



Synthesis of New Cyclophane Host Molecules and Crystal Structures of Their Compounds with Hydrocarbon Guests

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Abstract

Three new cyclophane host molecules **2**, **4**, and **6** are prepared by connecting the oxygen atoms of two α , α' -di(4-hydroxyphenyl)-1,4-diisopropylbenzene units with two di-, tetra-, and hexamethylene spacers, respectively. Solid-state structures are determined for host **2** with a hexane guest, host **4** with a toluene guest and a solvating toluene molecule, host **4** with a *p*-xylene guest, and host **6** with two *p*-xylene guests.

Introduction

In the design and synthesis of new receptors for complexation of molecular species, cyclophanes play an important role [1, 2]. Guest species are complexed within the central cavities of these macrocyclic receptors. To provide a new family of cyclophanes, we are using the relatively unexplored bisphenol **1** [3] as a π -electron rich, hydrophobic unit for the construction of hosts **2–6**. Rigidity of the two α , α' -di(4-oxyphenyl)-1,4-diisopropylbenzene units should provide open structures in which the dimensions of the central cavity can be systematically varied by changing the number of carbons in the multi-methylene spacers. Complexation of aromatic guests within their central cavities should be facilitated by π -interactions with the host molecules. Since it is envisioned that the aromatic guest would be contained within a walled enclosure, the cyclophane hosts **2–6** are termed “corrals”.

Recently, we described the synthesis of cyclophane host **3** and the solid-state structure for the complex of this corral with a *p*-xylene guest [4]. In this structure, the *p*-xylene guest was encapsulated within the central cavity of the host. We also reported the structure of **3** that contained a disordered dichloromethane solvent molecule. The conformations of **3** in the two structures were nearly identical, which demonstrates the rigidity of this small corral.

Very recently, we have reported the preparation of cyclophane host **5** and the solid-state structure for the complex of this corral with anthracene [5]. Unexpectedly, the planes of

the host and encapsulated guest were nearly coplanar in the complex.

We now report the synthesis of cyclophanes **2**, **4**, and **6** and additional structures of this host molecule series with hydrocarbon guests: **2**-hexane (**2-HEX**); **4**-toluene₂ (**4-2TOL**); **4**-*p*-xylene (**4-XYL**); and **6**-(*p*-xylene)₂ (**6-2XYL**).

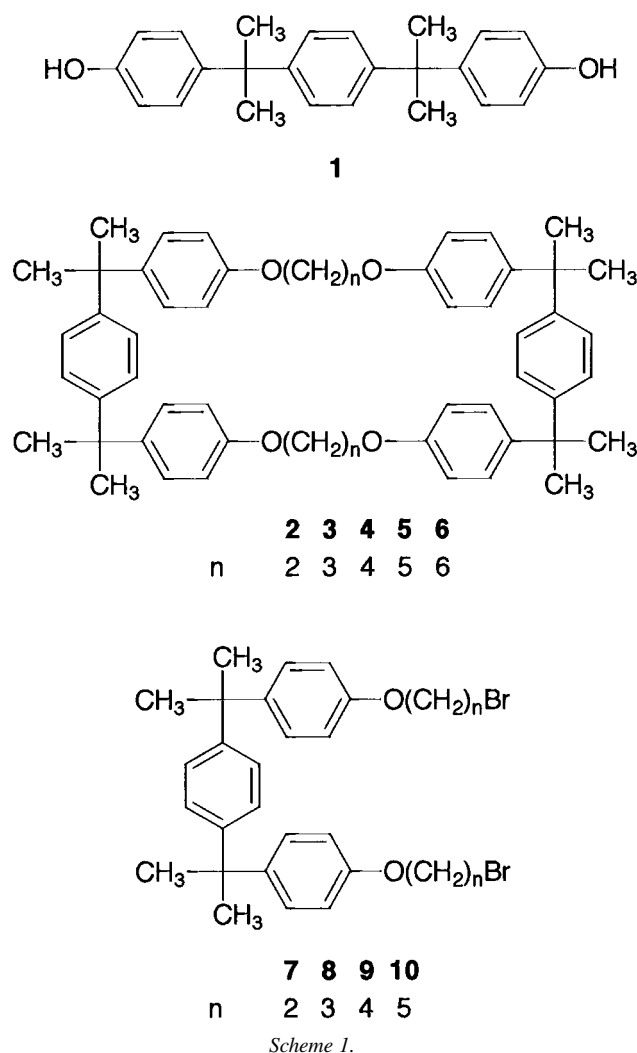
Experimental

IR spectra were taken as potassium bromide pellets with a Perkin Elmer Model 1600 infrared spectrophotometer. ¹H NMR spectra were recorded with an IBM AF-200 spectrometer and chemical shifts are reported in parts per million (δ) downfield from TMS. Combustion analysis was performed by Desert Analytics Laboratory of Tucson, Arizona.

