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2'-Substituted Meta-terphenyls as Building Blocks for Cyclophanes with Intra-Annular Functionality

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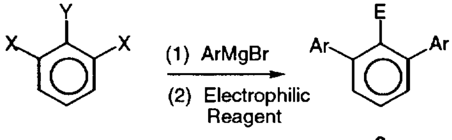
Abstract: 2'-Substituted m-terphenyls containing chloromethyl and/or thiomethyl groups at the 4,4" or 3,3" positions are used as building blocks for cyclophanes with intra-annular functionality. Syntheses are short and yields are good. The methodology, capable of wide structural variation, has been adapted to bi- and tricyclic cyclophanes.

Cyclophanes[1] and molecular clefts [2] with functionality directed toward the interior of the molecule can function as selective hosts.[3] We describe here a short, efficient synthesis of *m*-terphenyl-based cyclophanes with one or more functional groups directed inward. The methodology is general and capable of wide structural variation.

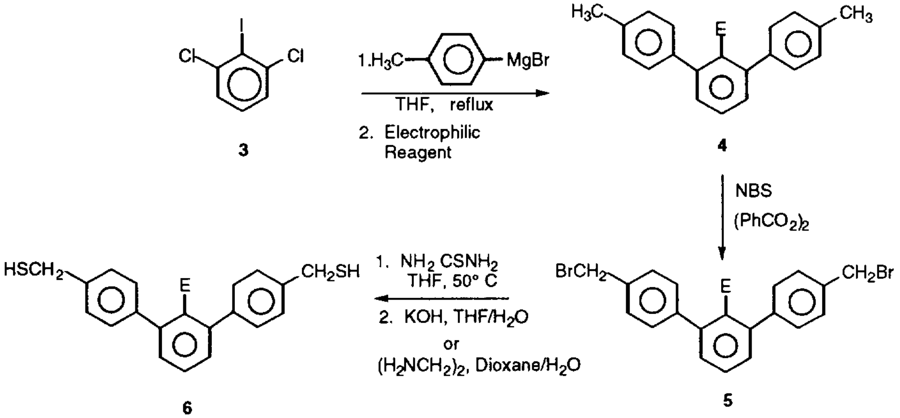
SYNTHESIS OF THE BUILDING BLOCKS

Tandem aryne reaction of aryl Grignard reagents with 1,2,3-trihalobenzenes[1] followed by electrophilic quenching gives *in one operation m*-terphenyls **2** with the electrophile at the 2' position. [4] With appropriate substitution on the Ar group, these *m*-terphenyls can be quickly converted to cyclophanes with E directed toward the interior of the ring. The building blocks can be constructed as outlined in Scheme 1.



1 **2** (1)

Scheme I

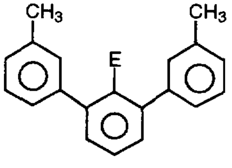


E = **a** (H), **b** (D), **c** (Br), **d** (I), **e** (CO_2H), **f** (CN), **g** (COCl), **h** (CO_2CH_3)

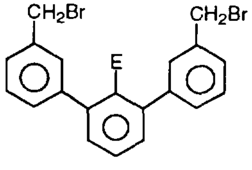
Addition of 2,6-dichloroiodobenzene **3** [5] to 3 equiv. of *p*-tolylmagnesium bromide in refluxing THF [6] gave a solution of 4,4"-dimethyl-*m*-terphenyl-2'-magnesium bromide which, with various electrophiles (H^+, D^+, Br_2, I_2, CO_2) gave **4** in 55-75% yield. The nitrile (**4f**) was obtained by treating **4c** or **4d** with cuprous cyanide in refluxing *N*-methylpiperidone. The methyl ester (**4h**) was obtained from **4e** either directly (CH_2N_2) or via the acid chloride **4g** and methanol.

Radical bromination with *N*-bromosuccinimide and benzoyl peroxide afforded the bromomethyl derivatives **5** (78-95%) which were converted to the corresponding bis-thiols **6** via the isothiouronium salts, in 38-86% yields. Except for **4a** [7] and **5a** [7] these 2'-substituted *m*-terphenyls are new; individual yields, melting points and spectra that support the structural assignments are given in the experimental section.

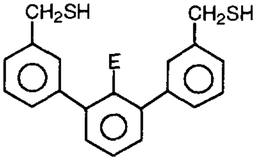
Using similar technology, but *m*-tolylmagnesium bromide in the first step, the *m*-building blocks **7-9** were also constructed.



7 (a, c, e, h)



8 (a, h)



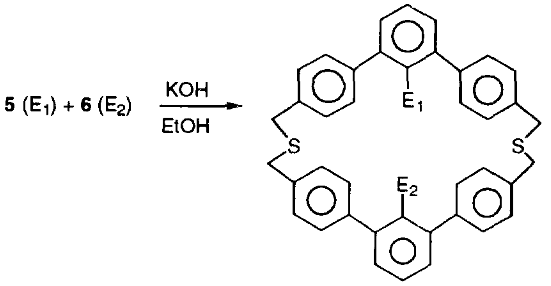
9a

Specialized building blocks used to construct *m*-terphenyl based bicyclophanes, etc. are described later in this paper, at the point where they are used.

ASSEMBLING THE BUILDING BLOCKS

Cyclophanes Constructed Solely from m-Terphenyls

Bis-bromides **5** and bis-thiols **6** were coupled with base to give dithiacyclophanes **10** in 45-60% yield. Symmetric cyclophanes ($E_1 = E_2$) were also prepared by the reaction of **5** with sodium sulfide. Not all possible



10

(2)

combinations were tried. Table 1 lists the examples that were, including yields, melting points of the products, and their ^{1}H NMR spectra.

All examples showed sharp singlets for the methylene protons at δ 3.8–3.9 (one 8 H singlet for **10aa** and two 4 H singlets for the remaining examples except for a few where these accidentally overlap). The internal proton E_2 (and with **10aa**, $E_1 = E_2$) in all examples appeared as the lowest field aromatic proton, easily identified as a triplet with meta coupling. This assignment was confirmed by synthesis of **10aa** with $E_1 = E_2 =$ D and of **10 ad, ae, af** with $E_2 =$ D; in each case, the ^{1}H spectrum was identical with that of the corresponding protio compound except that the low-field aromatic triplet was absent. The observed deshielding of this proton is presumably due to the two adjacent aryl rings.

The low field one-proton singlet that appeared in the spectra of haloesters **10 ch** and **10dh** had a *J* typical of ortho coupling. This peak can probably be assigned to the proton para to the carbomethoxy group.

Most of the spectra also showed various sets of doublets with characteristic ortho coupling constants due to protons on the 'outer' aryl rings of each *m*-terphenyl unit. Finally, the methyl esters (**10 ah, ch, dh, hh**) showed the expected singlets for the methyl groups.

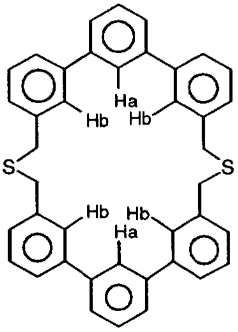
The data in Table 1 and additional data in the Experimental Section all suppport structures **10.**

Table 1. Yields and Properties of Cyclophanes **10.** [a]

Cpd.	E_1	E_2	Y[b]	mp[c]	^{1}H NMR		
					CH_2	E_2	Others
10aa	H	H	58	258	3.85[d]	7.62(1.7)[e]	7.01(8.3)[f], 7.33-7.41[g]
10ac	Br	H	55	247	3.92, 3.93[h]	7.56(1.9)[e]	6.96(8.2)[i], 7.20-7.51[j]
10ad	I	H	45	245	3.92, 3.93[h]	7.56(1.87)[e]	6.96(7.98)[i], 7.21(7.14)[i], 7.32-7.48[g]
10ae	CO_2H	H	50	238	3.84,3.89[h]	7.91(1.85)[e]	7.04(8.0)[i], 7.09(7.98)[i], 7.31-7.53[g]
10ah	CO_2Me	H	51	208	3.85,3.86[h]	7.98(1.83)[e]	6.88(8.04)[i], 7.15(8.04)[i] , 7.57(8.19)[i], 7.29-7.50[j], 3.42[k]
10af	CN	H	58	235	3.90,3.91[h]	8.02(1.86)[e]	6.50(8.25)[i], 7.20(8.0)[i], 7.27-7.54[g]
10ce	CO_2H	Br	45	252	3.79,3.84[h]		7.12(8.7)[i], 7.21-7.52[l]
10ch	CO_2Me	Br	40	243	3.84[d]		7.06(8.25)[i], 7.10(8.20)[i], 7.19-7.34[m], 7.42 (7.56)[n], 3.11[k]
10de	CO_2H	I	45	288	3.79, 3.84[h]		7.12(8.2)[i], 7.21-7.51[l]
10dh	CO_2Me	I	35	247	3.83[d]		7.06(8.22)[i], 7.10(8.19)[i], 7.19-7.34[m], 7.43(7.62)[n], 3.11[k]
10hh	CO_2Me	CO_2Me	30	180	3.66[d]		7.27-7.58[p], 3.39[q]

[a] Additional properties are given in the Experimental Section; [b] Yield, %; [c] °C, uncorrected; [d] s, 8 H; [e] t (*J*), 2 H for **10a**, 1 H for **10b-f**; [f] d(*J*), 8 H; [g] m, 14 H; [h] s, 4 H each; [i] d(*J*), 4 H; [j] m, 18 H; [k] s, 3 H; [l] m, 18 H; [m] m, 13 H; [n] t(*J*) 1 H; [o] from **5h** + **6h**; improved to 50% from **5h** + Na_2S; [p] m, 22 H; [q] s, 6 H.

Using similar methodology as for **10**, the all-meta cyclophane **11** and the mixed meta-para cyclophanes **12** were prepared, **11** by the coupling of **8a** with **9a** or by the self-coupling of **8a** with sodium sulfide, **12a** from dibromide **8a** with dithiol **6a**, and **12c** and **12f** by the coupling of dithiol **9a** with dibromides **5c** and **5f** respectively. Yields and selected properties are summarized in Table 2.



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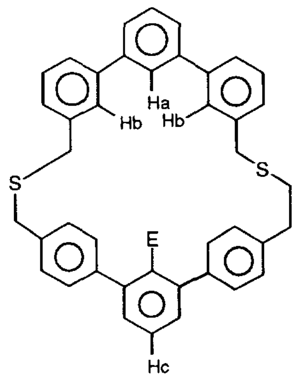


12 (a, c, f)

As expected, the methylene protons appeared as a sharp 8-proton singlet in **11** and as two 4-proton singlets in **12**. The internal aryl protons in **11** appeared in two sets, a 2-proton triplet with meta-coupling for H_a and a 4-proton broadened singlet (also meta-coupled) for H_b.

Compounds **12** all showed two 4-proton doublets with ortho coupling for the para-linked *m*-terphenyl unit. It is uncertain in **12a** whether the one-proton meta-coupled triplet at δ7.67 should be assigned to the internal proton at H_a or E. [8] In **12c**, the H_b protons are clearly discernible and their chemical shift is similar to that in **11**, but in **12a** and **12f** these protons are mixed in with the multiplet for other aryl protons. Finally, the two low-field one-proton triplets at δ 7.56 and 7.61 in **12f** are easily distinguished by their coupling constants, the former (H_a) being meta-coupled whereas the latter, para to the cyano group, is ortho-coupled. All these data and others given in the Experimental Section support the structural assignments.

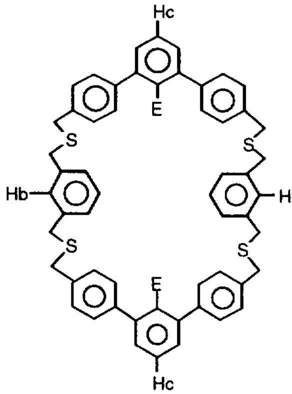
Table 2. Yields and Properties of Cyclophanes **11** and **12.** [a]

Cpd	Y[b]	mp[c]	^{1}H NMR				
			CH$_2$	H_a	H_b	H_c	Others
11	53	156	3.71[d]	7.46(1.68)[e]	7.17[f]		7.31-7.38[g]
12a	41	252	3.73, 3.76[h]	7.67(1.65)[e]			7.13(7.35)[i], 7.18(7.98)[i] ,7.29-7.49[j]
12c	60	198	3.65, 3.76[h]		6.95[k]		7.13(8.25)[l], 7.19(8.25)[i], 7.21-7.44[l]
12f	60	220	3.50, 3.74[h]	7.56(1.68)[e]		7.61(7.68)[e]	7.20(8.01)[i], 7.32(8.04)[i], 7.34-7.48[l]

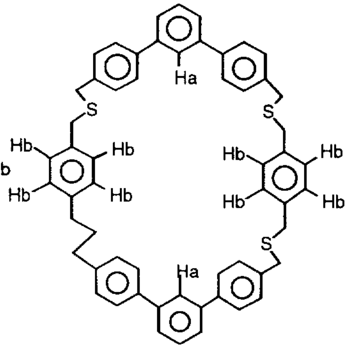
[a] Additional properties are given in the Experimental Section; [b] Yield, %; [c] °C; [d] s, 8 H; [e] t(*J*) 2 H for **11**, 1 H for **12a** and **12f**; [f] br s 4 H; [g] m, 18 H; [h] s, 4 H each; [i] d(*J*) 4 H; [j] m, 15 H; [k] br s, 2 H; [l] m, 13 H.

Cyclophanes from m-Terphenyls and Various Linking Units

The space 'inside' cyclophanes **10-12** is limited by the shortness of the link ($-CH_2SCH_2-$) between the two *m*-terphenyl units. It was possible to lengthen these connectors by using various other linking units to join the *m*-terphenyl moieties. For example, equimolar amounts of *m*-xylylene dithiol and *m*-terphenyl dibromide **5a** were coupled (KOH) to give cyclophane **13a** (E = H) in 65% yield. Similarly, *p*-xylylene dithiol and *o*-xylylene dithiol gave **14** and **15** respectively. Internal functionality could be incorporated, as in the analogous preparation of **13c** and **13h** (E=Br and CO_2Me, respectively). Yields and selected properties are summarized in Table 3.



