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Synthesis and solid-state structures of new cyclophane host molecules

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Abstract—Five new cyclophane host molecules (corrals) are prepared by linking together two α,α′-di(4-hydroxyphenyl)-1,4-diisopropylbenzene or α,α′-di(3,5-dimethyl-4-hydroxyphenyl)-1,4-diisopropylbenzene units with two permethylene spacers. Three small cyclophane hosts (boxes) are synthesized by cyclization of α,α′-di(4-hydroxyphenyl)-1,4-diisopropylbenzene with di(bromomethyl)benzene compounds. Solid-state structures of one corral and one box are reported.

1. Introduction

Recently, we described the preparation of a new family of cyclophanes[1–3] in which two units of α,α′-di(4-hydroxyphenyl)-1,4-diisopropylbenzene (**1**)[4] are connected through the phenolic oxygens with polymethylene bridges containing 2–6 carbons to give hosts **2**–**6** (Fig. 1).[5–7] It was envisioned that rigidity of the bisphenol units would provide open, hydrophobic cavities in which aromatic hydrocarbon guest molecules could be complexed. Since the aromatic guests would be contained within the central cavities of the receptors, such hosts were termed ‘corrals’. Complexes of corral hosts with toluene and *p*-xylene guests were isolated and their solid-state structures determined.[5,7] Of particular interest was a 1:1 complex of anthracene and the corral host **5** with edge-to-face interactions between the guest molecule and the two end benzene rings of the structural units derived from **1**.[6]

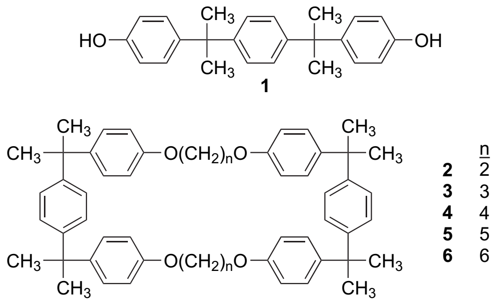

Figure 1. Structures of bisphenol **1** and previously reported corral hosts **2**–**6**.

In extension of this work, we now report the synthesis of two corrals with longer spacers between the two units derived from bisphenol **1**. In addition, a tetramethylated derivative of bisphenol **1** has been prepared and converted into two corral hosts. A hybrid corral molecule with one unit from bisphenol **1** and the other from its tetramethylated derivative was also synthesized. To provide related host molecules with small cavities, three cyclic hosts termed ‘boxes’ have been obtained by cyclization reactions of bisphenol **1** and di(bromomethyl)benzene compounds. Solid-state structures of one of the new corrals and one of the boxes are presented.

2. Results and discussion

2.1. Synthesis of corrals with elongated cavities

In our earlier work, cyclophanes **2**–**6** with 2–6 carbons bridging the phenolic oxygens of two bisphenol **1** molecules were reported.[5–7] Solid-state structures of these host molecules revealed open cavities with pronounced tendencies to form complexes with aromatic molecular guests. For further probing of such complexation phenomena, the preparation of analogues with 7- and 8-carbon bridges was undertaken.

Keywords: Cyclophane synthesis; Solid-state structures.
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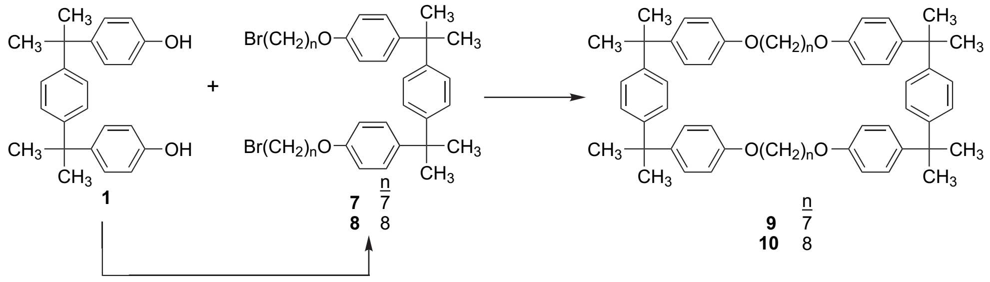


Scheme 1. Two-step synthesis of corrals **9** and **10** with elongated cavities.

