 H each)	3.46, 3.68 (J = 12.4 Hz, 4 H each)
H_a	5.47 (s, 1 H)	5.42 (s, 2 H)
bridgehead	5.55 (s, 2 H)	5.60 (s, 4 H)
	^{13}C Spectrum	
CH_2	28.71, 34.76	28.60, 34.52
bridgehead	52.79	52.76

In summary, we have shown that the "ate" complex from DIBAH and *n*-BuLi can reduce enedioic esters such as **1** to the corresponding enediols in high yield without overreduction. We have demonstrated the utility of the derived dihalides and dithiols such as **3** and **9** for medium ring

(13) The benzo analogue i was recently reported, but without conformational analysis. The corresponding hydrocarbon [2,2]orthometacyclophane exists as a 4:1 syn:anti mixture.



i

Bodwell, G.; Ernst, L.; Haenel, M. W.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *25*, 455–456. See also: Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5424–5428.

(14) Vinod, T.; Hart, H. *J. Org. Chem.* **1990**, *55*, 881–890 and earlier references cited therein.

construction. We have also described the conformational properties of **10** and **12–14**. Finally, although we do not plan to pursue the matter, we call attention to the possibility that elimination of anthracene from rings derived from **3** or **9** (i.e. **10**, **12–14** and so on) might provide a useful route to cycloalkynes.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with CH_2Cl_2 or the residual line of $CDCl_3$ as the internal reference (coupling constants, J, are given in hertz). Mass spectra were measured by the FAB technique and 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. Anhydrous $MgSO_4$ or Na_2SO_4 were the drying agents throughout, and the silica gel for chromatography was 60–200 mesh. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI, or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

11,12-Bis(hydroxymethyl)-9,10-etheno-9,10-dihydroanthracene (2). In flame-dried glassware under argon a solution of 150 mL of tetrahydrofuran (THF) and 78 mL (0.197 mol) of 2.5 M *n*-BuLi in hexanes[15] was cooled to −22 °C, and 197 mL (0.197 mol) of 1 M diisobutylaluminum hydride (DIBAL-H) in hexanes (or cyclohexane)[15] was added dropwise with stirring over 1 h. After 3 h of additional stirring at −22 °C, this solution of "ate" complex was added via cannula over 1 h to a stirred solution of diester **1**[1] (15.0 g, 0.0468 mol) in 100 mL of THF under argon kept at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and then was cooled to 0 °C and quenched (*CAUTION*: strong exotherm) with 40 mL of 50% aqueous CH_3OH. The mixture was added to a flask containing 35 g of powdered Glauber's salt ($Na_2SO_4 \cdot 10H_2O$), 250 mL of THF was added, and the slurry was stirred with gentle warming for 0.5 h, during which time the initial gel became a fine precipitate. The mixture was filtered, the filter cake was extracted with boiling THF (200 mL), and the combined filtrates were evaporated to yield crude **2** as a white solid. Trituration with 40 mL of ether afforded pure diol **2** as a white crystalline solid (11.2 g, 90%): mp 193–194 °C; recrystallization from $CHCl_3$ did not change the mp; ^1H NMR δ 1.57 (br s, 2 H, exchanges with D_2O), 4.30 (s, 4 H, methylenes), 5.18 (s, 2 H, bridgehead), 6.95–7.33 (AA'BB' m, 8 H, arom); ^{13}C δ 53.24 (bridgehead), 59.80 (methylene), 123.06, 124,88, 145.76, 145.97 (arom and vinyl); mass spectrum, m/e 264 ($M^{\bullet+}$). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 82.15; H, 6.47.