13 (a, c, h)



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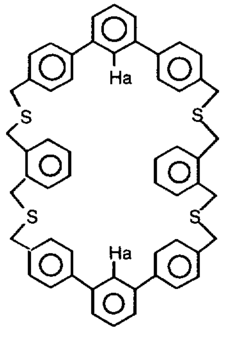

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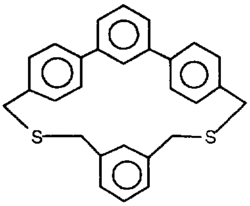
Table 3. Yields and Properties of Cyclophanes **13-15**. [a]

Cpd	Y[b]	mp[c]	^{1}H NMR				
			CH_2[d]	H_a[e]	H_b	H_c[e]	Others
13a	65	186-8	3.61, 3.64	7.65(1.65)	7.00[f]		7.26-7.47[g]
13c	70	181	3.62, 3.63		7.04[f]		7.16-7.34[g]
13h	70	216	3.59, 3.61		7.00[f]	7.38(7.62)	7.21-7.32[h], 3.19[i]
14	68	205	3.59, 3.61	7.80(1.65)	7.25[j]		7.35(8.16)[k], 7.48-7.55[l], 7.59(8.22)[k]
15	71	226	3.52, 3.54	7.74(1.65)			7.15-7.21[m], 7.31(8.01)[k], 7.50(8.20)[k], 7.53-7.56[l]

[a] Additional properties are given in the Experimental Section; [b] Yield, %; [c] °C; [d] s, 8 H each; [e] t(*J*) 2 H; [f] br s, 2 H; [g] m, 28 H; [h] m, 26 H; [i] s, 6 H; [j] s, 8 H; [k] d(*J*) 8 H; [l] m, 6 H; [m] m, 8 H.

The alternate 1:1 mode of coupling which might, for example, give cyclophane **16** instead of **13a** from **5a** and *m*-xylylene dithiol, was eliminated by observing that the fast atom bombardment (FAB) mass spectra showed in each case that two *m*-terphenyl units and two xylylene units were incorporated in the resulting cyclophane (see Experimental Section).

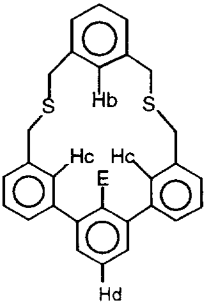


16

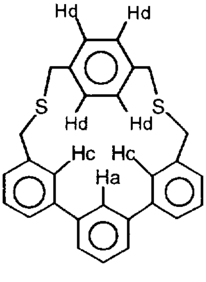
As with **10**, the lowest field (δ 7.65-7.8) aryl proton in **13-15** was the internal proton H_a (E in **13a**). On the other hand, the isolated proton H_b on the *m*-xylylene units of **13a, c, h** appeared at highest field (δ 7.0) as a broadened singlet, possibly suggesting some conformation such as that drawn, with these protons outside the large ring.

The *p*-xylylene protons H_b in **14** appeared as a sharp 8-proton singlet, showing that rotation of those rings is unrestricted at ambient temperatures. The spectrum of **13h** showed a two-proton triplet with ortho coupling for H_c, the protons para to the carbomethoxy substituents, as well as a six-proton singlet at δ 3.19 for the ester methoxyls. Finally, all five cyclophanes (**13-15**) showed two sharp eight-proton singlets at δ 3.5-3.6 for the two sets of methylene protons.

Although 1:1 cyclophanes such as **16** were *not* formed from 4,4"-disubstituted *m*-terphenyl precursors (for example, from **5a**) they were the sole products from 3,3"-disubstituted *m*-terphenyls such as **8**; in these cases, no 2:2 cyclophanes were isolated. Thus, treatment of **8a** or **8h** gave, with *m*-xylylene dithiol and base, exclusively the 1:1 cyclophanes **17**; analogous results (*i.e.*, **18** and **19**) were obtained with **8a** and *p*- or *o*-xylylene dithiols respectively. Yields and selected properties are summarized in Table 4. The mass spectra in each case showed that the products were 1:1, not 2:2 cyclophanes.



17 (a, h)



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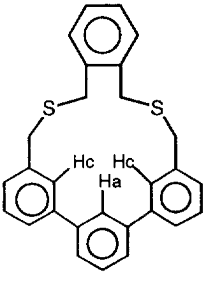

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Table 4. Yields and Properties of Cyclophanes **17-19**.[a]

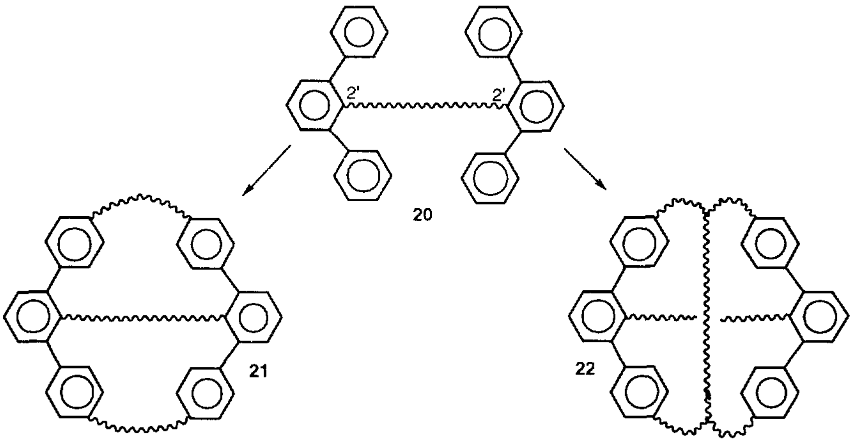
Cpd	Y[b]	%[c]	^{1}H NMR					
			CH$_2$[d]	H$_a$[e]	H$_b$[f]	H$_c$[g]	H$_d$	Others
17a	80	168	3.58, 3.74	7.98(1.71)	7.27	7.81		7.37-7.67[h]
17h	85	138	3.8		7.77	7.82	7.53(7.60)[i]	7.21-7.25[j],,7.37-7.43[k], 3.20[p]
18	88	110	3.52, 3.77	7.71[f]		7.37	7.10[l]	7.43-7.62[m]
19	87	196	3.94, 4.00	7.66(1.5)		7.71		7.14-7.17[n], 7.28(7.53)[o],7.42-7.63[m]

[a] Additional properties are given in the Experimental Section; [b] Yield, %; [c] °C; [d] s, 4 H each except for **17h**, which was a s, 8 H; [e] t(J) 1 H; [f] br s, 1 H; [g] br s, 2 H; [h] m, 12 H; [i] t(J) 1 H; [j] m, 5 H; [k] m, 6 H; [l] s, 4 H; [m] m, 9 H; [n] m, 2 H; [o] d(J) 2 H; [p] s, 3 H.

As with previously discussed examples, internal proton H$_a$ (in **17a**, E) appeared as a meta-coupled low-field triplet. H$_c$ appeared in all cases as a broad singlet (2 H), at higher field in **18** than in **17a,h** or **19**, presumably due to shielding by the *p*-xylylene ring. H$_b$ appeared at considerably lower field in **17h** than in **17a**, no doubt due to proximity to the carbomethoxy group in the former. Finally, all protons on the *p*-xylylene ring in **18** were equivalent, as expected. All data are consistent with the assigned structures.

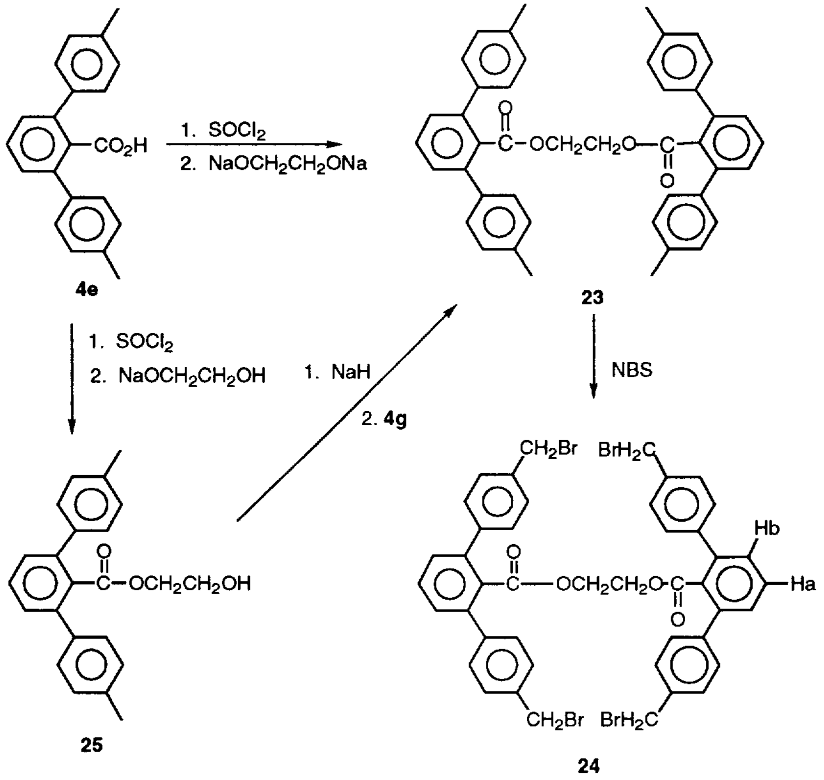
BICYCLIC AND TRICYCLIC CYCLOPHANES

By joining two *m*-terphenyl units through their 2'-positions, as in **20**, followed by connecting the outer rings with linking units, it was possible to readily adapt our technology to the construction of bicyclic cyclophanes **21** and tricyclic cage-like cyclophanes such as **22**. We describe here some specific examples in which the outer rings are linked at the 4,4"-positions as shown in **21** and **22**, but of course other loci for these connections could also easily be designed.



Construction of the Building Blocks

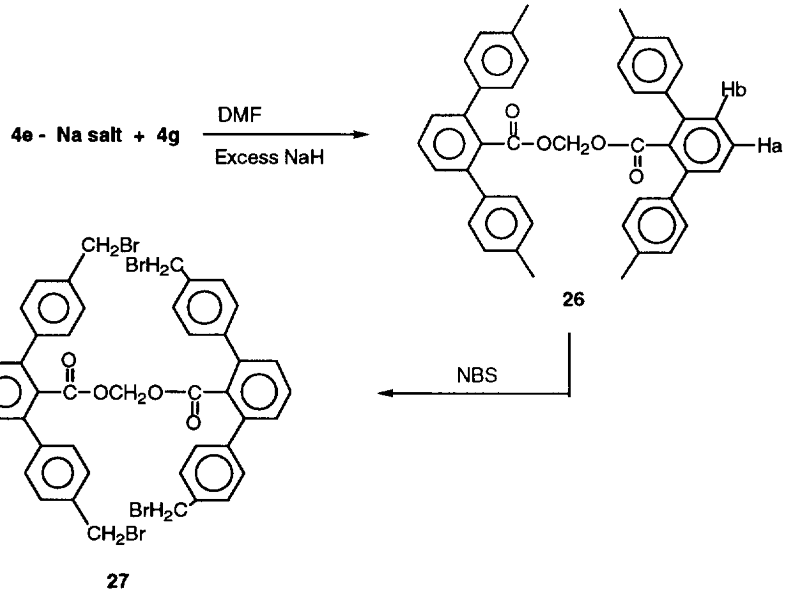
Carboxylic acid **4e** was used as the starting point for the diester **24**. Two equivalents of the acid chloride **4g** reacted with one equivalent of ethylene glycol disodium salt to give **23** directly in 87% yield.



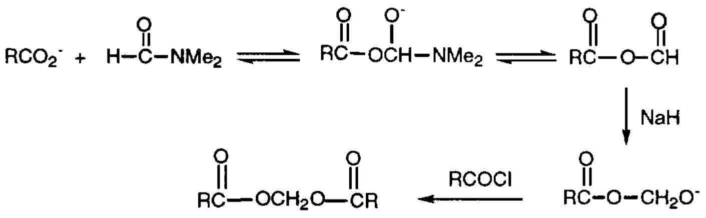
Alternatively, **4g** and the *mono*sodium salt of ethylene glycol gave ester-alcohol **25** in 98% yield, and its sodium salt, in turn, reacted with **4g** to give **23**, again in 98% yield. NBS bromination of **23** gave tetrabromide **24** in 80% crude yield, but purification necessary to remove other bromination products reduced the yield of **24** to 40%.

Tetrabromide **24**, mp 192 °C, showed singlets at δ 3.55 and 4.43 for the $-OCH_2$ and $-CH_2Br$ protons (4 H and 8 H respectively), and a doublet and triplet at δ 7.34 and 7.54 (4 H and 2 H respectively) for H_b and H_a, as well as a multiplet at δ 7.24-7.31 for the remaining 16 aryl protons, all consistent with the assigned structure.

An attempt to shorten the link between the two *m*-terphenyl moieties by preparing the anhydride from the sodium salt of **4e** and its acid chloride **4g** gave no useful product in THF, but in DMF the unexpected diester **26** was obtained in 86% yield. The ^1H NMR spectrum supported this structure assignment. Singlets at δ 2.23 and 5.23 (12 H and 2 H) could be assigned to the methyl and methylene protons, respectively.