Due to the poor quality of commercially available 1,7-dibromoheptane, this reactant was prepared in 89% yield by reaction of 1,7-heptanediol with 2.2 equiv of triphenylphosphine dibromide generated in situ.[8] Reactions of bisphenol **1** with an 8-fold excess of 1,7-dibromoheptane or 1,8-dibromooctane and K_2CO_3 in refluxing acetone for 5 h gave dibromides **7** and **8** in 81 and 84% yields, respectively (Scheme 1). Dilute solutions of dibromides **7** and **8** were refluxed with an equimolar amount of bisphenol **1** and K_2CO_3 in acetone for several days to provide the corresponding corrals **9** and **10** in 19 and 14% yields, respectively. The relatively low yields of **9** and **10** are consistent with the 21% yield obtained in the preparation of corral **6** with hexamethylene spacers between the two units derived from bisphenol **1**.[5]

To date, our attempts to form solid complexes of **9** and **10** with aromatic hydrocarbon guests have been unsuccessful.

2.2. Synthesis of corrals with deeper hydrophobic cavities

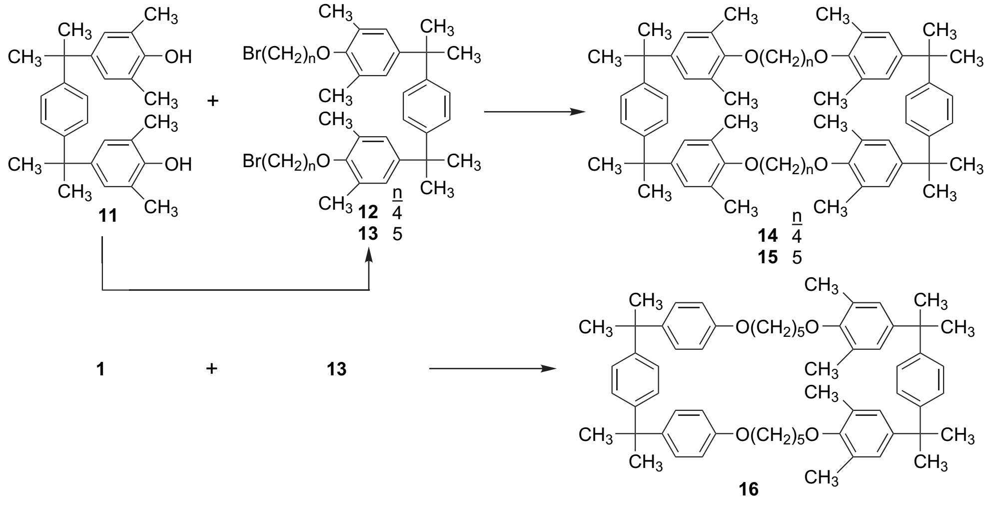
We envisioned that the introduction of methyl groups *ortho* to each phenolic oxygen in **1** would allow new corrals to be prepared in which the cavities would be more tubular than circular. To this end, tetramethylated bisphenol **11** was prepared in 73% yield by reaction of α,α,α′,α′-tetramethyl-1,4-benzenedimethanol, excess 2,6-dimethylphenol, and hydrogen chloride gas at 80 °C.

Reactions of tetramethylated bisphenol **11** with a 7-fold excess of 1,4-dibromobutane or 1,5-dibromopentane and K_2CO_3 in refluxing aqueous acetone for 2 days gave dibromides **12** and **13** in 59 and 44% yields, respectively (Scheme 2). Dilute solutions of dibromides **12** and **13** were cyclized with an equimolar amount of bisphenol **11** and K_2CO_3 in DMF at 50–70 °C for 6 days to produce the corresponding corrals **14** and **15** in 31 and 62% yields, respectively. These cyclization yields are appreciably lower than those for corrals **4** (71%) and **5** (79%) obtained from analogous reactions of bisphenol **1**.[6,7]

Corral **16** with end units derived from two different bisphenol units was also prepared. This hybrid corral was synthesized in 24% yield by reaction of dibromide **13**, bisphenol **1**, and K_2CO_3 in DMF at 50–70 °C for 6 days.