11,12-Bis(hydroxymethyl)-9,10-dimethyl-9,10-etheno-9,10-dihydroanthracene (5). The procedure was analogous to that described for **2**. The "ate" complex (0.012 mol) and 1 g (2.87 mmol) of 11,12-dicarbomethoxy-9,10-dimethyl-9,10-etheno-9,10-dihydroanthracene[7] (mp 188–189 °C) gave 0.73 g (88%) of **5**, recrystallized from $CHCl_3$: mp 215 °C; ^1H NMR δ 1.56 (s, 2 H exchangeable), 2.30 (s, 6 H, methyl), 4.32 (s, 4 H, methylene), 6.90–7.02 and 7.28–7.31 (AA'BB' m, 4 H each, arom); ^{13}C NMR δ 12.84 (CH_3), 50.14 (bridgehead), 57.33 (methylene), 120.16, 124.5, 149.24, 150.92 (arom and vinyl); mass spectrum, m/e 292 ($M^{\bullet+}$). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.08; H, 6.78.

2,3-Bis(hydroxymethyl)-9,10-diphenyl-1,4-etheno-1,4-dihydroanthracene (6). From 9.53 mmol of "ate" complex and 1.0 g (2.11 mmol) of 2,3-dicarbomethoxy-9,10-diphenyl-1,4-etheno-1,4-dihydroanthracene[7] there was obtained 0.70 g (80%) of **6**: mp 240 °C; ^1H NMR δ 1.80 (br s, 2 H, exchanges with D_2O), 4.13 (d, J = 12.6, 2 H, methylene), 4.23 (d, J = 12.6, 2 H, methylene), 4.75 (dd, J = 7.5, 1.2, 2 H, bridgehead), 6.79 (dd, J = 7.5, 1.2, 2 H, vinyl), 7.23–7.58 (m, 14 H, arom); ^{13}C NMR δ 48.72 (bridgehead),60.07 (methylene), 125.41, 126.47, 127.57, 128.62, 130.34, 130.70, 132.18, 138.74, 139.11, 140.77, 145.83 (arom and vinyls); high-resolution mass spectrum, m/e calcd for $C_{30}H_{24}O_2$ 416.17760, found 416.17826.

19,20-Bis(hydroxymethyl)-5,18:9,14-di-*o*-benzeno-7,16-etheno-5,7,9,14,16,18-hexahydroheptacene (7). To a mixture of 5,18:9,14-di-*o*-benzeno-5,9,14,18-tetrahydroheptacene[6,8] (1.0 g, 1.88 mmol) and DMAD (0.6 g, 4.22 mmol) in 25 mL of CH_2Cl_2 was added 0.56 g (4.22 mmol) of anhydrous $AlCl_3$. After 1 h at room temperature and 3 h at reflux, the dark reaction mixture was washed with water (25 mL) and 10% sodium bicarbonate (25 mL) and dried. Evaporation gave crude adduct as a yellow solid that was triturated with benzene to give 1.07 g (85%) of the pure cycloadduct which was recrystallized from hexane/benzene (1:2): mp 252 °C; ^1H NMR δ 3.66 (s, 6 H, methoxyls), 5.22 (s, 2 H, 7,16-bridgehead), 5.23 (s, 4 H, other bridgeheads), 6.80–6.83 (AA'BB' m, 4 H), 6.91–6.93 (AA'BB' m, 4 H), 7.18–7.20 (AA'BB' m, 4 H), 7.26–7.29 (AA'BB' m, 4 H), 7.31 (s, 4 H, arom at C-6,8,15,17).

The diester cycloadduct was reduced using a procedure analogous to that described for **2**. From 3.3 mmol of "ate" complex and 0.5 g (0.74 mmol) of diester cycloadduct there was obtained 0.40 g (87%) of diol **7**: mp 320–322 °C dec; ^1H NMR δ 1.51 (s, 2 H, exchanges with D_2O), 4.15 (s, 4 H, methylenes), 4.98 (s, 2 H, 7,16-bridgeheads), 5.23 (s, 4 H, other bridgeheads), 6.80–6.83, 6.90–6.93, 7.18–7.21, 7.28–7.31 (AA'BB' m, 4 H each, arom), 7.26 (s, 4 H, arom); ^{13}C NMR δ 51.87 and 52.45 (bridgeheads), 57.54 (methylenes), 118.96, 123.56, 123.64, 124.93, 141.69, 144.06, 144.84, 145.78, 148.25 (arom and vinyl); high-resolution mass spectrum, m/e calcd for $C_{46}H_{32}O_2$ 616.2402, found 616.2393.