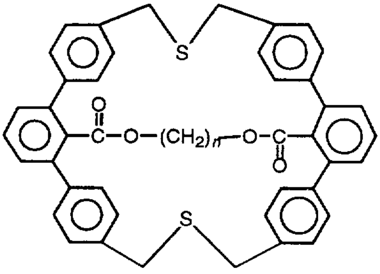
Aryl protons H_b and H_a appeared at δ 7.36 and 7.52 (doublet and triplet respectively) and the remaining aryl protons appeared as two doublets at δ 7.03 and 7.17 (8 H each). A possible mechanism for the formation of **26** which takes into account the need for DMF as the solvent, and for excess NaH, is shown:



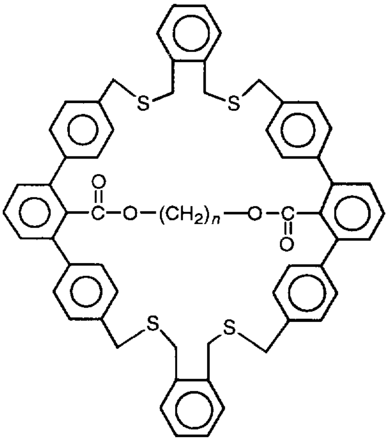
Diester **26** was converted to the tetrabromide **27**, mp 170 °C, with NBS in 39% yield. The spectral data support the assigned structure.

Bicyclic Cyclophanes

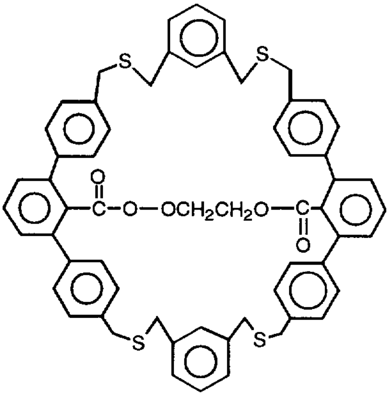
In a manner similar to that used to prepare the monocyclic cyclophanes described above (i.e. **10-15**, etc.), the bicyclic **28-31** were prepared from **24** and either sodium sulfide (**28**) or the appropriate xylylene



28 ($n = 2$)
32 ($n = 1$)



29 ($n = 2$)
33 ($n = 1$)



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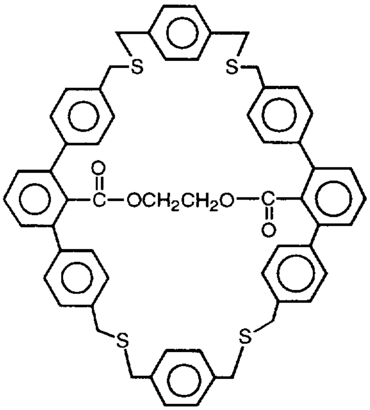


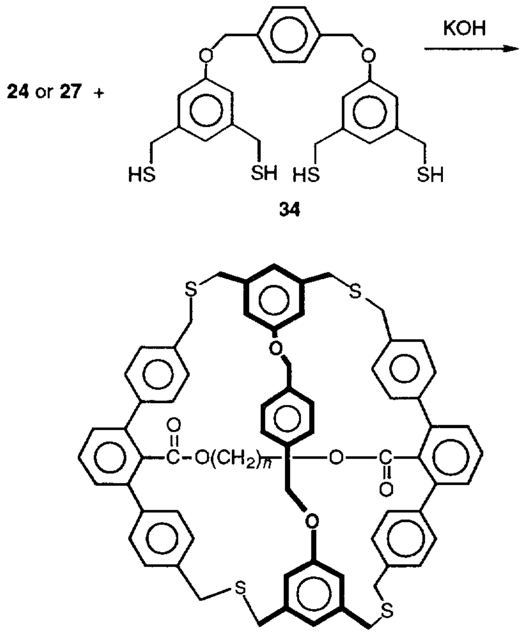
31

dithiol. Yields were 45-55%. The ^{1}H NMR spectra were consistent with the assigned structures (see Experimental Section) and in each example, the lowest field aromatic proton was on the central ring of the *m*-terphenyl moiety, para to the ester function (a triplet at δ 7.47, coupled to the two adjacent protons, $J = 7.65$ Hz). In **31**, the *p*-xylylene ring protons appeared as a sharp singlet at δ 7.22.

In a similar manner, **27** was converted to **32** and **33**. Yields were 40% and 30% respectively, and the ^{1}H NMR and other properties were consistent with the assigned structures. The aryl proton para to the ester function again appeared at the lowest field.

Tricyclic Cyclophanes

Tetrabromides **24** and **27** were treated with tetrathiol **34**[9] and base to give tricycles **35** and **36** in 60% and 30% yields, respectively.



34

35 (*n* = 2)
36 (*n* = 1)

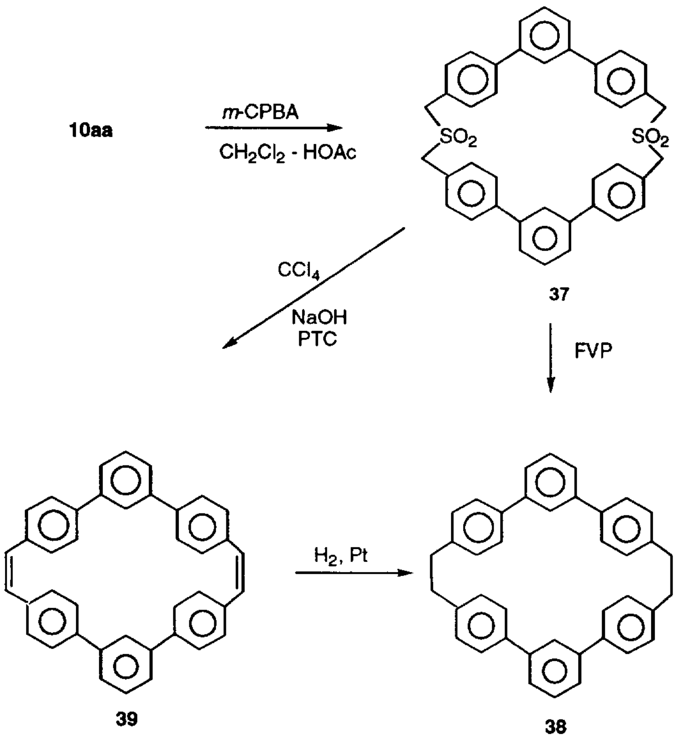
It was possible to assign all the peaks in the ^1H NMR spectra of these cage-like cyclophanes. In **35**, the $-OCH_2CH_2O-$ protons appeared as a sharp singlet (δ 3.18, 4 H). So, too, did the benzyloxy protons (δ 4.95, 4 H). On the other hand, the methylene groups attached to sulfur appeared as two AB quartets (δ 3.39 and 3.54, J = 14.3 Hz, 8 H and δ 3.68 and 3.78, J = 14.8 Hz, 8 H). The 'central' *p*-xylylene ring protons appeared as a sharp 4-proton singlet (δ 7.37) whereas the protons on the 'outer' rings of each *m*-terphenyl unit appeared as two doublets, 8 H each at δ 7.07 and 7.29. The remaining aryl protons of the *m*-terphenyl units, those on the central ring, appeared as a mutually coupled doublet (δ 7.25, 4 H) and triplet (δ 7.42, 2 H), the latter, *para* to the carbonyl group, being the lowest field aryl protons in the spectrum. Finally, the aryl protons on the phenoxy rings appeared as two broadened singlets (*meta* coupling) at δ 6.40 (4 H) and 7.02 (2 H).

In a similar manner, all peaks in the spectrum of **36** could be accounted for (see Experimental Section). Finally, the ir carbonyl frequency in **35** appeared at 1728 cm^{-1}, whereas that in **36** was at an expected[10] higher frequency, 1750 cm^{-1}.

REMOVAL OF THE SULFURS

Removal of the sulfurs from cyclophanes has been widely studied[11]. We illustrate here with just one example, the conversion of **10aa** to hydrocarbons **38** and **39**. Oxidation of **10aa** with *m*-CPBA gave an essentially quantitative yield of disulfone **37**. This could be converted by flash vacuum pyrolysis to the saturated cyclophane **38** (mp 228 °C, 28%) or to diene **39** (mp 370 °C, 30%) via the phase-transfer catalyzed Ramberg-Bäcklund procedure. Catalytic hydrogenation of **39** gave **38**.

The ^{1}H NMR spectra were diagnostic for these structural changes. The methylene singlet at δ 3.85 in **10aa** moved downfield to δ 4.43 (s, 8 H) in **37** and to δ 2.96 (s, 8 H) in **38**, and became a four-proton vinyl singlet at δ 6.81 in **39**. The internal protons on the central rings of the *m*-terphenyl moieties appeared at lowest field, as triplets at δ 7.80 in **38** and at δ 7.59 in **39**; this assignment was verified by preparing the deuterio analogues.



CONCLUSIONS

We have shown that the readily prepared *m*-terphenyl building blocks **5**, **6**, **8**, and **9** can be used to assemble cyclophanes with internal substituents. Yields in the cyclization steps are high, the number of steps required is small, and through the use of other linking agents many structural variations are possible (**10-15**, **17-**

19). The methodology has been adapted to bi- and tricyclic cyclophanes **28-33**, **35**, **36** and to desulfurized cyclophanes **38**, **39**. Clearly the *m*-terphenyl moiety is well-designed for cyclophane construction.[12]

EXPERIMENTAL SECTION[13]

4, 4"-Dimethyl-1, 1': 3', 1"-terphenyl (4a). A general procedure[4] was followed. To a solution of 4-methylphenylmagnesium bromide [prepared from 28.0 g (165 mmol) of 4-bromotoluene and 4.4 g (180 mmol) of magnesium in 500 mL of dry THF] heated at reflux under Ar was added dropwise a solution of 2,6-dichloroiodobenzene[5] (15.0 g, 55 mmol) in 100 mL of dry THF. After 3 h additional heating at reflux, the mixture was cooled, quenched with 6N HCl (150 mL) and extracted with ether (3 x 200 mL). The combined extracts were washed with water, saturated sodium bicarbonate, and dried ($MgSO_4$). The crude product obtained after solvent removal was chromatographed (silica gel, hexanes) to give 10.1 g (71%) of **4a**, mp 115 °C (hexanes) (lit[7] 114 °C); ^{1}H NMR δ 2.44 (s, 6 H), 7.30 (d, *J* = 7.8 Hz, 4 H), 7.48-7.59 (m, 7 H), 7.81 (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR δ 20.9, 125.8, 125.9, 127.16, 127.24, 129.3, 129.7, 137.3, 141.9; mass spectrum, *m/e* (relative intensity) 258 (M^+, 100).

Alternate Procedure. Commercial[14] vinylmagnesium bromide (11.1 mL of a 1.0 M solution in THF) was added to a stirred solution of 2,6-dichloroiodobenzene (3.0 g, 11.0 mmol) in THF (40 mL) under Ar at -18 °C. After being stirred at that temperature for 2 h the mixture was added (20 min) under Ar to a refluxing solution of 4-methylphenylmagnesium bromide [prepared from 3.8 g (22.2 mmol) of 4-bromotoluene and 0.55 g (22.6 mmol) of magnesium in THF (80 mL)]. After 3 h of additional reflux, workup as above gave 1.96 g (69%) of **4a** identical in all respects with product described above.

4,4"-Dimethyl-1,1':3',1"-terphenyl-2'-d (4b). The same procedure was followed as for **4a** except that the reaction was quenched with D_2O (5 mL on a 33 mmol scale); mp 115 °C; ^{1}H NMR δ 2.44 (s, 6 H), 7.30 (d, *J* = 7.95 Hz, 4 H), 7.49-7.60 (m, 7 H); mass spectrum, *m/e* (relative intensity) 259 (M^+, 100).

2'-Bromo-4,4"-dimethyl-1,1':3',1"-terphenyl (4c). The alternate procedure for **4a** was followed except that prior to aqueous quench the reaction mixture was added dropwise to bromine (1.76 g, 11 mmol in 50 mL of CCl_4) and stirred for 30 min. Workup as above except for a sodium bisulfite wash to remove excess bromine gave 2.80 g (75%) of **4c** as a colorless solid, mp 118 °C (hexanes); ^{1}H NMR δ 2.44 (s, 6 H), 7.24-7.41 (m, 11 H); ^{13}C NMR δ 21.1, 127.7, 128.8, 129.46, 129.54, 130.2, 137.5, 143.1, 148.3; mass spectrum, *m/e* (relative intensity) 338 (M^+, 100), 336 (M^+, 100), 257 (80), 242 (80), 226 (20). Anal. Calcd for $C_{20}H_{17}Br$: C, 71.23; H, 5.08. Found: C, 70.95: H, 5.23.

2'-Iodo-4,4"-dimethyl-1,1':3',1"-terphenyl (4d). The alternate procedure for **4a** was followed but scaled up four-fold, and prior to aqueous quench iodine (7.62 g, 60 mmol in 50 mL of CCl_4) was added and the mixture was stirred for an additional hour. Workup as above except for a sodium thiosulfate wash to remove the excess iodine gave 10.14 g (60%) of **4d** as a white solid, mp 120 °C (hexanes); ^{1}H NMR δ 2.43 (s, 6 H), 7.23-7.41 (m, 11 H); ^{13}C NMR δ 21.1, 104.3, 127.7, 128.76, 128.77, 129.5, 137.5, 143.1, 148.3; mass spectrum, *m/e* (relative intensity) 384 (M^+, 100), 257 (M^+-I, 45), 242 (44). Anal. Calcd for $C_{20}H_{17}I$: C, 62.51; H, 4.46. Found: C, 62.39; H, 4.45.