All X-ray data were obtained using a Siemens R3m/V automated diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). All structures were solved using the direct methods program contained in the SHELXTL-PLUS program package [6]. Final refinement and display of the structures were performed using the SHELXTL-PC program package [7]. Crystal data and experimental details for the four structures are contained in Tables 1 and 2. The solid-state structures and atom-numbering schemes for **2-HEX**, **4-2TOL**, **4-XYL** (two conformations), and **6-2XYL** are displayed in Figures 1–5, respectively. The guest of **2-HEX** and the toluene solvent molecule in **4-2TOL** are omitted from the figures. Positions of the hydrogen atoms bonded to carbon atoms were calculated or located in difference maps with exception of the hydrogen atoms of the disordered hexane molecule in **2-HEX** and the disordered toluene solvent molecule in **4-2TOL**. The hydrogen atoms were allowed to ride on their neighboring carbon atoms during refinement.

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Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1E2, UK) [8].

Materials

Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. Bisphenol **1** and cesium carbonate were obtained from TCI America and Chemetall GMBH (marketed in the USA by CM Chemical Products, Inc. of Berkeley Heights, New Jersey), respectively. DMF was distilled from calcium hydride.

Synthesis of hosts **2**, **4**, and **6**

Preparation of intermediates **7**–**10**

Method A

A mixture of bisphenol **1** (5.0 mmol), the 1, ω -dibromoalkane (0.10 mol), and 5.0 g of freshly ground potassium carbonate in 50 mL of DMF was stirred at room temperature for 12–15 hours and the mixture was filtered. The filtrate was evaporated to dryness *in vacuo* and the residue was dissolved in dichloromethane. The dichloromethane

Table 1. Crystal data and experimental details for **2**-HEX and **6**-2XYL

	2 -HEX	6 -2XYL
Formula	C ₅₂ H ₅₆ O ₄ ·C ₆ H ₁₄	C ₆₀ H ₇₂ O ₄ ·2C ₈ H ₁₀
Formula weight	831.28	1069.50
F(000)	1800	580
Crystal size, mm	0.50 × 0.34 × 0.10	0.50 × 0.20 × 0.12
μ , mm ⁻¹	0.07	0.07
Temperature, °C	20	20
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P $\bar{1}$
a, Å	22.821(8)	6.620(4)
b, Å	6.363(2)	11.391(4)
c, Å	34.160(8)	21.842(13)
α , °	90.00	83.56(4)
β , °	100.68(2)	82.77(4)
γ , °	90.00	78.95(4)
V, Å ³	4874	1597
Z	4	1
ρ , kg/m ³	1.133	1.112
Max 2 θ , °	45	45
Total data	3279	4637
Unique data	3182 ($R_{\text{int}} = 2.46\%$)	4196 ($R_{\text{int}} = 2.22\%$)
R	8.53%	5.57%
R_w	19.22%	12.95%
Goodness of fit	1.046	1.029
Largest peak, $\Delta\mu_{\text{map}}$, eÅ ⁻³	0.418	0.153
Largest hole, $\Delta\mu_{\text{map}}$, eÅ ⁻³	-0.27	-0.16
Extinction coefficient	0.0002(4)	0.006(2)

solution was washed with water twice, dried over magnesium sulfate, and evaporated *in vacuo*. Chromatography of the residue on silica gel with hexane-dichloromethane (1:1) as eluent gave a white solid.

Method B

A mixture of bisphenol **1** (29 mmol), the 1, ω -dibromoalkane (0.20 mol), 20 g of freshly ground potassium carbonate, 20 mL of acetone, and 8 mL of water was stirred at reflux for 48 hours and the mixture was evaporated to dryness *in vacuo*. To the residue, dichloromethane and water were added. The dichloromethane layer was separated, washed with water, dried over magnesium sulfate, and evaporated *in vacuo*. Chromatography of the residue on silica gel first with hexane to remove the residual unreacted 1, ω -dibromoalkane and then with dichloromethane gave a white solid.