11,12-Bis(bromomethyl)-9,10-etheno-9,10-dihydroanthracene (3). A suspension of diol **2** (9.0 g, 0.034 mol), CH_2Cl_2 (180 mL) and *s*-collidine (8.8 g) was cooled to −20 °C, and a solution of PBr_3 (9.0 g, 0.033 mmol) in CH_2Cl_2 (70 mL) was added dropwise over 1 h with vigorous stirring. After an additional 6 h the mixture was allowed to warm to room temperature and then cooled to 0 °C as 40 mL of ice-cold 1 N HBr was added (10 min). The organic layer was washed with ice-cold saturated sodium bromide (2 × 100 mL) and cold 10% copper sulfate (2 × 100 mL) and dried. Evaporation of the solvent gave crude **3** as a yellow solid which was taken up in 25 mL of 1:1 CH_2Cl_2–hexanes and passed through a 1-in. pad of neutral alumina and quickly eluted with the same solvent (150 mL). Evaporation gave 8.5 g (63%) of **3** as a white crystalline solid: mp 203–205 °C dec; ^1H NMR δ 4.23 (s, 4 H, methylene), 5.11 (s, 2 H, bridgehead), 7.0–7.37 m, 8 H, arom); mass spectrum, m/e 390 ($M^{\bullet+}$). Anal. Calcd for $C_{18}H_{14}Br_2$: C, 55.39; H, 3.62. Found: C, 55.41; H, 3.64.

11,12-Bis(methylene)-9,10-dihydro-9,10-ethanoanthracene (4). A mixture of dibromide **3** (8.5 g, 0.021 mol), THF (150 mL), and zinc dust (5.0 g, 0.077 mol, 325 mesh) was stirred and heated at reflux for 8 h. The cooled mixture was concentrated (rotavap), and the residue was taken up in CH_2Cl_2 (150 mL) and filtered through a 1-in. pad of Celite. The Celite was washed with 50 mL of CH_2Cl_2, and the combined organic layers were washed with water (2 × 100 mL) and dried. Evaporation of the solvent gave crude diene **4** as a yellow solid in nearly quantitative yield (95% pure by NMR). Recrystallization from 1:20 CH_2Cl_2–hexanes gave 4.7 g (93%) of **4** as a white solid, mp 157 °C (lit.[2] mp 157 °C), identical in all respects to previously reported material.[2,4-6]

11,12-Bis(mercaptomethyl)-9,10-dihydro-9,10-etheno-anthracene (9). To dibromide **3** (3.9 g, 0.01 mol) in THF (25 mL) was added a suspension of thiourea (1.52 g, 0.02 mol) in 20 mL of 1:1 ethanol–THF, and the mixture was stirred at reflux for 2 h. The mixture was concentrated (rotavap) and filtered, and the solid was washed with ether (20 mL) and dried to give 5.4 g (nearly 100%) of bisisothiouronium salt **8**, mp 290 °C dec, which analyzed correctly as a monohydrate. Anal. Calcd for $C_{20}H_{22}N_4S_2H_2O$: C, 42.83; H, 4.28; N, 9.99. Found: C, 43.01; H, 3.95; N, 9.81.

The salt was suspended in water (50 mL), KOH was added (2.6 g, 0.04 mol), and the mixture was stirred at reflux under argon for 2 h. The mixture was cautiously acidified with concentrated HCl (argon), extracted with CH_2Cl_2 (3 × 75 mL), and dried. Evaporation gave crude dithiol as a yellow solid. Solution in benzene (25 mL), filtration through 2 in. of silica gel, and evaporation gave 2.30 g (67%) of **9** as a white air sensitive solid: mp 152 °C; recrystallized from 1:20 CH_2Cl_2/hexanes; ^1H NMR δ 1.30 (t, J = 7.2, 2 H, thiol), 3.42 (d, J = 7.2, 4 H, methylene), 5.14 (s, 2 H, bridgehead), 6.99–7.07 and 7.34–7.40 (AA'BB' m, 4 H, each, arom); ^{13}C NMR δ 24.40 (methylene), 54.67 (bridgehead), 122.75, 124.78, 142.66, 145.75 (arom and vinyl); high-resolution mass spectrum, m/e calcd for $C_{18}H_{16}S_2$ 296.06934, found 296.06998.