4,4"-Dimethyl-1,1':3',1"-terphenyl-2'-carboxylic acid (4e). The alternate procedure for **4a** was followed but scaled up four-fold, and prior to aqueous quench dry CO_2 was bubbled through the reaction mixture overnight. The resulting yellow mass was treated with 6N HCl (150 mL) and worked up as usual. Chromatography [silica gel, hexanes: CH_2Cl_2 (1:4 v/v)] gave 7.36 g (55%) of **4e** as a pale yellow solid, mp 135 °C (hexanes: CH_2Cl_2 1:1 v/v); IR (neat) 3854, 3748, 1701, 1653 cm^{-1}; ^{1}H NMR δ 2.41 (s, 6 H), 7.19-7.51 (m, 11 H); ^{13}C NMR δ 21.0, 128.5, 128.9, 129.1, 129.3, 129.8, 137.5, 137.7, 140.5, 174.7; mass spectrum, *m/e* (relative intensity) 302 (M^+, 100), 285 (60), 269 (10), 242 (20). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.49; H, 6.07.

2'-Cyano-4,4"-dimethyl-1,1":3',1"-terphenyl (4f). A mixture of **4d** (11.52 g, 30 mmol), copper (I) cyanide (16.12 g, 180 mmol) in 400 mL of *N*-methylpiperidone was heated at reflux for 2 d. The mixture was poured onto ice and 200 mL of concentrated aqueous ammonia was added. The dark solid was filtered, air-dried and extracted with CH_2Cl_2 (soxhlet, 400 mL). Evaporation of the solvent left a dark solid which was chromatographed (hexanes: CH_2Cl_2 5:4 v/v) to give 4.84 g (57%) of **4f** as a colorless solid, mp 145 °C; IR (neat) 3030, 2916, 2216, 1587, 1516 cm^{-1}; ^{1}H NMR δ 2.43 (s, 6 H), 7.27-7.67 (m, 11 H); ^{13}C NMR δ 21.1, 118.4, 128.7, 129.1, 129.5, 132.4, 136.0, 138.8, 147.2 (one overlapped); mass spectrum *m/e* (relative intensity) 283 (M$^+$, 100), 268 (75), 140 (30), 133 (40). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.95. Found: C, 89.01; H, 6.07; N, 4.97.

Methyl 4,4"-dimethyl-1,1':3',1"-terphenyl-2'-carboxylate (4h). Via the acid chloride 4g. To a solution of **4e** (12.08 g, 40 mmol) in 20 mL of CH_2Cl_2 was added a solution of thionyl chloride[15] (2.92 mL, 40 mmol) in 20 mL of CH_2Cl_2, followed by 4-5 drops of pyridine. The mixture was stirred (2h) and the solvent removed to give **4g** as a pale yellow solid, mp 120 °C (hexanes: CH_2Cl_2, 2:1 v/v); IR (neat) 1794 cm^{-1}; ^{1}H NMR δ 2.42 (s, 6 H), 7.24 (d, J = 7.9 Hz, 4 H), 7.31-7.38 (m, 6 H), 7.53 (t, J = 7.7 Hz, 1 H); ^{13}C NMR δ 21.2, 128.8, 129.1, 129.3, 130.3, 136.3, 137.3, 138.0, 139.1, 170.1; mass spectrum, *m/e* (relative intensity) 285 (M$^+$ - Cl, 100), 269 (40). Without further purification, **4g** in 50 mL of methanol was heated at reflux for 3h. Removal of the solvent and recrystallization from hexanes gave ester **4h** (10.75 g, 85%), mp 99 °C; IR (neat) 1732 cm^{-1}; ^{1}H NMR δ 2.37 (s, 6 H), 3.40 (s, 3 H), 7.19 (d, J = 7.9 Hz, 4 H), 7.27-7.34 (m, 6 H), 7.46 (t, J = 7.6 Hz, 1 H); ^{13}C NMR δ 21.2, 51.8, 128.2, 128.4, 128.7, 129.0, 129.3, 137.2, 137.6, 140.2, 170.1; mass spectrum, *m/e* (relative intensity) 316 (M$^+$, 50), 285 (100), 242 (25), 165 (10), 58 (50). Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.82; H, 6.37. **From Diazomethane.** To a solution of **4e** (12.08 g, 40 mmol) in ether (50 mL) was added slowly an ether solution of diazomethane (4.2 g, 100 mmol in 250 mL of ether) prepared from *N,N'*-dinitroso-*N,N'*-dimethylterephthalamide (37.5 g, 150 mmol), ether (400 mL), ethanol (50 mL) and KOH (10 g, 180 mmol in 15 mL of water). The mixture was left overnight in the hood, then Ar was bubbled through it to drive off the excess diazomethane. The organic layer was evaporated to dryness. Chromatography (silica gel, hexanes: CH_2Cl_2 3:2 v/v) gave 12.39 g (98%) of **4h** with properties as described above.

3,3"-Dimethyl-1,1':3',1"-terphenyl (7a). Following the alternate procedure for **4a** but scaling up three-fold and using 3-methylphenylmagnesium bromide, there was obtained 5.80 g (68%) of **7a**, mp 54 °C (hexanes); ^{1}H NMR δ 2.46 (s, 6 H), 7.21 (d, J = 9.9 Hz, 2 H) 7.37 (t, J = 7.7 Hz, 2 H), 7.46-7.59 (m, 7 H), 7.82 (t, J = 1.6 Hz, 1 H); ^{13}C NMR δ 21.5, 124.4, 126.0, 126.2, 128.0, 128.1, 128.7, 129.0, 138.3, 141.2, 141.8; mass spectrum, *m/e* (relative intensity) 258 (M$^+$, 100), 243 (10), 228 (10), 194 (40), 165 (30). Anal . Calcd for $C_{20}H_{18}$: C, 92.97; H, 7.02. Found: C, 92.52; H, 7.19.

2'-Bromo-3,3"-dimethyl-1,1':3',1"-terphenyl (7c). Following the procedure for **4a** at half-scale but using 3-phenylmagnesium bromide, and adding the mixture dropwise to a solution of bromine (4.4 g, 27.5 mmol) in 200 mL of CCl_4 (see procedure for **4c**), gave after workup 5.26 g (70%) of **7c** as a colorless solid, mp 88 °C (hexane): ^{1}H NMR δ 2.42 (s, 6 H), 7.20-7.37 (m, 11 H); ^{13}C NMR δ 21.5, 123.1, 126.6, 126.7, 127.8, 128.2, 130.0, 130.2, 137.5, 142.1, 143.9; mass spectrum, *m/e* (relative intensity) 336 (100), 320 (10), 253 (15), 241 (40), 164 (30). Anal. Calcd for $C_{20}H_{17}Br$: C, 71.23; H, 5.08. Found: C, 71.34; H, 5.08.

3,3"-Dimethyl-1,1': 3',1"-terphenyl-2'-carboxylic acid (7e). The procedure for **4e** was followed, but with 3-methylphenylmagnesium bromide, to give 6.42 g (48%) of **7e**, mp 164 °C; IR (neat) 3622, 1698 cm^{-1}; ^{1}H NMR δ 2.40 (s, 6 H), 7.17-7.29 (m, 8 H), 7.37 (d, J = 7.7 Hz, 2 H), 7.51 (t, J = 7.7 Hz, 1 H); ^{13}C NMR δ 21.4, 125.4, 128.2, 128.4, 128.9, 129.2, 129.5, 131.4, 137.9, 140.2, 140.4, 173.8; mass spectrum, *m/e* (relative intensity) 302 (M$^+$, 100), 285 (70), 269 (10), 242 (20), 165 (25). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.29; H, 6.02.

Methyl 3,3"-dimethyl-1,1':3',1"-terphenyl-2'-carboxylate (7h). The same procedure as for **4h** was followed, but starting with **7e**, to give 11.38 g (90%) of **7h**, mp 138 °C; IR (neat) 1731 cm^{-1}; ^{1}H NMR δ 2.39 (s, 6 H), 3.41 (s, 3 H), 7.16-7.31 (m, 8 H), 7.37 (d, *J* = 7.7 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR δ 21.4, 51.7, 125.3, 128.2, 128.3, 128.7, 129.1, 129.3, 132.7, 137.9, 140.4, 140.5, 170.0 mass spectrum, *m/e* (relative intensity) 315 (10), 284 (33), 241 (20), 165 (50), 134 (50), 119 (100). Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.56; H, 6.14.

General Procedure for Bromination of 4. *N*-bromosuccinimide (NBS) was added in 5 or 6 equal portions 5h apart to a solution of **4** in CCl_4 heated at reflux, each portion being immediately followed by a few mg of benzoyl peroxide. After additional reflux (total 40h) the mixture was cooled and the precipitated succinimide removed by filtration. The residue obtained after solvent removal was chromatographed (silica gel, hexanes: CH_2Cl_2 8:2 v/v) and the final product recrystallized (hexanes or hexanes: CH_2Cl_2).

4,4"-Bis(bromomethyl)-1,1':3',1"-terphenyl (5a). From 12.5 g (70.5 mmol) of NBS and 8.65 g (33.5 mmol) of **4a** in 300 mL of CCl_4 there was obtained 11.5 g (83%) of **5a** as a colorless solid, mp 108 °C (lit[7] 105 °C); ^{1}H NMR δ 4.56 (s, 4 H), 7.49 (d, *J* = 8.2 Hz, 4 H), 7.56-7.63 (m, 7 H), 7.77 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR δ 33.1, 126.2, 126.5, 127.6, 127.8, 129. 5, 129.7, 137.2, 141.3; mass spectrum, (FAB), *m/e* 416 (M^{+}); Anal. Calcd. for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88. Found: C, 57.56; H, 3.92.

4,4"-Bis(bromomethyl)-1,1':3'1"-terphenyl-2'-d (5b). From 1.295 g (5 mmol) of **4b**, 1.86 g (10.5 mmol) of NBS in 50 mL of CCl_4 there was obtained 1.67 g (80%) of **5b**, mp 102 °C; ^{1}H NMR δ 4.57 (s, 4 H), 7.50 (d, *J* = 8.2 Hz, 4 H), 7.57-7.67 (m, 7 H); ^{2}H NMR (DMSO) δ 7.907; mass spectrum, (FAB), *m/e* 417 (M^{+}).

2'-Bromo-4,4"-bis(bromomethyl)-1,1':3',1"-terphenyl (5c). From 10.11 g (30 mmol) of **4c**, 11.04 g (62 mmol) of NBS in 250 mL of CCl_4 there was obtained 11.58 g (78%) of **5c**, mp 112 °C; ^{1}H NMR δ 4.57 (s, 4 H), 7.25 (d, *J* = 8.3 Hz, 4 H), 7.34-7.49 (m, 7 H); ^{13}C NMR δ 33.1, 126.4, 128.0, 128.9, 129.0, 130.1, 137.3, 145.8, 147.9; mass spectrum, *m/e* (relative intensity) 495 (M^{+}, 100). Anal. Calcd for $C_{20}H_{15}Br_3$: C, 48.52; H, 3.05. Found C, 48.57; H, 2.95.

2'-Iodo-4,4"-bis(bromomethyl)-1,1':3',1"-terphenyl (5d). From 15.36 g (40 mmol) of **4d**, 14.60 g (82 mmol) of NBS in 300 mL of CCl_4 there was obtained 18.86 g (87%) of **5d**, mp 138 °C; ^{1}H NMR δ 4.57 (s, 4 H), 7.25 (d, *J* = 8.3 Hz, 4 H), 7.34-7.49 (m, 7 H); ^{13}C NMR δ 33.3, 103.1, 127.8, 128.7, 128.8, 129.9, 137.1, 145.5, 147.4; mass spectrum, *m/e* (relative intensity) 542 (M^{+}, 60), 462 (90), 461 (100), 415 (12), 382 (28), 334 (8), 255 (52). Anal. Calcd for $C_{20}H_{15}Br_2I$: C, 44.31; H, 2.79. Found C, 44.17; H, 2.73.

4,4'-bis(bromomethyl)-1,1':3',1"-terphenyl-2'-carboxylic acid (5e). From 15.1 g (50 mmol) of **4e**, 18.69 g (105 mmol) of NBS in 350 mL of CCl_4 there was obtained 21.16 g (92%) of **5e** as a light pale yellow solid, mp 162 °C (hexanes: CH_2Cl_2 7:3 v/v); IR (neat) 3400, 1695 cm^{-1}; ^{1}H NMR δ 4.52 (s, 4 H), 7.37-7.55 (m, 11 H); ^{13}C NMR δ 33.0, 129.1, 129.3, 129.4, 130.1, 130.9, 137.5, 140.0, 140.6, 173.7; mass spectrum, *m/e* (relative intensity) 460 (M^{+}, 20), 301 (100), 283 (40). Anal. Calcd. for $C_{21}H_{16}Br_2O_2$: C, 54.81; H, 3.51. Found: C, 54.64; H, 3.24.

2'-Cyano-4,4'-bis(bromomethyl)-1,1':3',1"-terphenyl (5f). From 9.43 g (33.3 mmol) of **4f**, 12.5 g (70.5 mmol) of NBS in 300 mL of CCl_4 there was obtained 13.97 g (95%) of **5f**, mp 178 °C; IR (neat) 2226 cm^{-1}; ^{1}H NMR δ 4.56 (s, 4 H), 7.49 (d, *J* = 7.7 Hz, 4 H), 7.52-7.72 (m, 7 H): ^{13}C NMR δ 32.7, 117.9, 129.2, 129.5, 129.7, 132.7, 138.5, 138.8, 146.5, 157.3; mass spectrum, *m/e* (relative intensity) 441 (M^{+}, 25), 380 (100), 281 (80), 140 (50). Anal. Calcd for $C_{21}H_{15}Br_2N$: C, 57.17; H, 3.43; N, 3.18. Found: C, 57.47; H, 3.47; N, 3.07.