Dibromide **7** with mp = 102–104 °C was obtained in 43% yield by Method B. ¹H NMR (CDCl₃) δ 1.62 (s, 12H), 3.60 (t, 4H, J = 6.3 Hz), 4.35 (t, 4H, J = 6.3 Hz), 6.79, 7.10 (dd, J = 8.8 Hz), 7.08 (s, 4H). *Anal. Calcd* for C₂₈H₃₂O₂Br₂: C, 60.01; H, 5.75. *Found*: C, 60.26; H, 5.69.

Dibromide **8** [4] was obtained in 49% yield by Method A and in 79% yield by Method B.

Dibromide **9** with mp = 105–107 °C was obtained in 92% yield by Method A. ¹H NMR (CDCl₃) δ 1.62 (s, 12H), 1.90–2.10 (m, 8H), 3.47 (t, 4H, J = 6.5 Hz), 3.96 (t, 4H, J = 5.7

Table 2. Crystal data and experimental details for 4-HEX and 4-XYL

	4-2TOL	4-XYL
Formula	C ₅₆ H ₆₄ O ₄ ·C ₇ H ₈	C ₅₆ H ₆₄ O ₄ ·2C ₈ H ₁₀
Formula weight	985.34	907.23
F(000)	532	490
Crystal size, mm	0.45 × 0.20 × 0.30	0.38 × 0.20 × 0.09
μ , mm ⁻¹	0.07	0.07
Temperature, °C	20	-150
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
a, Å	11.505(2)	5.813(5)
b, Å	11.872(2)	12.127(4)
c, Å	13.018(2)	18.469(4)
α , °	107.37(1)	95.52(8)
β , °	115.92(1)	90.95(7)
γ , °	95.72(1)	97.02(8)
V, Å ³	1470	1286
Z	1	1
ρ , kg/m ³	1.133	1.172
Max 2 θ , °	50	45
Total data	5337	3780
Unique data	5032 ($R_{\text{int}} = 2.14\%$)	3381 ($R_{\text{int}} = 3.95\%$)
R	6.30%	6.83%
R_w	14.41%	13.38%
Goodness of fit	1.053	1.052
Largest peak, $\Delta\mu_{\text{map}}$, eÅ ⁻³	0.210	0.236
Largest hole, $\Delta\mu_{\text{map}}$, eÅ ⁻³	-0.180	-0.295
Extinction coefficient	0.012(3)	0.013(3)

Hz), 6.77, 7.13 (dd, 8H, J = 8.4 Hz), 7.09 (s, 4H). *Anal. Calcd* for C₃₂H₄₀O₂Br₂: C, 62.40; H, 6.54. *Found*: C, 62.68; H, 6.77.

Dibromide **10** with mp = 83–85 °C was obtained in 79% yield by Method B. ¹H NMR (CDCl₃) δ 1.63 (s, 12H), 1.45–1.95 (m, 16H), 3.41 (t, 4H), 3.92 (t, 4H), 6.78, 7.13 (dd, 8H, J = 8.8 Hz), 7.09 (s, 4H). *Anal. Calcd* for C₃₆H₄₈O₂Br₂: C, 64.29; H, 7.19. *Found*: C, 64.11; H, 7.17.

Preparation of cyclophanes **2**, **4**, and **6**

A mixture of the appropriate dibromide (1.00 mmol), bisphenol **1** (1.00 mmol), cesium carbonate (2.15 g), and DMF (400 mL) was stirred at 50–70 °C for 5–7 days under nitrogen. The solvent was removed in vacuo and dichloromethane and water were added to the residue. The dichloromethane layer was separated, washed with water, dried over magnesium sulfate, and evaporated *in vacuo*. Chromatography of the residue on silica gel with hexane-dichloromethane (1:1) as eluent gave a white solid.

Host **2** with mp > 260 °C was obtained in 50% yield. ¹H NMR (CDCl₃) δ 1.63 (s, 24H), 4.24 (s, 8H), 6.76, 7.04 (dd, 16H, J = 8.8 Hz), 7.06 (s, 8H). IR (KBr) 3038, 2970, 2932, 2872, 1609, 1528, 1510, 1474, 1400, 1382, 1362, 1298, 1252, 1225, 1186, 1092, 1024, 932, 832, 731, 592, 558 cm⁻¹. *Anal. Calcd* for C₅₂H₅₆O₄: C, 83.83; H, 7.57. *Found*: C, 83.53; H, 7.36.