(15) Aldrich Chemical Co.

Anal. Calcd for $C_{18}H_{16}S_2$: C, 72.92; H, 5.44. Found: C, 72.46; H, 5.32.

General Procedures for Thiol–Bromide Cyclizations. A solution of dithiol and di- or tetrabromide in the appropriate ratio and approximately 1–3-mmol scale in 80 mL of benzene was added slowly, using a laboratory pump or precision dropping funnel, over 5–6 h to a vigorously stirred solution of KOH (2-fold excess) in 300 mL of 90% aqueous ethanol. After addition, the reaction was quenched with 30 mL of 3 N HCl. The mixture was concentrated to dryness, water was added (100 mL), and the product was extracted with CH_2Cl_2 (3 × 75 mL). The organic layer was dried and evaporated, and the crude product was chromatographed on silica gel using 2:3 CH_2Cl_2–hexanes as eluent to give the desired thiacyclophanes as white or off-white solids. Most of the thiacyclophanes readily crystallized on concentration.

5,18:9,14-Di-*o*-benzeno-5,6,8,9,14,15,17,18-octahydrodinaphtho[2′,3′-*c*:2″,3″-*h*][1,6]dithiecin (10). From 0.5 g (1.28 mmol) of dibromide **3**, 0,38 g (1.28 mmol) of dithiol **9** and 0.5 g of KOH there was obtained 0.29 g (44%) of disulfide **10**: mp 252 °C; ^{1}H NMR δ 2.28 (d, J = 14.2, 4 H, methylene), 2.55 (d, J = 14.2, 4 H, methylene), 5.20 (s, 4 H, bridgehead), 6.8–7.4 (m, 16 H, arom); ^{13}C NMR δ 28.47 (methylene), 53.33 (bridgehead), 122.77, 122.82, 124.65, and 124.79 (H-bearing aryl carbons), 142.16 (vinyl), 146.05 and 146.20 (quaternary aromatic); high-resolution mass spectrum, m/e calcd for $C_{36}H_{28}S_2$ 524.1632, found 524.16088. Anal. Calcd for $C_{36}H_{28}S_2 \cdot H_2O$: C, 79.66; H, 5.57. Found: C, 79.22; H, 5.92.

8,13-*o*-Benzeno-5,7,8,13,14,16-hexahydrobenzo[*c*]naphtho[2′,3′-*h*][1,6]dithiecin (12). From 0.9 g (2.3 mmol) of dibromide **3**, 0.4 g (2.3 mmol) of *o*-xylylenedithiol,[16,17] and 0.6 g of KOH there was obtained 0.71 g (78%) of disulfide **12**: mp 248 °C; ^{1}H NMR (toluene-d_8) room temperature δ 2.6–3.2 (m, 8 H, methylenes), 54.20 (s, 2 H, bridgehead), 6.7–7.4 (m, 12 H, arom); −20 °C δ 2.38 and 2.84 (d, J = 14.5, 2 H each, methylenes), 2.49 and 2.59 (d, J = 15.0, 2 H each, methylenes), 5.20 (s, 2 H, bridgehead), 6.80–6.83, 6.85–6.88, 6.89–6.92, and 7.04–7.07 (AA′BB′ m, 2 H each, arom), 7.36–7.40 (m, 4 H, arom); 110 °C δ 2.63 (s, 4 H, methylene), 2.69 (s, 4 H, methylene), 5.20 (s, 2 H, bridgehead), 6.7–7.4 (m, 12 H, arom); a VT NMR study gave a coalescence temperature T_c of 41 °C and $\Delta G^{\ddagger}$ = 15.03 kcal mol^{-1} for the first set of methylene signals and a T_c 16 °C, $\Delta G^{\ddagger}$ 14.90 kcal mol^{-1} for the second set of methylene signals; ^{13}C NMR ($CDCl_3$) δ 27.7 and 28.55 (methylenes), 53.88 (bridgehead), 122.71, 124.67, 127.13, 129.37, 136.88, 142.32, 146.00 (arom and vinyl); mass spectrum, m/e 398 ($M^{\bullet+}$). Anal. Calcd for $C_{26}H_{22}S_2$: C, 78.33; H, 5.56. Found: C, 78.11; H, 5.50.