2.3. Synthesis of small cyclophanes

Examination of CPK (Corey–Pauling–Kortun) space-filling models indicated that it might be possible to prepare small cyclophanes[9,10] by cyclization of bisphenol **1** with di(bromomethyl)benzenes. In these cyclophanes, planes of adjacent aromatic rings would be nearly perpendicular forming box-like structures. Hence, we term them 'boxes'. Reactions of bisphenol **1** with di-1,4-, di-1,3- or di-1,2-(bromomethyl)benzenes and Cs_2CO_3 in DMSO at 60 °C for 2 days gave small-ring cyclophanes **17–19** (Fig. 2) in 4, 3, and 5% yields.



Scheme 2. Two-step syntheses of new corral compounds.

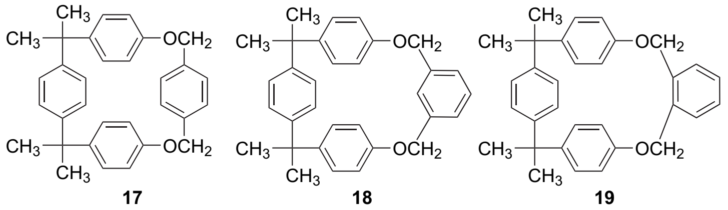


Figure 2. Structures of boxes.

These low yields are consistent with the formation of small cyclophane ring systems.

2.4. Solid-state structures of corral 15 and box 17

The solid-state structures of bisphenols **1** and **11** show *anti* conformations.[11,12] However, these change to *syn* conformations when bisphenol **1** is incorporated into corrals.[5–7]

The solid-state structure of corral **15** contains a disordered toluene molecule and is identified as **15**·TOL (Fig. 3). The presence of the methyl groups bonded to the lateral benzene units causes the conformation of **15** to differ from that of **5**. The cavity dimensions in **15**·TOL are nearly equilateral with interatomic distances C4–C4A=13.1 Å and C20–C23A=13.2 Å. The toluene guest is not contained in the cavity of **15**. The toluene guest is disordered with one orientation of the molecule related to the other by a shift of approximately 1.4 Å in the direction of the C aromatic–C methyl bond. One toluene consists of C42A, C43, C41A, C45, C42, C44, and C41 and the other includes C42, C43A, C41A, C44A, C42A, C45A, and C41. Because the shift of orientations is approximately the length of an aromatic C–C bond, atoms C41, C42, and their symmetry related atoms of one orientation are approximately superimposed on the other. The methyl atom C42A may interact weakly with benzene ring C8–C14 since C42A points at that benzene and the plane of that benzene is nearly perpendicular (83°) to the plane of the toluene (see Fig. 3). Such an interaction would be weak since the distance between C42A and the center of benzene ring C8–C14 is 4.3 Å. C42 has the same relationship to the C8–C14 benzene ring of **15** in the neighboring unit cell, so the toluene guest is sandwiched between two molecules of corral **15**.

The solid-state structure of box **17**, which contains a mirror plane perpendicular to benzene rings C1–C3 and C15–C17, is shown in Figure 4. This structure verifies that box **17** is the product of reaction between bisphenol **1** and 1,4-di(bromomethyl)benzene. The structure resembles a slightly rectangular box of dimensions 6.9 by 6.4 Å with a benzene ring on each side of the box. These dimensions are the distances between the centers of the benzene rings on opposite sides of the box with the longer distance between benzene ring C6–C11 and its opposing benzene ring. The dihedral angle between the least-squares planes of these benzene rings is 69°, while the dihedral angle between the least-squares planes of the other pair of benzene rings is 158°.

CIF files for corral **15**·TOL and box **17** have been deposited with the Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge CB2 1E2, UK) with identification numbers CCDC 185207 and CCDC 185208, respectively.

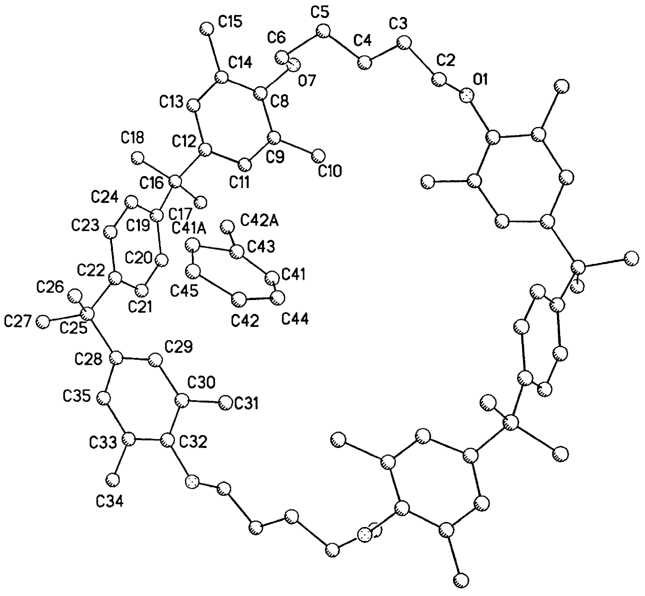


Figure 3. Solid-state structure and numbering scheme for corral **15**·TOL showing one orientation of the disordered toluene.