Host **4** with mp = 241–245 °C was formed in 30% yield. ¹H NMR (CDCl₃) δ 1.63 (s, 24H), 1.90 (br s, 8H), 3.97 (br s, 8H), 6.74, 7.08 (dd, 16H, J = 8.7 Hz), 7.09 (s, 8H). IR (KBr) 3048, 2966, 2942 (sh), 2931 (sh), 2872, 1607, 1513, 1478, 1396, 1361, 1290, 1249, 1184, 1090, 1055, 1014, 826, 814, 738, 585 cm⁻¹. *Anal. Calcd* for C₅₆H₆₄O₄: C, 83.96; H, 8.05. *Found*: C, 83.77; H, 8.05.

Host **6** with mp = 228–232 °C was obtained in 21% yield. ¹H NMR (CDCl₃) 1.64 (s, 24H), 1.40–1.90 (m, 16H), 3.92 (t, 8H), 6.76, 7.10 (dd, 16H, J = 8.8 Hz), 7.07 (s, 8H). IR (KBr) 3042, 2965, 2944, 2868, 1609, 1579, 1560, 1509, 1474, 1468, 1383, 1360, 1301, 1247, 1183, 1070, 1051, 1016, 935, 829, 732, 596 cm⁻¹. *Anal. Calcd* for C₆₀H₇₂O₄·H₂O: C, 82.33; H, 8.52. *Found*: C, 82.21; H, 8.29.

Preparation of host–guest compounds

Crystallization of **2** from dichloromethane-hexane gave **2-HEX**. Crystallization of **4** from toluene and *p*-xylene gave **4-2TOL** and **4-XYL**, respectively. Crystallization of **6** from *p*-xylene gave **6-2XYL**.

Structure determinations

Three of the four structures (**2-HEX**, **4-2TOL**, and **4-XYL**) contained disorder. The guests of **2-HEX** and **4-2TOL** were disordered; while both the guest and the host of **4-XYL** were disordered. All four of the host molecules contain centers of inversion. The disorder of the guest molecules in **2-HEX** and **4-2TOL** results from the absence of an inversion center in each guest.

Structure of 2-hexane (2-HEX)

It was not expected that **2-HEX** would contain a guest since the cavity of **2** is rather small. However, the direct method solution of **2-HEX** yielded the expected molecule plus several peaks in the cavity of the molecule. These peaks were assumed to be carbon atoms of a disordered solvent hexane molecule. The seven largest peaks were included in the refinement as carbon atoms, six with 0.5 occupancies and the seventh with an occupancy of 0.25. Inclusion of these carbon atoms in the structure reduced the R value by approximately 5%. It was not possible to make chemical sense out of the disordered atoms that were refined isotropically. The heavy atoms of **2** were refined anisotropically. The least-squares plane calculated for the disordered atoms was almost perpendicular (94.5°) to the least-squares plane of the host. None of the disordered atoms of the guest interact with those of the host molecule.

Structure of 4-toluene₂ (4-2TOL)

The structure of **4-TOL** contained a disordered toluene of solvation and a disordered toluene guest. The guest toluene was located about the same center of inversion as the host. To comply with this symmetry, the methyl group of half of the guest molecules point in one direction, while the other half are rotated by 180°. The aromatic rings of the guest are superimposable. This results in a guest that resembles a *p*-xylene molecule. In the refinement, occupancy factors for

the methyl groups were required to have values of 0.50. The disorder of the toluene of solvation, which lies on another inversion center, was resolved using difference maps.

Structure of 4-*p*-xylene (4-XYL)

It was apparent from the direct method solution for 4-XYL that portions of both the host and guest molecules were badly disordered. In an effort to resolve the disorder, single crystal data were collected at 150 ± 3 °K. These data provided good resolution of the host, but only an approximate structure for the guest. In the host molecule, the disorder of atoms O1 and C21 to C30 could be resolved. The disordered atoms C42 and C43 were resolved in the guest, but the bond lengths and angles of the guest indicated that the resolution of the disorder for that molecule was not very good. Occupancies of the disordered atoms in both the guest and the host were approximately 0.5. The resulting two conformations are displayed in Figures 3 and 4. The guest and host contain the same center of inversion.