Methyl 4,4"-bis(bromomethyl)-1,1':3',1"-terphenyl-2'-carboxylate (5h). From 15.8 g (50 mmol) of **4h**, 18.69 g (105 mmol) of NBS in 400 mL of CCl_4 there was obtained 20.8 g (88%) of **5h** as a colorless solid, mp 50 °C; IR (neat) 1722 cm^{-1}; ^{1}H NMR δ 3.38 (s, 3 H), 4.52 (s, 4 H), 7.35-7.44 (m, 10 H), 7.51 (t, *J* = 7.7 Hz, 1 H); ^{13}C NMR δ 33.2, 51.9, 128.8, 128.98, 129.03, 129.5, 132.7, 137.1, 139.7, 140.5, 169.6; mass spectrum, *m/e* (relative intensity) 473 (30), 395 (100), 314 (45), 283 (15), 252 (33), 239 (45), 157 (50). Anal. Calcd for $C_{22}H_{18}O_2Br_2$: C, 55.72; H, 3.82, Found: C, 55.20; H, 3.72.

3,3"-Bis(bromomethyl)-1,1':3',1"-terphenyl (8a). From 12.5 g (70.5 mmol) of NBS and 8.65 g (33.5 mmol) of **7a** in 300 mL of CCl_4 there was obtained 9.70 g (70%) of **8a** as a colorless solid, mp 114 °C; ^{1}H NMR δ 4.56 (s, 4 H), 7.38-7.65 (m, 11 H), 7.76 (t, *J* = 1.6 Hz, 1 H); ^{13}C NMR δ 33.5, 126.1, 126.4, 127.4, 128.0, 128.1, 129.3, 138.4, 141.2, 141.7; mass spectrum, *m/e* (relative intensity) 416 (15), 335 (20), 256 (40), 239 (45), 167 (50), 128 (100). Anal. Calcd for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88. Found: C, 58.05; H, 3.94.

Methyl 3,3"-bis(bromomethyl)-1,1':3',1"-terphenyl-2'-carboxylate (8h). From 15.8 g (50 mmol) of **7h**, 18.69 g of NBS in 400 mL of CCl_4 there was obtained 17.7 g (75%) of **8h** as a colorless solid, mp 118 °C (hexanes: CH_2Cl_2 3:1 v/v); IR (neat) 1730 cm^{-1}; ^{1}H NMR δ 3.42 (s, 3 H), 4.49 (s, 4 H), 7.32-7.42 (m, 10 H), 7.51 (t, *J* = 7.7 Hz, 1 H); ^{13}C NMR δ 33.2, 52.1, 128.2, 128.4, 128.8, 129.0, 129.1, 129.5, 132.9, 137.9, 139.7, 141.0, 169.5; mass spectrum, *m/e* (relative intensity) 474 (5), 393 (18), 363 (15), 283 (55), 252 (57), 239 (100), 226 (48), 215 (35), 202 (40). Anal. Calcd for $C_{22}H_{18}O_2Br$: C, 55.72; H, 3.82. Found: C, 55.49; H, 3.87.

General Procedure for Bis(mercaptomethyl) Compounds 6. 4,4"-Bis (mercaptomethyl)-1,1':3',1"-terphenyl (6a). A solution of **5a** (10.5 g, 25.2 mmol) and thiourea (4.5 g, 53.1 mmol) in THF (250 mL) was stirred for 20 h at 50 °C under Ar. After cooling, the precipitated bis(isothiouronium) bromide was filtered and dried under vacuum (11.33 g, 88%). This salt was suspended in degassed THF (350 mL) under Ar and treated with deoxygenated aqueous KOH (4.5 g, 80 mmol in 100 mL of H_2O). This mixture was stirred (Ar, rt) for 15 h, then neutralized with 6N HCl (400 mL) with cooling, and extracted with CH_2Cl_2 (2 x 300 mL). The combined organic layers were dried ($MgSO_4$), solvent was removed, and the residue was chromatographed (silica gel, hexanes: CH_2Cl_2 3:1 v/v) to give 7.0 g (86%) of **6a** as a white solid, mp 107 °C; ^{1}H NMR δ 1.82 (t, *J* = 7.59 Hz, 2 H), 3.81 (d, *J* = 7.58 Hz, 4 H), 7.43 (d, *J* = 8.01, 4 H), 7.53-7.62 (m, 7 H), 7.78 (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR δ 28.5, 125.9, 126.3, 127.0, 127.7, 128.7, 129.4, 137.5, 141.6; mass spectrum, *m/e* (relative intensity) 322 (M$^+$, 20) 290 (100), 257 (20), 154 (90), 136 (60). Anal. Calcd for $C_{20}H_{18}S_2$: C, 74.49; H, 5.63. Found: C, 74.53; H, 5.73.

4,4"-Bis(mercaptomethyl)-1,1':3',1"-terphenyl-2'-d (6b). From 4.17g (10 mmol) of **5b** and 1.52 g (20 mmol) of thiourea, followed by hydrolysis of the resulting bis(isothiouronium) salt with KOH (1.79 g, 31.8 mmol) and workup as above there was obtained 2.57 g (78%) of **6b**, mp 106 °C; ^{1}H NMR δ 1.82 (t, *J* = 7.55 Hz, 2 H), 3.82 (d, *J* = 7.7 Hz, 4 H), 7.43 (d, *J* = 8.2, 4 H), 7.50-7.64 (m, 7 H); ^{2}H NMR (DMSO) δ 7.884; mass spectrum, *m/e* (relative intensity) 323 (M$^+$, 20), 306 (90), 289 (100).

2'-Bromo-4,4"-bis(mercaptomethyl)-1,1':3',1"-terphenyl (6c). From bis (bromomethyl) compound **5c** (4.95 g, 10 mmol), thiourea (1.52 g (20 mmol) and for the hydrolysis, KOH (1.79 g, 31.8 mmol) there was obtained 2.73 g (68%) of **6c** as a white solid, mp 115 °C; ^{1}H NMR δ 1.83 (t, *J* = 7.69 Hz, 2 H), 3.82 (d, *J* = 7.59 Hz, 4 H), 7.23-7.42 (m, 11 H); ^{13}C NMR δ 28.6, 127.8, 128.8, 128.9, 129.4, 129.86, 129.92, 130.0 (one overlapped); mass spectrum, *m/e* (relative intensity) 401 (M$^+$, 80). Anal. Calcd for $C_{20}H_{17}BrS_2$: C, 59.84; H, 4.27. Found: C, 59.80; H, 4.18.

2'-Iodo-4,4"-bis(mercaptomethyl)-1,1':3',1"-terphenyl (6d). From 5.42 g (10 mmol) of bis(bromomethyl) compound **5d**, 1.52 g (20 mmol) of thiourea and for the hydrolysis, 1.79 g (31.8 mmol) of KOH there was obtained 2.24 g (50%) of **6d**, mp 110 °C; ^{1}H NMR δ 1.81 (t, *J* = 7.59 Hz, 2 H), 3.79 (d, *J* = 7.65 Hz, 4 H), 7.20-7.39 (m, 11 H); ^{13}C NMR δ 28.6, 127.77, 127.84, 128.9, 129.7, 129.9, 140.7, 144.6, 147.9; mass spectrum, *m/e* (relative intensity) 448 (M$^+$, 55), 416 (90), 383 (100). Anal. Calcd for $C_{20}H_{17}IS_2$: C, 53.57; H, 3.82. Found: C, 53.58; H, 3.80.

4,4"-Bis(mercaptomethyl)-1,1':3',1"-terphenyl-2'-carboxylic acid (6e). The bis (isothiouronium) salt obtained from 4.60 g (10 mmol) of bis(bromomethyl) compound **5e** and 1.52 g (20 mmol) of thiourea was hydrolyzed by treating a suspension of the salt in 400 mL of dioxane-water (4:1 v/v) with 1.80 g (30 mmol) of ethylenediamine for 15 h at rt, followed by neutralization with 6N HCl

(30 mL). The mixture was extracted with CH_2Cl_2 (3 x 200 mL), combined organic layers were dried ($MgSO_4$) and the residue obtained after evaporation of the solvent was chromatographed (silica gel, hexanes-CH_2Cl_2 1:9 v/v) to give 1.39 g (38%) of bis-thiol **6e** as a pale yellow solid, mp 120 °C; IR (neat) 3600, 3000, 1700, 1605 cm^{-1}; ^1H NMR δ 1.81 (t, *J* = 7.56, Hz, 2 H), 3.79 (d, *J* = 7.53 Hz, 4 H), 7.35-7.55 (m, 11 H); ^{13}C NMR δ 28.7, 128.1, 128.8, 129.0, 129.6, 129.7, 139.1, 139.9, 140.5, 172.5; mass spectrum, *m/e* (relative intensity) 366 (M^+, 80), 333 (87), 301 (100), 255 (25), 239 (20), 150 (65). Anal. Calcd for $C_{21}H_{18}O_2S_2$: C, 68.82; H, 4.95. Found: C, 68.72; H, 5.01.

Methyl 4,4"-bis(mercaptomethyl)-1,1':3',1"-terphenyl-2'-carboxylate (6h). The bis(isothiouronium) salt obtained from 4.74 g (10 mmol) of **5h** and 1.90 g (25 mmol) of thiourea was hydrolyzed with 1.80 g (30 mmol) of ethylenediamine in 400 mL of dioxane-water (4:1 v/v). After the usual workup followed by chromatography (silica gel, hexanes: CH_2Cl_2 1:1 v/v) there was obtained 1.14 g (30%) of **6h**, mp 107 °C; IR (neat) 1729 cm^{-1}; ^1H NMR δ 1.82 (t, *J* = 7.6 Hz, 2 H), 3.42 (s, 3 H), 3.81 (d, *J* = 7.5 Hz, 4 H), 7.37-7.39 (m, 10 H), 7.52 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR δ 28.7, 51.8, 128.0, 128.5, 128.7, 128.9, 129.4, 132.7, 139.2, 139.9, 140.4, 169.8; mass spectrum, *m/e* (relative intensity) 380 (M^+, 10), 347 (30), 314 (10), 283 (10), 269 (15), 239 (25), 226 (15), 157 (100), 119 (30). Anal. Calcd for $C_{22}H_{20}S_2O_2$: C, 69.44; H, 5.30. Found: C, 69.48; H, 5.34.

3,3"-Bis(mercaptomethyl)-1,1':3',1"-terphenyl (9a). From 5.25 g (12.6 mmol) **8a** and 2.25 g (26.6 mmol) of thiourea, followed by hydrolysis of the resulting bis(isothiouronium) salt with KOH (2.25 g, 40 mmol) and workup as with **5a** there was obtained 3.0 g (75%) of **9a**, mp 43 °C; ^1H NMR δ 1.83 (t, *J* = 7.6 Hz, 2 H), 3.82 (d, *J* = 7.6 Hz, 4 H), 7.34 (d, *J* = 7.6 Hz, 2 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.52-7.60 (m, 7 H), 7.79 (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR δ 29.0, 126.0, 126.1, 126.3, 127.0, 127.1, 129.15, 129.20, 141.5, 141.6, 141.7; mass spectrum, *m/e* (relative intensity) 322 (M^+, 100), 289 (98), 256 (60), 239 (30), 128 (97). Anal. Calcd for $C_{20}H_{18}S_2$: C, 74.49; H, 5.62. Found: C, 74.54; H, 5.61.

General Procedure for Coupling Bis(bromomethyl) Compounds 5 or 8 with Bis (mercaptomethyl) Compounds 6 or 9. A solution of the required bis(bromomethyl) terphenyl (6.5 mmol) and the required bis(mercaptomethyl) terphenyl (6.5 mmol) in Ar-degassed benzene (450 mL) was added dropwise over 18-20 h to a solution of KOH (13 mmol) in 500 mL of 95% aqueous ethanol under Ar with vigorous stirring. After addition was complete, the mixture was stirred for an additional 4h, then evaporated to dryness. The crude product was chromatographed (silica gel) and recrystallized.

Properties of Cyclophanes 10, 11 and 12. Yields, melting points and ^1H NMR spectra are summarized in Tables 1 and 2. Additional data follow.

For 10aa: ^{13}C NMR δ 37.3, 125.5, 125.9, 127.0, 127.5, 129.2, 129.5, 129.7, 138.9; mass spectrum, *m/e* (relative intensity) 576 (M^+, 40), 287 (40), 256 (100), 243 (10). Anal. Calcd for $C_{40}H_{32}S_2 \cdot 0.8\ CH_2Cl_2$: Calcd C, 76.01; H, 5.25. Found: C, 76.20; H, 5.22.

For 10ab: Prepared from dibromide **5b** (0.834 g, 2.0 mmol) and dithiol **6a** (0.644 g, 2.0 mmol), yield 0.693 g (60%), mp 258 °C; ^1H NMR same as for **10aa** except that the peak at δ 7.62 integrated for only 1 H; ^2H NMR δ 7.53 (s); mass spectrum (FAB) 577 (M^+) and 578 (M^++1).

For 10bb: Prepared from dibromide **5b** (0.834 g, 2.0 mmol) and dithiol **6b** (0.646 g, 2.0 mmol), yield 0.671 g (58%), mp 258 °C; ^1H NMR same as for **10aa** except that the peak at δ 7.62 was absent; ^2H NMR δ 7.51 (s); mass spectrum (FAB) 578 (M^+), 579 (M^++1).

For 10ac: ^{13}C NMR δ 37.7, 39.5, 125.2, 125.5, 126.7, 126.9, 127.3, 128.4, 128.8, 128.9, 129.7, 138.7, 139.2, 139.5, 140.7, 144.2, 147.7; mass spectrum, *m/e* (FAB) 655 (M^+). Anal. Calcd for $C_{40}H_{31}BrS_2$: C, 73.27; H, 4.77. Found: C, 72.91; H, 4.88.

For 10ad: ^{13}C NMR δ 37.7, 39.5, 103.6, 125.2, 125.5, 126.9, 127.7, 128.4, 128.85, 128.94, 129.1, 129.7, 138.7, 139.2, 139.5, 140.8, 144.2, 147.7; mass spectrum, *m/e* (relative intensity) 702 (M$^+$, 95), 575 (10), 415 (20), 384 (40), 288 (70), 258 (100). Anal. Calcd for $C_{40}H_{31}IS_2$: C, 68.37; H, 4.45. Found: C, 68.40; H, 4.40.