***m*-Dithiacyclophane 13.** From 0.9 g (2.3 mmol) of dibromide **3**, 0.4 g (2.3 mmol) of *m*-xylylenedithiol,[16,18] and a 0.6 g of KOH there was obtained 0.53 g (58%) of disulfide **13**: mp 226–228 °C; ^{1}H NMR ($CDCl_3$, room temperature) δ 2.73 (br s, 4 H, methylene), 3.49 (br s, 4 H, methylene), 5.43 (s, 2 H, bridgehead), 5.66 (br s, 1 H, arom), 6.97–7.16 (m, 6 H, arom), 7.34–7.40 (m, 5 H, arom); −40 °C δ 2.64 and 2.80 (d, J = 14.5, 2 H each, methylene), 3.38 and 3.57 (d, J = 12.2, 2 H each, methylenes), 5.47 (s, 2 H, bridgehead), 5.55 (br s, 1 H, arom), 6.9–7.4 (m, 11 H, arom); a VT NMR study gave a T_c of 2 °C for each set of methylene protons, and $\Delta G^{\ddagger}$ = 13.51 and 13.41 kcal mol^{-1}; ^{13}C NMR δ 28.71 and 34.76 (methylenes), 52.79 (bridgehead), 123.17, 124.77, 126.99, 129.48, 132.96, 135.33, 142.22, 146.15 (arom and vinyl); mass spectrum, m/e 398 ($M^{\bullet+}$). Anal. Calcd for $C_{26}H_{22}S_2$: C, 78.33; H, 5.56. Found: C, 78.46; H, 5.41.

***p*-Dithiacyclophane 14.** From 0.9 g (2.3 mmol) of dibromide **3**, 0.4 g (2.3 mmol) of *p*-xylylenedithiol,[19] and 0.6 g of KOH there was obtained 0.60 g (66%) of disulfide **14**: mp 245 °C; ^{1}H NMR δ 2.56 (s, 4 H, methylene), 2.70 (s, 4 H, methylene), 5.30 (s, 2 H, bridgehead), 6.65 (s, 4 H, *p*-xylylene ring), 6.98–7.01 and 7.36–7.39 (AA′BB′ m, 4 H each, arom); ^{13}C NMR δ 29.25 and 32.90 (methylenes), 54.31 (bridgehead), 122.63, 124.56, 128.63, 136.29, 141.89, 145.95 (arom and vinyl); mass spectrum, m/e 398 ($M^{\bullet+}$). Anal. Calcd for $C_{26}H_{22}S_2$: C, 78.33; H, 5.56. Found: C, 78.19; H, 5.63.

Tetrathiacuppedophane 17. From 1.0 g (1.69 mmol) of tetrabromide **16**,[14] 1.0 g (3.37 mmol) of dithiol **9**, and 0.7 g of KOH there was obtained 0.60 g (41%) of cuppedophane **17**: mp 245 °C; ^{1}H NMR δ 2.85 and 3.17 (d, J = 10.5, 4 H each, methylenes), 3.15 and 3.20 (d, J = 11.9, 4 H each, methylenes), 5.08 (s, 4 H, bridgeheads), 6.60 (t, J = 1.8, 1 H, isolated arom), 6.8–7.0 (m, 8 H, arom), 7.1–7.5 (m, 17 H, arom); ^{13}C NMR δ 33.88 and 35.13 (methylenes), 54.28 (bridgeheads), 122.92, 124.88, 126.80, 127.17, 127.83, 128.40, 134.54, 135.96, 137.79, 141.74, 145.49, 145.81 (arom and vinyl); high-resolution mass spectrum (M + H)$^+$ calcd for $C_{58}H_{47}S_4$ 871.25606, found 871.25731.