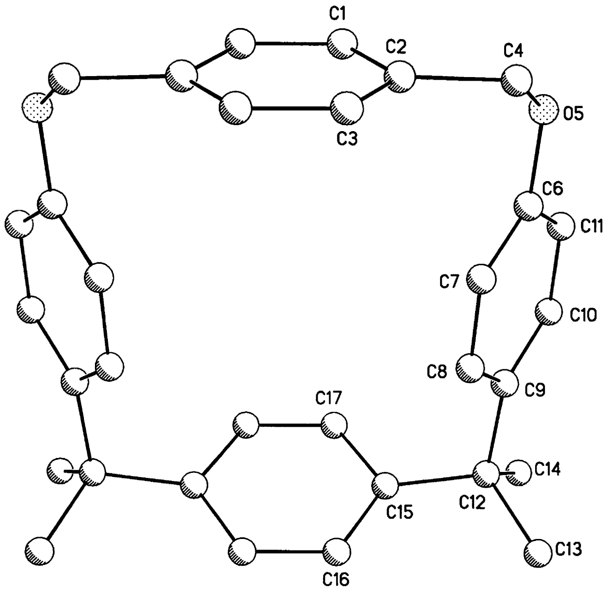


Figure 4. Solid-state structure and numbering scheme for box **17**.

3. Experimental

3.1. General

Melting points were determined with a Fisher–Johns melting point apparatus. NMR spectra were obtained with 200 MHz Varian or Bruker spectrometers. Spectra were taken in $CDCl_3$ and chemical shifts are reported in parts per million (ppm) downfield from TMS.

3.2. Synthesis

Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. Bisphenol **1** and Cs_2CO_3 were obtained from TCI America and Chemetall GMBH (marketed in the USA by CM Chemical Products, Inc. of Berkeley Heights, New Jersey), respectively. Both Cs_2CO_3 and K_2CO_3 were dried overnight in an oven and freshly powdered before use.

THF was distilled from sodium metal with benzophenone ketyl as indicator. Acetone was distilled from and stored over anhydrous K_2CO_3. DMF was distilled from BaO or CaH_2 and stored over 4 Å molecular sieves. DMSO was stored over 4 Å molecular sieves.

3.2.1. Dibromides 7 and 8. A mixture of bisphenol **1** (2.00 g, 5.70 mmol), the 1,ω-dibromoalkane (29.0 mmol), K_2CO_3 (1.57 g, 11.4 mmol), and acetone (50 mL) was refluxed for 5 h and evaporated in vacuo. To the residue, CH_2Cl_2 was added and the mixture was filtered. The filtrate was evaporated in vacuo to provide a pale yellow oil, which was purified by flash chromatography on silica gel with EtOAc–hexanes (3:17) as eluent.

Dibromide 7: obtained in 81% yield as a white solid with mp 69–70 °C. ^1H NMR ($CDCl_3$): δ 1.40–1.45 (m, 12H), 1.62 (s, 12H), 1.75 (m, 4H), 1.85 (m, 4H), 3.40 (t, J=6.8 Hz, 4H), 3.90 (t, J=6.4 Hz, 4H), 6.77 (d, J=6.7 Hz, 4H), 7.08 (s, 4H), 7.12 (d, J=6.7 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 25.9, 28.1, 28.5, 29.2, 30.9, 32.7, 33.9, 41.8, 67.6, 113.7, 126.2, 127.7, 142.7, 147.8, 156.8. Anal. Calcd for $C_{38}H_{52}O_2Br_2$: C, 65.31; H, 7.51. Found: C, 65.24; H, 7.71.