For 10ae: IR (neat) 3219, 1705 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.91 (s, 4 H), 3.93 (s, 4 H), 6.76 (d, *J* = 8.2 Hz, 4 H), 7.26 (d, *J* = 8.2 Hz, 4 H), 7.36-7.58 (m, 14 H), 8.01 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 36.4, 37.9, 124.5, 125.1, 126.5, 128.5, 128.8, 129.1, 129.4, 129.6, 134.2, 137.6, 138.3, 138.7, 139.9, 140.2, 140.3, 170.0. Spectra of the carboxylate ion, obtained by adding 1.1 equiv of NaOMe to the above solutions: ^{1}H NMR δ 3.83 (s, 4 H), 3.89 (s, 4 H), 6.50 (d, *J* = 7.8 Hz, 4 H), 7.14-7.77 (m, 19 H); ^{13}C NMR δ 35.8, 38.4, 124.3, 124.6, 124.8, 126.7, 128.7, 128.9, 129.1, 129.2, 129.4, 129.6, 136.2, 136.9, 138.6, 139.8, 141.6, 166.8; mass spectrum, *m/e* (relative intensity) 620 (M$^+$, 80), 588 (10), 301 (60), 257 (80), 84 (100). Anal. Calcd for $C_{41}H_{32}O_2S_2{\bullet}H_2O$; C, 77.08; H, 5.04. Found: C, 77.14; H, 4.94.

For 10ah: IR (neat) 1725 cm^{-1}; ^{13}C NMR δ 37.7, 38.6, 51.8, 125.4, 125.7, 127.1, 127.3, 127.8, 128.66, 128.73, 128.8, 129.0 129.3, 129.5, 133.0, 139.1, 139.2, 139.7, 141.1, 169.7; mass spectrum, *m/e* (relative intensity) 634 (M$^+$, 15), 603 (10), 346 (60), 329 (75), 315 (90), 285 (60), 271 (100), 257 (65), 228 (45), 207 (95). Anal. Calcd for $C_{42}H_{34}O_2S_2.H_2O$: C, 77.27; H, 5.56. Found C, 77.14; H, 5.49.

For 10af: IR (neat) 2227 cm^{-1}; ^{13}C NMR δ 37.9, 38.3, 118.0; 125.2, 125.3, 127.0, 128.8, 128.98, 129.08, 129.14, 132.2, 137.0, 138.4, 138.8, 140.3, 140.8, 146.6; mass spectrum, *m/e* (relative intensity) 601 (M$^+$, 40), 569 (20), 289 (60), 257 (100). Anal. Calcd for $C_{41}H_{31}NS_2$: C, 81.82; H, 5.19; N, 2.33. Found: C, 81.85; H, 5.15; N, 2.33.

For 10ce: IR (neat) 3434, 1742 cm^{-1}; ^{13}C NMR δ 36.5, 36.6, 121.7, 127.3, 127.8, 128.0, 128.58, 128.63, 129.25, 129.33, 129.5, 136.4, 138.9, 139.08, 139.16, 140.3, 144.6, 147.3, 169.0; mass spectrum (FAB) 699 (M$^+$). Anal. Calcd for $C_{41}H_{31}BrO_2S_2$: C, 70.37; H, 4.47. Found: C, 70.16; H, 4.60.

For 10ch: ^{13}C NMR δ 37.4, 37.5, 52.5, 127.4, 127.6, 128.2, 128.3, 128.6, 128.7, 129.0, 129.3, 129.5, 129.8, 138.8, 138.9, 139.0, 140.3, 144.2, 147.6, 169.3; mass spectrum, *m/e* (relative intensity) 714 (M$^+$+1, 20), 634 (20), 414 (25), 383 (30), 346 (25), 315 (100), 271 (25), 239 (40). Anal. Calcd for $C_{42}H_{33}BrO_2S_2$: C, 70.68; H, 4.66. Found: C, 70.55; H, 4.44.

For 10de: IR (neat) 3434, 1742 cm^{-1}; ^{13}C NMR δ 36.5, 36.6, 107.2, 127.7, 127.8, 128.0, 128.58, 128.62, 129.3, 129.5, 138.9, 139.1, 139.2, 140.3, 144.6, 147.3, 169.0 (two overlapped); mass spectrum (FAB) 746 (M$^+$). Anal. Calcd for $C_{41}H_{31}IO_2S_2{\bullet}H_2O$: C, 64.39; H, 4.08. Found: C, 64.57; H, 3.93.

For 10dh: IR (neat) 1738 cm^{-1}; ^{13}C NMR δ 37.4, 37.5, 52.5, 106.2, 127.4, 127.7, 128.2, 128.3, 128.7, 129.0, 129.3, 129.5, 129.8, 138.8, 138.9, 139.0, 140.3, 144.2, 147.6, 169.3; mass spectrum, *m/e* (relative intensity) 760 (M$^+$, 90) 728 (10), 634 (10), 383 (40), 345 (30), 315 (100), 285 (20), 239 (30). Anal. Calcd for $C_{42}H_{33}IO_2S_2$: C, 66.31; H, 4.37. Found: C, 66.38; H, 4.27.

For 10hh: IR (neat) 1730 cm^{-1}; ^{13}C NMR δ 35.4, 51.8, 128.5, 128.8, 129.0, 129.4, 132.7, 137.4, 139.2, 140.0, 169.8; mass spectrum, *m/e* (relative intensity) 692 (M$^+$, 10), 647 (10), 600 (30), 474 (20), 395 (62), 329 (65), 315 (100), 283 (10), 255 (20), 239 (25). Anal. Calcd for $C_{44}H_{36}O_4S_2$: C, 76.27; H, 5.24. Found: C, 75.90; H, 5.28.

For 11: ^{13}C NMR δ 35.9, 125.8, 125.9, 126.0, 127.7, 128.4, 128.9, 129.0, 138.3, 141.1, 141.2; mass spectrum, *m/e* (relative intensity) 576 (M$^+$, 80), 350 (30), 289 (30), 271 (100), 253 (20), 239 (20), 226 (20). Anal. Calcd for $C_{40}H_{32}S_2{\bullet}0.8CH_2Cl_2$: C, 76.01; H, 5.25. Found: C, 76.23; H, 5.16.

For 12a: ^{13}C NMR δ 36.2, 36.7, 124.7, 124.9, 125.4, 126.0, 126.9, 127.3, 127.6, 128.0, 128.7, 129.0, 129.1, 129.52, 137.7, 139.1, 139.6, 140.4, 141.0, 141.3 mass spectrum, *m/e* (relative intensity) 576 (M$^+$, 95), 319 (20), 287 (90), 257 (100), 239 (40), 165 (30). Anal. Calcd for $C_{40}H_{32}S_2{\bullet}0.8\,CH_2Cl_2$: C, 76.01; H, 5.25. Found: C, 76.25; H, 5.06.

For 12c: ^{13}C NMR δ 34.8, 36.1, 125.5, 125.8 126.3, 127.2, 128.15, 128.18, 128.5, 128.6, 128.9, 129.2, 129.3, 137.1, 138.4, 140.6, 141.1, 141.6 143.4; mass spectrum, *m/e* (relative intensity) 656 (20), 575 (10), 399 (10), 367 (20), 335 (20), 288 (30), 258 (100), 239 (40). Anal. Calcd for $C_{40}H_{31}BrS_2$: C, 73.27; H, 4.77. Found: C, 72.86; H, 4.54.

For 12f: IR (neat) 2220 cm^{-1}; ^{13}C NMR δ 34.6, 35.4, 117.2, 126.2, 126.5, 126.9, 127.0, 127.5, 128.1, 128.4, 129.0, 129.3, 131.9 137.2, 137.9, 138.7, 141.5, 146.6 (two overlapped); mass spectrum, *m/e* (relative intensity) 601 (M$^+$, 58), 568 (12), 537 (10), 344 (10), 319 (28), 314 (54), 312 (54), 288 (70), 281 (100), 258 (55), 256 (30). Anal. Calcd for $C_{41}H_{31}NS_2$: C, 81.83; H, 5.19. Found: C, 81.69; H, 5.32.

General Procedure for Coupling 5 or 8 with Xylylene Dithiols. A solution of the particular bis(bromomethyl) terphenyl (2.40 mmol) and xylylene dithiol (2.41 mmol) in Ar-degassed benzene (500 mL) was added dropwise over 18-20 h with vigorous stirring to a solution of KOH (13 mmol) in 900 mL of 95% aqueous ethanol under Ar. After addition was complete, the mixture was stirred for an additional 4 h, then evaporated to dryness. The crude product, after the usual workup, was chromatographed (silica gel) and recrystallized. Yields, mp and ^{1}H NMR spectra are summarized in Tables 3 and 4. Additional data follow.

For 13a: ^{13}C NMR δ 35.4, 35.7, 125.7, 125.9, 127.2, 127.5, 128.9, 129.1, 129.4, 129.8, 137.3, 138.1, 139.7, 141.2; mass spectrum (FAB) 849 (M$^+$+1). Anal. Calcd for $C_{56}H_{48}S_4$: C, 79.20; H, 5.70. Found: C, 78.85; H, 5.68.

For 13c: ^{13}C NMR δ 35.3, 35.6, 123.0, 126.8, 127.7, 128.6, 129.1, 129.6, 130.0, 130.1, 137.3, 138.1, 140.7, 143.4; mass spectrum (FAB) 1007 (M$^+$+1). Anal. Calcd for $C_{56}H_{46}Br_2S_4$: C, 66.79; H, 4.60. Found: C, 66.44; H, 4.44.

For 13h: IR (neat) 1719 cm^{-1}; ^{13}C NMR δ 35.3, 35.6, 51.6, 127.7, 128.5, 128.7, 128.9, 129.0, 129.3, 129.8, 132.7, 137.3, 138.1, 139.2, 139.9, 169.6; mass spectrum (FAB) 965 (M$^+$+1). Anal. Calcd for $C_{60}H_{52}O_4S_4$: C, 74.65; H, 5.43. Found: C, 74.67; H, 5.38.

For 14: ^{13}C NMR δ 34.9, 125.8, 125.9, 127.2, 129.2, 129.3, 129.5, 136.8, 137.4, 139.7, 141.3; mass spectrum (FAB) 849 (M$^+$+1). Anal. Calcd for $C_{56}H_{48}S_4$: C, 79.20; H, 5.70. Found: C, 78.78; H, 5.47.

For 15: ^{13}C NMR δ 32.8, 36.6, 125.8, 126.1, 127.3, 127.5, 129.2, 129.4, 130.6, 135.9, 137.8, 139.8, 141.3; mass spectrum (FAB) 849 (M$^+$+1). Anal. Calcd for $C_{56}H_{48}S_4$: C, 79.20; H, 5.70. Found: C, 78.81; H, 5.62.

For 17a: ^{13}C NMR δ 35.2, 35.3, 125.4, 125.7, 125.8, 126.0, 127.1, 127.4, 128.1, 128.3, 129.4, 129.6, 138.1, 138.9, 140.6, 141.0; mass spectrum (FAB) 425 (M$^+$+1). Anal. Calcd for $C_{28}H_{24}S_2$: C, 79.20; H, 5.70. Found: C, 79.26; H, 5.66.

For 17h: IR (neat) 1730 cm^{-1}; ^{13}C NMR δ 35.8, 35.9, 52.1, 125.6, 127.9, 128.0, 128.1, 128.5, 128.6, 129.3, 130. 4, 131.3, 132.9, 137.6, 138.1, 140.8, 141.3, 169.1; mass spectrum (FAB) 482 (M$^+$). Anal. Calcd for $C_{30}H_{26}O_2S_2$: C, 74.65; H, 5.43. Found: C, 74.77; H, 5.46.

For 18: ^{13}C NMR δ 34.2, 35.4, 125.3, 125.4, 125.7, 128.0, 128.9, 129.0, 129.2, 129.3, 137.1, 138.1, 140.1, 140.8; mass spectrum, *m/e* (relative intensity) 424 (M$^+$- 1, 10), 287 (10), 257 (20), 256 (60), 239 (30), 165 (20), 135 (100). Anal. Calcd for $C_{28}H_{24}S_2$: C, 79.20; H, 5.70. Found: C, 79.51; H, 5.78.

For 19: ^{13}C NMR δ 34.3, 37.9, 124.8, 125.2, 127.2, 127.3, 127.6, 128.7, 129.0, 129.35, 129.39, 135.2, 139.7, 140.9, 141.0; mass spectrum (FAB) 425 (M$^+$+1). Anal. Calcd for $C_{28}H_{24}S_2$: C, 79.20; H, 5.70. Found: C, 78.76; H, 5.57.

2-Hydroxyethyl 4,4"-dimethyl-1,1':3',1"-terphenyl-2'-carboxylate (25). Acid chloride **4g**, obtained from 10.0 g (33.1 mmol) of **4e** and $SOCl_2$ (2.5 mL, 34.3 mmol) was added in 4 portions to the monosodium salt of ethylene glycol (from 2.23 g, 36.0 mmol of ethylene glycol and 1.73 g, 36 mmol, of sodium hydride, 50% in oil) in 700 mL of anhydrous DMF under Ar. The mixture was stirred overnight and the residue obtained after removing the solvent was taken up in benzene (500 mL), washed with water (2 x 200 mL), dried ($MgSO_4$) and evaporated to dryness. Chromatography (silica gel, hexane: CH_2Cl_2 1:2 v/v) gave 11.23 g (98%) of **25** as a white solid, mp 155 °C: IR (neat) 3365, 1730 cm^{-1}; ^{1}H NMR δ 1.04 (br s, 1 H, exchanges with D_2O), 2.38 (s, 6 H), 3.37 (t, *J* =

4.5 Hz, 2 H), 3.96 (t, J = 4.5 Hz, 2 H), 7.21 (d, J = 7.9 Hz, 4 H), 7.30 (d, J = 7.9 Hz, 4 H), 7.34 (d, J = 7.7 Hz, 2 H), 7.48 (t, J = 7.7 Hz, 1 H); ^{13}C NMR δ 21.1, 60.6, 66.6, 128.3, 128.8, 129.1, 132.4, 137.5, 137.7, 140.3, 169.4; mass spectrum, *m/e* (relative intensity) 346 (M$^+$, 100), 302 (60), 285 (95), 257 (10), 242 (20). Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.80; H, 6.32.