3,5,3″,5″-Tetramethyl-1,1′:3′,1″-terphenyl. Vinylmagnesium bromide (7.3 g, 55.5 mmol as a 1 M THF solution) was added to a stirred solution of 2,6-dichloroiodobenzene[20] (15.0 g, 55 mmol) in 200 mL of THF maintained at −18 to −20 °C. After 2 h of additional stirring at that temperature, this solution was added via a cannula over 30 min to a refluxing solution of (3.5-dimethylphenyl)magnesium bromide (prepared from 20.6 g, 0.111 mol, of 3.5-dimethylbromobenzene[15] and 2.75 g, 0.114 g-atom, of magnesium in 300 mL of THF). The mixture was stirred at reflux for an additional 3 h and then quenched with 50 mL of 0.1 N aqueous HCl. The product was extracted with CH_2Cl_2, dried, and chromatographed over silica gel using hexanes as the eluent to give 13.0 g (82%) of the desired *m*-terphenyl as a white crystalline solid, recrystallized from hexanes: mp 111–113 °C; ^{1}H NMR δ 2.40 (s, 12 H, methyl), 7.03 (br s, 2 H, 4.4″ arom), 7.27 (s, 4 H, 2,6,2″,6″ arom), 7.4–7.6 (m, 3 H, 4′,5′,6′ arom), 7.77 (t, J = 2, 2′ arom). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.86.

3,5,3″,5″-Tetrakis(bromomethyl)-1,1′:3′,1″-terphenyl (18). Freshly recrystallized *N*-bromosuccinimide (12.44 g, 0.069 mol) was added in 4 equal portions over 12 h to a solution of the tetramethylterphenyl (5.0 g, 0.017 mol) in 250 mL of CCl_4 at reflux; each addition was immediately followed by adding a few milligrams of benzoyl peroxide. After 4 h of additional reflux, the mixture was cooled and filtered, and the crude product was chromatographed over silica gel using 1:6 CH_2Cl_2–hexanes as eluent to give 2.76 g (27%) of **18** as colorless crystals: mp 162 °C; ^{1}H NMR δ 4.56 (s, 8 H, methylene), 7.46 (t, J = 1.6, 1 H, 2′ arom), 7.5–7.75 (m, 7 H, arom), 7.74 (s, 2 H). Anal. Calcd for $C_{22}H_{18}Br_4$: C, 43.89; H, 3.01. Found: C, 43.93; H, 3.10.

Tetrathiabis-*m*-cyclophane 19. From 0.5 g (0.845 mmol) of tetrabromide **18**, 0.5 g (1.69 mmol) of dithiol **9**, and 0.4 g of KOH there was obtained 0.37 g (52%) of **19**: mp 248 °C dec; ^{1}H NMR (room temperature) δ 2.75 (br s, 8 H, methylenes), 3.60 (br s, 8 H, methylenes), 5.60 (br s, 6 H, 4,4″ arom of the *m*-terphenyl moiety and bridgehead protons), 7.05 (br s, 8 H, arom), 7.2–7.6 (m, 15 H, arom), 7.76 (br s, 1 H, 2′ arom of the *m*-terphenyl moiety); −40 °C δ 2.66 and 2.82 (d, J = 15.1, 4 H each, methylenes), 3.46 and 3.68 (d, J = 12.4, 4 H each, methylenes), 5.42 (br s, 2 H, 4,4″ arom of the *m*-terphenyl moiety), 5.60 (s, 4 H, bridgehead), 6.95–7.04, 7.06–7.14, 7.30–7.36 (m, 4 H each, arom), 7.43 (br s, 4 H, arom), 7.46–7.60 (m, 7 H, arom), 7.76 (br s, 1 H, 2′ arom of the *m*-terphenyl moiety); ^{13}C NMR δ 28.60 and 34.52 (methylenes), 52.76 (bridgeheads), 123.25, 124.90, 125.70, 125.86, 126.48, 129.32, 132.65, 135.82, 141.19, 142.32, 142.48, 146.27 (arom and vinyl); high-resolution mass spectrum (M + H)$^+$ calcd for $C_{58}H_{47}S_4$ 871.2538, found 871.2560.

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