Dibromide 8: obtained in 84% yield as a white solid with mp 59–61 °C. ^1H NMR ($CDCl_3$): δ 1.30–1.40 (m, 16H), 1.66 (s, 12H), 1.75 (m, 4H), 1.85 (m, 4H), 3.40 (t, J=6.8 Hz, 4H), 3.91 (t, J=6.4 Hz, 4H), 6.77 (d, J=6.8 Hz, 4H), 7.09 (s, 4H), 7.13 (d, J=6.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 26.0, 28.1, 28.7, 29.2, 29.3, 30.9, 32.8, 34.0, 41.8, 67.4, 113.7, 126.2, 127.7, 142.7, 147.8, 156.9. Anal. Calcd for $C_{40}H_{56}O_2Br_2$: C, 66.09; H, 7.77. Found: C, 66.41; H, 7.60.

3.2.2. Corral 9. A mixture of bisphenol **1** (124 mg, 0.36 mmol), dibromide **7** (250 mg, 0.36 mmol), K_2CO_3 (149 mg, 1.10 mmol), and acetone (300 mL) was stirred at reflux for 6 days and evaporated in vacuo. To the residue, CH_2Cl_2 (50 mL) was added and the mixture was filtered. The filtrate was washed with 10% HCl (3×25 mL), 1 M NaOH (3×25 mL), and distilled water (25 mL). After drying over $MgSO_4$ and evaporation in vacuo, the resultant white residue was purified by flash chromatography on silica gel with EtOAc–hexanes (3:17) as eluent to provide a white powder (60 mg, 19%) with mp 217–218 °C. ^1H NMR ($CDCl_3$): δ 1.35–1.45 (m, 12H), 1.62 (s, 24H), 1.73 (m, 8H), 3.87 (t, J=6.4 Hz, 8H), 6.75 (d, J=6.7 Hz, 8H), 7.08 (s, 8H), 7.11 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 26.0, 29.1, 29.2, 30.8, 41.8, 67.7, 113.7, 126.2, 127.7, 142.8, 147.8, 156.8. Anal. Calcd for $C_{66}H_{84}O_4\cdot EtOAc$: C, 81.44; H, 8.70. Found: C, 81.80; H, 9.13.

3.2.3. Corral 10. A mixture of bisphenol **1** (475 mg, 1.40 mmol), dibromide **8** (1.00 g, 1.40 mmol), K_2CO_3 (0.40 g, 2.80 mmol), and acetone (600 mL) was stirred at reflux for 9 days. The workup was identical to that given above for corral **9**. A white powder (195 mg, 14%) with mp 187–191 °C was obtained. ^1H NMR ($CDCl_3$): δ 1.30–1.40 (m, 16H), 1.62 (s, 24H), 1.73 (m, 8H), 3.90 (t, J=6.4 Hz, 8H), 6.75, (d, J=8.9 Hz, 8H), 7.08 (s, 8H), 7.11 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 25.8, 29.2, 30.8 (predicted to be two peaks by calculation), 41.8, 67.7, 113.7, 126.2, 127.7, 142.7, 147.8, 156.8. Anal. Calcd for $C_{64}H_{80}O_4\cdot 0.1EtOAc$: C, 83.94; H, 8.85. Found: C, 83.63; H, 8.75.

3.2.4. Bisphenol 11. A 500-mL, 3-necked flask was charged with α,α,α′,α′-tetramethyl-1,4-benzenedimethanol (50.0 g, 0.26 mol) and 2,6-dimethylphenol (317.2 g, 2.6 mol). The reaction vessel was fitted with a mechanical stirrer and heated to 80 °C. Upon melting of the reactants, stirring was initiated and HCl gas was bubbled directly into the reaction mixture through a 1/4-inch glass tube. (The HCl gas was generated by slowly dripping concentrated HCl into concentrated H_2SO_4.) The reaction mixture was saturated with HCl for 30 min at which point HCl introduction was terminated. Stirring at 80 °C was continued for 3 h and the mixture was poured into water (500 mL). Repeated washing of the crude oil with water gave a light brown solid. Recrystallization of the solid from EtOH gave **11** (76.0 g, 73%) as very large prisms. ^1H NMR ($CDCl_3$): δ 1.62 (s, 12H), 2.19 (s, 12H), 4.46 (s, 2H), 6.83 (s, 4H), 7.11 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 16.1, 30.8, 41.6, 122.2, 126.1, 126.9, 142.4, 147.8, 149.9. Anal. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.79; H, 8.50.