Ethylene 1,2-bis (4,4"-dimethyl-1,1':3',1"-terphenyl-2'-carboxylate (23). From 4e: Acid chloride **4g**, obtained from 10.0 g (33.1 mmol) of **4e** and $SOCl_2$ (2.5 mL, 34.3 mmol) was added in 4 portions to the disodium salt of ethylene glycol (from 0.99 g, 16.0 mmol of ethylene glycol and 1.63 g, 34.0 mmol, of sodium hydride, 50% in oil) in 500 mL of anhydrous DMF under Ar. The mixture was stirred overnight at 50 °C and the DMF was then removed under reduced pressure. The residue was dissolved in benzene (2 x 300 mL), washed with water (2 x 100 mL) dried ($MgSO_4$) and evaporated to give a dark solid. Chromatography (silica gel, hexanes: CH_2Cl_2, 1:1 v/v) gave 9.10 g (87%) of **23** as a colorless solid, mp 212 °C (hexanes: CH_2Cl_2, 3:1 v/v): IR (neat) 1736 cm^{-1}; ^{1}H NMR δ 2.37 (s, 12 H), 3.68 (s, 4 H), 7.11 (d, J = 8.2 Hz, 8 H), 7.27 (d, J = 8.0 Hz, 8 H), 7.38 (d, J = 7.5 Hz, 4 H), 7.53 (t, J = 7.6 Hz, 2 H); ^{13}C NMR δ 21.10, 21.14, 61.9, 128.3, 128.6, 128.9, 129.3, 132.5, 137.2, 137.5, 140.3, 169.2; mass spectrum, *m/e* (relative intensity) 630 (M$^+$, 20), 329 (25), 285 (100), 269 (5). Anal. Calcd for $C_{44}H_{38}O_4$: C, 83.78; H, 6.07. Found: C, 83.67; H, 6.14. **From 25:** Acid chloride **4g** prepared as above was added in 4 portions to the monosodium salt of **25** (from 11.45 g, 33.1 mmol of **25** and 1.73 g, 36 mmol of sodium hydride, 50% in oil) in 500 mL of anhydrous DMF. Workup as above gave 20.44 g (98%) of **23** with properties as described above.

Tetrabromide 24. From 6.30 g (10.0 mmol) of **23** and 7.12 g (40 mmol) of NBS in 300 mL of CCl_4, following the general bromination procedure above, there was obtained 7.58 g (80%) of crude **24** as a pale yellow solid. Recrystallization 4X from hexanes: CH_2Cl_2 (3:2 v/v) gave 3.79 g (40%) of pure **24** as a colorless solid, mp 192 °C: IR (neat) 1730 cm^{-1}; ^{1}H NMR δ 3.55 (s, 4 H), 4.43 (s, 8 H), 7.24-7.31 (m, 16 H) 7.34 (d, J = 7.6 Hz, 4 H), 7.54 (t, J = 7.6 Hz, 2 H); ^{13}C NMR δ 33.1, 62.0, 126.5, 128.9, 129.0, 129.8, 132.3, 137.3, 139.9, 140.3, 168.6; mass spectrum (FAB) 947 (M$^+$+1). Anal. Calcd for $C_{44}H_{34}Br_4O_4$: C, 55.84; H, 3.62. Found: C, 55.74; H, 3.62.

Methylene bis (4,4"-dimethyl-1,1':3',1"-terphenyl-2'-carboxylate) (26). Acid chloride **4g**, obtained as described for **23**, was added in 4 portions to the sodium salt of **4e** (prepared from 10.0 g, 33.1 mmol of **4e** and 3.17 g, 66.04 mmol of NaH,[16] 50% in oil) in 900 mL of DMF[17] under Ar. The mixture was stirred overnight at 65 °C. The DMF was removed under reduced pressure, and the residue was dissolved in benzene (2 x 450 mL), washed with water (2 x 200 mL), dried ($MgSO_4$) and evaporated to give a dark viscous oil. Chromatography (silica gel, hexanes: CH_2Cl_2 2:1 v/v) gave 17.5 g (86%) of **26** as a white solid, mp 164 °C (hexanes: CH_2Cl_2 3:1 v/v): IR (neat) 1756 cm^{-1}; ^{1}H NMR δ 2.23 (s, 12 H), 5.23 (s, 2 H), 7.03 (d, J = 8.4 Hz, 8 H), 7.17 (d, J = 8.0 Hz, 8 H), 7.36 (d, J = 7.5 Hz, 4 H), 7.52 (t, J = 7.6 Hz, 2 H); ^{13}C NMR δ 21.1, 81.5, 128.3, 128.6, 129.0, 129.5, 131.7, 137.0, 137.3, 140.5, 167.8; mass spectrum, *m/e* (relative intensity) 616 (M$^+$, 10), 285 (100), 284 (90), 242 (50), 165 (30). Anal. Calcd for $C_{43}H_{36}O_4$: C, 83.74; H, 5.88. Found: C, 83.76; H, 5.81.

Tetrabromide 27: From 6.16 g (10.0 mmol) of **26** and 7.12 g (40.0 mmol) of NBS in 300 mL of CCl_4, following the general bromination procedure above, there was obtained 7.46 g (80%) of crude **27** as a pale yellow solid. Four recrystallizations from hexanes: CH_2Cl_2 (3:2 v/v) gave pure **27** (2.8 g, 30%), mp 170 °C: IR (neat) 1748 cm^{-1}; ^{1}H NMR δ 4.34 (s, 8 H), 5.14 (s, 2 H), 7.19-7.26 (br s, 16 H), 7.40 (d, J = 7.5 Hz, 4 H), 7.57 (t, J = 7.7 Hz, 2 H); ^{13}C NMR δ 33.0, 81.4, 126.6, 128.7, 128.8, 129.0, 130.0, 137.3, 139.8, 140.0, 147.3; mass spectrum (FAB) 932 (M$^+$). Anal. Calcd for $C_{43}H_{32}Br_4O_4$: C, 55.39; H, 3.46. Found: C, 55.33: H, 3.52.

Bicyclophane 28. A solution of tetrabromide **24** (0.946 g, 1.0 mmol) in Ar-degassed benzene (500 mL) was added dropwise over 20-30 h to a solution of $Na_2S{\bullet}9H_2O$ (0.48 g, 2.0 mmol) in 1600 mL of 95% aqueous ethanol with vigorous stirring under Ar. After addition was complete, the mixture was stirred for an additional 4h, then evaporated to dryness. The crude product was extracted with CH_2Cl_2 (2 x 200 mL), dried and evaporated. The residue was chromatographed (silica gel, CH_2Cl_2: CH_3OH 250 mL:

6 drops) to give 0.31 g (45%) of **28** as a colorless solid, mp 340 °C (dec; hexanes: CH_2Cl_2 1:4 v/v): IR (neat) 1722 cm^{-1}; ^1H NMR δ 3.75 (s, 4 H), 3.84 (s, 8 H), 6.96 (d, *J* = 8.0 Hz, 8 H), 7.27 (d, *J* = 8.2 Hz, 8 H), 7.39 (d, *J* = 8.2 Hz, 4 H), 7.47 (t, *J* = 7.6 Hz, 2 H); ^{13}C NMR δ 38.6, 62.8, 128.1, 128.8, 129.1, 129.6, 133.0, 139.1, 140.07, 140.10, 169.7; mass spectrum, *m/e* (relative intensity 690 (M^+, 100), 658 (20), 627 (30), 595 (40), 551 (30), 368 (30), 314 (50), 284 (90), 264 (50), 236 (50), 111 (50). Anal. Calcd for $C_{44}H_{34}O_4S_2$: C, 76.49; H, 4.96. Found: C, 76.23; H, 5.07.

Bicyclophane 29. A solution of tetrabromide **24** (0.94 g, 1.0 mmol) and *o*-xylylenedithiol (0.34 g, 2.0 mmol) in Ar-degassed benzene (500 mL) was added dropwise over 24-30 h to a solution of KOH (0.23 g, 4.1 mmol) in 1600 mL of 95% aqueous ethanol with vigorous stirring under Ar. After addition was complete, the mixture was stirred for an additional 6h. The usual workup (as with **28**) gave 0.53 g (55%) of **29** as a colorless solid, mp 223 °C (hexanes: CH_2Cl_2 1:5 v/v): IR (neat) 1734 cm^{-1}; ^1H NMR δ 3.44 (s, 4 H), 3.63 (s, 8 H), 3.65 (s, 8 H), 7.20-7.35 (m, 28 H), 7.47 (t, *J* = 7.7 Hz, 2 H); ^{13}C NMR δ 33.2, 36.2, 61.2, 127.4, 128.5, 128.9, 129.0 129.5 130.5, 132.0, 136.1 137.9, 139.1, 140.1, 168.7; mass spectrum (FAB) 963 (M^++1). Anal. Calcd for $C_{60}H_{50}O_4S_4$: C, 74.81; H, 5.23. Found: C, 74.92; H, 5.29.

Bicyclophane 30. Coupling of tetrabromide **24** (0.946 g, 1.0 mmol) with *m*-xylylenedithiol (0.34 g, 2.0 mmol) as with **29** gave 0.48 g (50%) of **30**: IR (neat) 1728 cm^{-1}; ^1H NMR δ 3.45 (s, 4 H), 3.56 (s, 8 H), 3.66 (s, 8 H), 7.23-7.34 (m, 28 H), 7.47 (t, *J* = 7.7 Hz, 2 H); ^{13}C NMR δ 34.7, 35.8, 61.8, 127.7, 128.4, 128.7, 128.9, 129.0 129.5, 137.2, 138.2, 139.1, 140.0, 168.8; mass spectrum (FAB) 963 (M^++1). Anal. Calcd for $C_{60}H_{50}O_4S_4$: C, 74.81; H, 5.23. Found: C, 74.76; H, 5.28.

Bicyclophane 31. Following the procedure for **29** but using p-xylylenedithiol, there was obtained 0.48 g (50%) of **31** as a white solid (hexanes: CH_2Cl_2, 1:5 v/v) mp > 360 °C: IR (neat) 1734 cm^{-1}; ^1H NMR δ 3.42 (s, 8 H), 3.49 (s, 4 H), 3.67 (s, 8 H), 7.07 (d, *J* = 7.9 Hz, 8 H), 7.20 (d, *J* = 8.0 Hz, 8 H), 7.22 (s, 8 H), 7.31 (d, *J* = 7.5 Hz, 4 H), 7.47 (t, *J* = 7.6 Hz, 2 H); ^{13}C NMR δ 34.0, 35.4, 61.8, 128.4, 128.7 128.9, 129.45, 129.54, 132.2 136.6, 137.1, 139.2 140.2, 168.8; mass spectrum (FAB) 963 (M^++1). Anal. Calcd for $C_{60}H_{50}O_4S_4$: C, 74.81; H, 5.23. Found: C, 74.71; H, 5.25.

Bicyclophane 32. Following the procedure for **28**, from 0.932 g (1.0 mmol) of tetrabromide **27** and the same amounts of reagents and solvents as for **28**, there was obtained 0.27 g (40%) of **32** as a white solid, mp >320 °C (dec) (hexanes: CH_2Cl_2, 1:4 v/v): IR (neat) 1748 cm^{-1}; ^1H NMR δ 3.89 (s, 8 H), 4.78 (s, 2 H), 7.09 (d, *J* = 8.2 Hz, 8 H), 7.23 (d, *J* = 8.2 Hz, 8 H), 7.33 (d, *J* = 7.7 Hz, 4 H), 7.46 (t, *J* = 7.7 Hz, 2 H); ^{13}C NMR δ 39.0, 84.7, 126.1, 128.0, 128.5, 128.8, 129.7, 138.5, 139.7, 139.9, 167.4; mass spectrum, *m/e* (relative intensity) 676 (100, M^+), 660 (20), 628 (30), 602 (50), 569 (20), 368 (15), 315 (50), 283 (50), 257 (60). Anal. Calcd for $C_{43}H_{32}O_4S_2{\bullet}H_2O$: C, 74.32; H, 4.93. Found: C, 74.68; H, 4.84.

Bicyclophane 33. Following the procedure for **29**, from 0.932 g (1.0 mmol) of tetrabromide **27** and the same amounts of reagents and solvents as for **29**, there was obtained 0.375 g (30%) of **33** as a white solid, mp 220 °C (hexanes: CH_2Cl_2, 1:4 v/v); IR (neat) 1752 cm^{-1}; ^1H NMR δ 3.43 (s, 8 H), 3.52 (s, 8 H), 5.07 (s, 2 H), 7.08 (d, *J* = 8.2 Hz, 8 H), 7.19 (d, *J* = 8.2 Hz, 8 H), 7.21-7.24 (m, 4 H), 7.29-7.33 (m, 4 H), 7.38 (d, *J* = 7.7 Hz, 4 H), 7.54 (t, *J* = 7.7 Hz, 2 H); ^{13}C NMR δ 32.1, 35.7 81.1, 127.4, 128.4, 128.9, 130.0, 130.2, 131.4, 136.1, 137.9, 138.6, 140.4, 167.6(one carbon overlapped); mass spectrum (FAB) 949 (M^++1). Anal. Calcd for $C_{59}H_{48}O_4S_4$: C, 74.66; H, 5.10. Found: C, 74.71; H, 5.18.