3.2.5. Dibromides 12 and 13. A mixture of bisphenol **1** (10.00 g, 29 mmol), the 1,ω-dibromoalkane (0.20 mol), freshly ground K_2CO_3 (20 g), acetone (20 mL), and water (8 mL) was refluxed for 48 h and evaporated in vacuo. To the residue, CH_2Cl_2 and water were added. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated in vacuo. Chromatography of the residue on silica gel first with hexane to remove the residual 1,ω-dibromoalkane and then with CH_2Cl_2 gave the product.

Dibromide 12: obtained 59% yield of white solid with mp 152–154 °C. ^1H NMR ($CDCl_3$): δ 1.62 (s, 12H), 1.90–2.20 (m, 8H), 2.20 (s, 12H), 3.51 (t, J=6.4 Hz, 4H), 3.76 (t, J=6.6 Hz, 4H), 6.83 (s, 4H), 7.09 (s, 4H). Anal. Calcd for $C_{36}H_{48}O_2Br_2$: C, 64.29; H, 7.19. Found: C, 64.35; H, 7.35.

Dibromide 13: obtained 44% yield of white solid with mp 131–134 °C. ^1H NMR ($CDCl_3$): δ 1.62 (s, 12H), 1.60–2.00 (m, 12H), 2.21 (s, 12H), 3.45 (t, J=6.3 Hz, 4H), 3.74 (t, J=6.7 Hz, 4H), 6.83 (s, 4H), 7.09 (s, 4H). Anal. Calcd for $C_{38}H_{52}O_2Br_2$: C, 65.12; H, 7.48. Found: C, 65.17; H, 7.47.

3.2.6. Corrals 14 and 15. A mixture of bisphenol **11** (1.00 mmol), dibromide **12** or **13** (1.00 mmol), Cs_2CO_3 (2.15 g), and DMF (400 mL) was stirred at 50–70 °C for 6 days. The solvent was evaporated in vacuo and CH_2Cl_2 and water were added to the residue. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2–hexane (1:1) as eluent.

*Corral **14***: obtained in 31% yield as a white solid with mp>260 °C. ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 24H), 1.80–2.00 (m, 8H), 2.18 and 2.20 (overlapped s, 24H), 3.82 (m, 8H), 6.75 and 6.82 (overlapped s, 8H), 7.11 (s, 8H). Anal. Calcd for $C_{64}H_{80}O_4$: C, 84.16; H, 8.83. Found: C, 84.15; H, 8.90.

*Corral **15***: obtained in 62% yield as a white solid with mp 278–280 °C. ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 24H), 1.60–1.90 (m, 12H), 2.19 (s, 24H), 3.74 (t, J=6.5 Hz, 8H), 6.80 (s, 8H), 7.09 (s, 8H). ^{13}C NMR ($CDCl_3$): δ 16.4, 23.1, 30.3, 30.9, 41.8, 71.9, 126.2, 127.2, 129.8, 145.7, 147.8, 153.6. Anal. Calcd for $C_{66}H_{84}O_4$: C, 84.21; H, 8.98. Found: C, 83.88; H, 8.97.

3.2.7. Unsymmetrical corral 16. Using the same procedure as for the synthesis of corral **15**, except with bisphenol **1** in place of bisphenol **11**, corral **16** was obtained in 24% yield as a white solid with mp 210–215 °C. ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 24H), 1.50–1.90 (m, 12H), 2.18 (s, 12H), 3.73 (t, J=6.5 Hz, 4H), 3.93 (t, J=6.5 Hz, 4H), 6.78 (s, 4H), 6.76 (d, J=8.6 Hz, 4H), 7.09 (d, J=8.6 Hz, 4H), 7.10 (s, 8H). Anal. Calcd for $C_{62}H_{76}O_4$: C, 84.12; H, 8.65. Found: C, 84.12; H, 8.61.

3.2.8. Boxes 17–19. A solution of bisphenol **1** (3.46 g, 10.0 mmol) and the appropriate di(bromomethyl)benzene (2.64 g, 10.0 mmol) in DMSO (75 mL) was added dropwise over a 30-min period to a stirred suspension of Cs_2CO_3 (3.48 g, 10.7 mmol) in DMSO (80 mL) at 60 °C. The mixture was heated at this temperature for 48 h. The solvent was evaporated in vacuo and the residue was partitioned between $CHCl_3$ and water. The organic layer was separated, washed three times with water, and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by column chromatography.