Tricyclophane 35. A solution of tetrabromide **24** (0.955 g, 1.01 mmol) and tetrathiol **34**[9] (0.48 g, 1.01 mmol) in Ar-degassed benzene (500 mL) was added dropwise over 25-30h to a solution of KOH (0.23 g, 4.11 mmol) in 1600 mL of 95% aqueous ethanol with vigorous stirring under Ar. After stirring an additional 4h, the mixture was evaporated to dryness. The crude product, after the usual workup, was chromatographed (silica gel, CH_2Cl_2; CH_3OH 250 mL: 6 drops) to give 0.60 g (60%) of **35**, mp >340 °C (becomes a black powder at 320 °C); IR (neat) 1728 cm^{-1}; ^1H NMR δ 3.18 (s, 4 H), 3.54 and 3.39 (ABq, *J* = 14.3 Hz, 8 H), 3.68 and 3.78 (ABq, *J* = 14.8 Hz, 8 H), 4.95 (s, 4 H), 6.40 (br s, 4 H), 7.02 (br s, 2 H), 7.07 (d, *J* = 8.0 Hz, 8 H), 7.25 (d, *J* = 7.0 Hz, 4 H), 7.29

(d, *J* = 7.6 Hz, 8 H), 7.37 (s, 4 H), 7.42 (t, *J* = 7.7 Hz, 2 H); ^{13}C NMR δ 35.7, 36.4, 62.1, 69.4, 113.6 121.75, 121.80, 127.2 128.5, 128.7, 128.8, 129.4, 132.4, 136.8, 138.0, 138.5, 139.5, 158.3, 168.9; mass spectrum (FAB) 1097 (M^+). Anal. Calcd for $C_{68}H_{56}O_6S_4$: C, 74.43; H, 5.14. Found: C, 74.41; H, 4.97.

Tricyclophane 36. From 0.941 g (1.01 mmol) of tetrabromide **27** and tetrathiol **34**, following the same procedure as for **35**, there was obtained after chromatography (silica gel, hexanes: CH_2Cl_2 1:3 v/v) 0.18 g (30%) of **36**, mp >340 °C (becomes red at 280 °C and a black powder at 320 °C); IR (neat) 1750 cm^{-1}; ^{1}H NMR δ 3.49 and 3.72 (ABq, *J* = 14.4 Hz, 8 H), 3.62 and 3.66 (ABq, *J* = 13.9 Hz, 8 H), 5.01 (s, 4 H), 5.10 (s, 2 H), 6.63 (br s, 4 H), 6.98 (d, *J* = 8.2 Hz, 8 H), 7.14 (d, *J* = 8.1 Hz, 8 H), 7.21 (br s, 2 H), 7.327 (s, 4 H), 7.333 (d, *J* = 7.47 Hz, 4 H), 7.48 (t, *J* = 7.7 Hz, 2 H); ^{13}C NMR δ 34.2, 35.7 69.2, 85.9, 114.4, 122.0, 127.1, 128.4, 128.5, 128.6, 129.9, 131.7, 136.9, 137.8, 138.2, 139.4, 139.8, 159.0, 166.9; mass spectrum (FAB) 1083 (M^++1). Anal. Calcd for $C_{67}H_{54}O_6S_4$: C, 74.23; H, 5.02. Found: C, 74.33; H, 5.11.

Disulfone 37. To a solution of **10aa** (1.15 g, 2.0 mmol) in 300 mL of CH_2Cl_2-glacial acetic acid (1:1 v/v) at 0 °C was added with stirring a solution of *m*-CPBA (85%, 1.73 g, 10 mmol) in 100 mL of glacial acetic acid. The mixture slowly warmed to rt and was stirred for 3 d. The precipitated disulfone was filtered and washed several times with $CHCl_3$ to give 1.24 g (97%) of **37**, mp > 350 °C; ^{1}H NMR δ 4.43 (s, 8 H), 7.32-7.61 (m, 24 H); ^{13}C NMR: too insoluble: mass spectrum, *m/e* (relative intensity) 640 (M^+, 10), 512 (M^+-2SO_2, 100), 497 (10), 383 (15), 257 (50). Anal. Calcd for $C_{40}H_{32}S_2O_4 \cdot H_2O$: C, 72.92; H, 5.20. Found: C, 72.89; H, 5.27.

Flash vacuum pyrolysis of 37. Cyclophane 38. Disulfone **37** (1.15 g, 1.8 mmol) was heated to 400-450 °C at 10^{-2} torr in a quartz pyrolysis apparatus. The product that sublimed to cooler zones was dissolved in CH_2Cl_2 and chromatographed (silica gel, hexanes) to give 0.26 g (28%) of **38**, mp 228 °C (hexanes); ^{1}H NMR δ 2.96 (s, 8 H), 6.82 (d, *J* = 8.2 Hz, 8 H), 7.37 (d, *J* = 8.0 Hz, 8 H), 7.48-7.57 (m, 6 H), 7.80 (t, *J* = 1.7 Hz, 2 H); ^{13}C NMR δ 37.7, 125.1, 126.6, 127.5, 129.2, 129.7, 138.9, 139.6, 141.8; mass spectrum, *m/e* (relative intensity) 512 (M^+, 100), 257 (50). Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.96; H, 6.30.

Diene 39. From Disulfone 37. To a suspension of **37** (2.56 g, 4.0 mmol) in CH_2Cl_2: $CHCl_3$ (150 mL, 2:1 v/v) was added 2.0 mL of CCl_4 and 100 mL of 10% aqueous NaOH and 0.69 g (2 mmol) of cetyltrimethylammonium chloride. The mixture was heated at reflux with vigorous stirring for 3 d. After cooling, the organic layer was separated, washed with water and saturated NaCl and dried (Na_2SO_4). Removal of the solvent left a dark yellow solid which was chromatographed (silica gel, hexanes: CH_2Cl_2 4:1 v/v) to give 0.61 g (30%) of **39**, mp 370 °C; ^{1}H NMR δ 6.81 (s, 4 H), 7.12 (d, *J* = 8.4 Hz, 8 H), 7.42 (d, *J* = 8.4 Hz, 8 H), 7.48-7.57 (m, 6 H), 7.59 (t, *J* = 1.9 Hz, 2 H); ^{13}C NMR δ 124.9, 125.0, 126.9, 129.2, 129.8, 131.0, 136.6, 140.2, 141.6; mass spectrum (FAB) 508 (M^+). Anal. Calcd for $C_{40}H_{28}$: C, 94.45; H, 5.55. Found: C, 94.60; H, 5.57. **From Disulfide 10aa.** To a solution of **10aa** (5.76 g, 10 mmol) in CH_2Cl_2 (150 mL) was added $(CH_3)_3O^+ BF_4^-$ (3.60 g, 24.34 mmol) in CH_2Cl_2 (30 mL) at -30 °C under Ar. The mixture was stirred (4h), then ethyl acetate (20 mL) was added and the mixture stirred for an additional 30 min. The crystalline bis(sulfonium) salt was collected, washed with CH_2Cl_2, and dried as a white powder (7.56 g, 97%), mp 280 °C (dec): ^{1}H NMR δ 3.19 (s, 6 H), 4.87 and 4.94 (AB q, *J* = 13.2 Hz, 8 H), 7.25-7.44 (m, 22 H), 7.58 (t, *J* = 1.8 Hz, 2 H); ^{13}C NMR δ 25.7, 25.8 47.2, 123.7 123.9, 125.9, 126.77, 126.84, 128.7 130.16, 130.24, 139.5. To a stirred suspension of this salt (7.0 g, 8.98 mmol) in dry THF (200 mL) was added with stirring K O-t-Bu (2.02 g, 17.96 mmol). After 10 min stirring at room temperature, the mixture was acidified (HCl) and extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated to leave a dark yellow residue that was chromatographed over silica gel to give a mixture of S-methyl isomers (2.71 g, 50%). This mixture was methylated with $(CH_3)_3O^+BF_4^-$ (1.48 g, 10 mmol) as above to give the bis (sulfonium) salt (3.27 g, 90%) which was again treated with KO-t-Bu (1.13 g, 10 mmol) as above to give, after workup, 0.41 g (20%) of diene **39** whose properties agreed with those above.

Diene 39-d. Cyclophane **10ab** (0.577 g, 1.0 mmol) was oxidized to **37-d** with *m*-CPBA; treatment with KOH-CCl$_4$ and cetyltrimethylammonium bromide gave 0.153 g (30%), mp 370 °C; ^{1}H NMR same as for **39** except that the peak at δ 7.59 integrated for 1 H; ^{2}H NMR (DMSO) δ 7.56 (s); mass spectrum (FAB) 509 (M$^+$).

Diene 39-d$_2$. Cyclophane **10bb** (0.578 g, 1 mmol) was oxidized to **37-d**$_2$ with *m*-CPBA, then rearranged with base as for **39** to give 0.153 g (30%) of **39-d**$_2$, mp 371 °C; ^{1}H NMR same as **39** except that the peak at δ 7.59 was absent; ^{2}H NMR (DMSO) δ 7.57 (s); mass spectrum, *m/e* (relative intensity) 510 (100), 493 (10), 255 (20).

Catalytic Hydrogenation of 39. A solution of diene **39** (0.51 g, 1.0 mmol) in ethyl acetate (20 mL) was hydrogenated at 40 psi over platinum at rt. After removal of the catalyst and solvent, the residue was chromatographed (silica gel, hexanes) to give 0.50 g (98%) of **38**, mp 228 °C, identical in all respects with the pyrolysis product of disulfone **37**.

REFERENCES AND NOTES

1. For reviews and some recent examples see (a) Cram, D.J.*Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1009-1020. (b) Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1988,** *27*, 362-386. (c) Ferguson, S.B.; Seward, E.M.; Sanford, E.M.; Hester, M.; Uyeki, M.; Diederich, F. *Pure Appl. Chem.* **1989**, *61*, 1523-1528. (d) Gutsche, C.D. *Acc. Chem. Res.* **1983,** *16*, 161-170. (e) Moneta, W.; Baret, P.; Pierce, J.L. *Bull. Soc. Chim. France* **1988**, 995-1004. (f) Jimenez, L.; Diederich, F.*Tetrahedron Lett.* **1989**, *30*, 2759-2762. (g) Kimura, E.; Yoshiyama, Y.; Shionoya, M.; Shiro, M. *J. Org. Chem.* **1990**, *55*, 764-766. (h) Campbell, M.; Unrau, C.; Cox, P.; Snieckus, V. 200th ACS Meeting, Washington, D.C. Aug. 26-31, **1990,** Abstract ORGN 187. (i) Lüning, U.; Wangnick, C.; Peters, K.; von Schnering, H.G. *Chem. Ber.* **1991**, *124*, 397-402. (j) Breitenbach, J.; Vögtle, F.*Synthesis* **1992**, 41-43. (k) Schmohel, E.; Ott, F.; Breitenbach, J.; Nieger, M.; Vögtle, F. *Chem. Ber.* **1993**, *126*, 2477-2452. (l) Lee, W.Y.; Park, C.H.; Kim, H.J,; Kim, S.S.*J. Org. Chem.* **1994**, *59*, 878-884. (m) Diederich, F.; Carcanague, D.R. *Helv. Chim. Acta* **1994**, *77*, 800-818.
2. Rebek, J., Jr. *Pure Appl. Chem.* **1989**, *61*, 1517-1522; Rebek, J., Jr. *Acc. Chem. Res.* **1990**, 23, 399-404.
3. Forces other than functionality may also serve for recognition, among them π-bonding. For example, see: (a) Schneider, H-J.; Blatter, T.; Zimmerman, P.*Angew. Chem. Int. Ed. Engl.* **1990,** *29*, 1161-1162. (b) Zimmerman, S.C.; Mrksich, M.; Baloga, M.*J. Am. Chem. Soc.* **1989**, *111*, 8528-8530. (c) Vögtle, F.; Papkalla, T.; Koch, H.; Nieger,*M. Chem. Ber.* **1990**, *123*, 1097-1103.
4. Du, C.-J.F.; Hart, H.; Ng, K.-K.D. *J. Org. Chem.* **1986**, *51*, 3162-3165.
5. Readily prepared from commercially available 2,6-dichloroaniline. See Bolton, R.; Sandell, J.P.B. *J. Chem. Soc., Perkin Trans. 2* **1977**, 278-280. Other 1,2,3-trihalobenzenes can also be used.[4]
6. Alternatively, one equiv. of vinylmagnesium bromide in THF (commercial) can be added to **3** at -18°C (2h) followed by addition of the resulting 2,6-dichlorophenylmagnesium halide to 2 equiv. of *p*-tolylmagnesium bromide in refluxing THF. *cf* Vinod, T.; Hart, H. *J. Org. Chem.* **1990**, *55*, 881-890.
7. Vögtle, F.; Staab, H.A. *Chem. Ber.* **1968**, *101*, 2709-2716.
8. Chemical shift arguments suggest that the signal is more likely due to E than Ha, but the matter would have to be settled by deuterium labelling.
9. Vinod, T.K.; Hart, H. *J. Org. Chem.* **1991**, *56*, 5630-5640.

10. Guthrie, R.D. *J. Chem. Soc.* **1961**, 2525-2528.
11. For a review and leading references, see V. Boekelheide, *Topics in Current Chemistry* **1983**, *113*, 87-143.
12. Some extensions of this work have already been published in preliminary form. See Rajakumar, P.; Kannan, A. *Tetrahedron Lett.* **1993**, *34*, 4407-4410 and 8317-8320.
13. For general procedures, see references 6 and 9.
14. Aldrich Chemical Company.
15. Excess thionyl chloride must be avoided; otherwise cyclization of the acyl cation to the fluorenone (1-p-tolyl-7-methyl), a bright yellow solid, occurs.
16. No reaction with a lesser amount of NaH; excess is required.
17. No reaction in THF.

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