*Box **17***: chromatography on alumina with $CHCl_3$ as eluent afforded crystalline box **17** in 4% yield with mp 269–271 °C. ^{1}H NMR ($CDCl_3$): δ 1.66 (s, 12H), 5.14 (s, 4H), 6.48 (d, J=8.6 Hz, 4H), 6.79 (d, J=8.9 Hz, 4H), 6.87 (s, 4H), 7.13 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 30.3, 43.0, 71.2, 116.8, 127.648, 128.658, 129.1, 139.0, 145.6, 150.2, 156.8. Anal. Calcd for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19. Found: C, 85.53; H, 7.32.

*Box **18***: chromatography on silica gel with $CHCl_3$–hexane (3:2) as eluent gave box **18** in 3% yield as an amorphous solid with mp 281–283 °C. ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 12H), 5.10 (s, 4H), 6.87 (d, J=8.8 Hz, 4H), 7.11 (s, 4H), 7.15 (d, J=8.8 Hz, 4H), 7.32–7.57 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 32.72, 43.72, 69.87, 116.12, 128.28, 129.86, 130.5, 131.1, 137.5, 145.5, 149.9, 158.6. Anal. Calcd for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19. Found: C, 85.59; H, 7.25.

*Box **19***: chromatography on silica gel with $CHCl_3$–hexane (3:2) as eluent produced box **19** in 5% yield as a foam. ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 12H), 5.04 (s, 4H), 6.86 (d, J=8.5 Hz, 4H), 7.11 (s, 4H), 7.13 (d, J=8.8 Hz, 4H), 7.38 (s, 4H), 7.49 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 32.6, 43.7, 71.7, 116.2, 128.3, 129.0, 129.8, 130.8, 139.7, 145.4, 149.9, 158.7. Anal. Calcd for $C_{32}H_{32}O_2\cdot 0.25CHCl_3$: C, 80.96; H, 6.79. Found: C, 80.82; H, 6.81.

3.3. Solid-state structure determination for corral 15 and box 17

Suitable crystals for structure determinations of **15** and **17** were obtained by crystallization from toluene and by slow diffusion of petroleum ether vapors into an EtOAc solution, respectively. Crystal and intensity data for the structural studies were obtained with a Siemens R3m/V automated diffractometer, which utilized graphite monochromated Mo Kα radiation. The structures were solved and initially refined using programs contained in the SHELXTL PLUS® program package.[13] Final refinement and the display of structures was accomplished using the SHELXTL PC® program package.[14] The crystal data and experimental details are listed in Table 1. The solution of **15** showed that the crystal structure included a disordered toluene molecule.

All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms bonded to carbon atoms were calculated with the exception of those bonded to the disordered toluene guest in **15**·TOL. Because of the disorder of the guest, no attempt was made to locate those hydrogen atoms. All hydrogen atoms were allowed to ride on their neighboring atoms during the refinement process. Molecule **15** and the solvent toluene molecule lie on separate inversion centers with the toluene molecule being disordered in order to contain a center of symmetry. Compound **17** contains a mirror plane that is perpendicular to and bisects the central benzene ring of the unit derived from bisphenol **1**.

Table 1. Crystallographic data for corral **15**·TOL and box **17**

	15·TOL	**17**
Formula	$C_{66}H_{84}O_4\cdot C_7H_8$	$C_{32}H_{32}O_2$
FW (g mol^{-1})	1033.47	448.58
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnma*
a (Å)	6.379(2)	18.849(10)
b (Å)	15.429(8)	20.884(11)
c (Å)	16.936(6)	6.489(3)
α (°)	110.83(3)	90
β (°)	93.76(3)	90
γ (°)	96.60(3)	90
Volume (Å^3)	1538.4(1.1)	2554.5(2.2)
Z	1	4
$m\mu$ (mm^{-1})	0.067	0.071
F(000)	562	960
Crystal size (mm)	0.5×0.4×0.4	0.50×0.14×0.12
$2\theta_{max}$ (°)	45.0	45.0
Reflections collected	4029	1721
Reflections observed	2093	846
Number of parameters	391	161
Goodness-of-fit on F^2	1.064	1.043
R ($I>2\sigma(I)$)	0.0937	0.0561
Largest difference peak and hole (eÅ^3)	0.303, −0.233	0.157, −0.144

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