Structure of 6-(*p*-xylene)₂ (6-2XYL)

The host molecule of 6-2XYL lies about a center of inversion and do not lie on inversion centers. Unlike the two compounds of 4, the two guest molecules are related by that center of inversion. These guest molecules are not contained entirely within the cavity of the host (see Figure 5). Positions for all hydrogen atoms were calculated with the hydrogen atoms riding on neighboring carbon atoms during refinement.

Results and discussion

Synthesis of cyclophanes 2, 4, and 6

The new molecular receptors 2, 4, and 6 were prepared in two steps from commercially available α, α' -di(hydroxyphenyl)-1,4-diisopropylbenzene (1). Reaction of 1 with a large excess of the appropriate 1, ω -dibromoalkane and potassium carbonate in DMF or aqueous acetone gave the intermediate dibromides 7, 9, and 10. Cyclization of equivalent amounts of the dibromide and bisphenol 1 with cesium carbonate in DMF gave 43, 92, and 79% yields of cyclophanes 2, 4, and 6, respectively. Structures of the new cyclophane hosts were verified by NMR and IR spectroscopy and by combustion analysis.

Structure determinations

The four reported solid-state structures consist of molecules containing two rigid α, α' -di(4-oxophenyl)-1,4-diisopropylbenzene units connected by two-, four-, and six-methylene spacers with various hydrocarbon guests. The size and conformation of the cavity is varied by changing the length of the spacers and the guest in the cavity. In an earlier paper [4], we discussed the structures of two three-spacer complexes, one that contained a *p*-xylene guest (3-XYL) and the other with a disordered dichloromethane guest (3-DCM). The aromatic guest fit snugly in the cavity of corral

3, but the dichloromethane did not. Despite the difference of the guest, the conformations of the hosts were nearly identical. This established that the host molecule was rigid. It was expected that corral 2 would also be rigid, but that larger corrals 4 and 6 would be more flexible with significantly different conformations. To compare and describe the conformational features of the corral molecules with increasing spacer length and different guests, three intramolecular distances were calculated and are presented in Table 3. These distances are: O1–O26, a measure of the rigidity of the aromatic portions of the host; C12–C13A, a measure of the cavity length; and, the distance between the approximate middles of the two methylene-group spacers, a measure of the cavity width. Similar data for the two complexes of the previously reported corral 3 are included in Table 3 for comparison.

Rigid corral 2 (Figure 1) contained a disordered guest that was not an aromatic molecule. Since the complex was crystallized from dichloromethane-hexane, it seemed reasonable that the guest was a disordered hexane molecule. (There was no evidence for the presence of a chlorine atom in the guest.) Unfortunately, the disorder of the guest molecule could not be resolved. There did not appear to be any interactions between the guest and host molecule. As in the case of 3-XYL and also in the two complexes of corral 4, the guest and host lie about the same center of inversion. Unlike those complexes, the least-squares planes of the guest is nearly perpendicular to the least-squares plane of the host in 2-HEX. As would be expected, the O1–O26 and C12–C13A distances for 2-HEX are the shortest of all of the molecules listed in Table 3. However, it was surprising that the cavity width of corral 2 is larger than that in corral 6. This feature will be discussed later in the description of 6.

Table 3. Interatomic distances showing the cavity sizes of the corral complexes

Complex	O1–O26 (Å)	C12–C13A (Å)	Width (Å)	
2-HEX	7.90	12.67	C27–C28A ^a	9.38
3-XYL	11.44	10.91	C28–C28A	14.28
3-DCM	10.99	11.10	C28–C28A	13.85
4-2TOL	8.99	14.48	C28–C29A	11.03
4-XYL (I)	10.08	13.07	C28–C29A	10.51
4-XYL (II)	10.12 ^b	13.07	C28'–C29B	11.26
6-2XYL	8.18	16.78	C30–C31A	7.85

^a The letters A or B following an atom name refer to an atom related to the atom named by an inversion center. A prime following an atom name refers to a corresponding disordered atom.

^b The O1'–O26' distance.

The O1–O26 distances in the two complexes of corral 3 are the larger than those in the complexes of 2, 4, and 6. At least for 3-XYL, this can be explained by direction of the methyl groups of the *p*-xylene guest toward the aliphatic spacers of the host. However, a large O1–O26 distance is also noted for 3-DCM, which reveals that with or without a *p*-xylene guest this conformation of 3 is the lowest energy structure. The addition of another methylene group to the spacers for 3 gives increased flexibility and a longer cavity for corral 4. While the guests in 4-2TOL and 4-XYL are

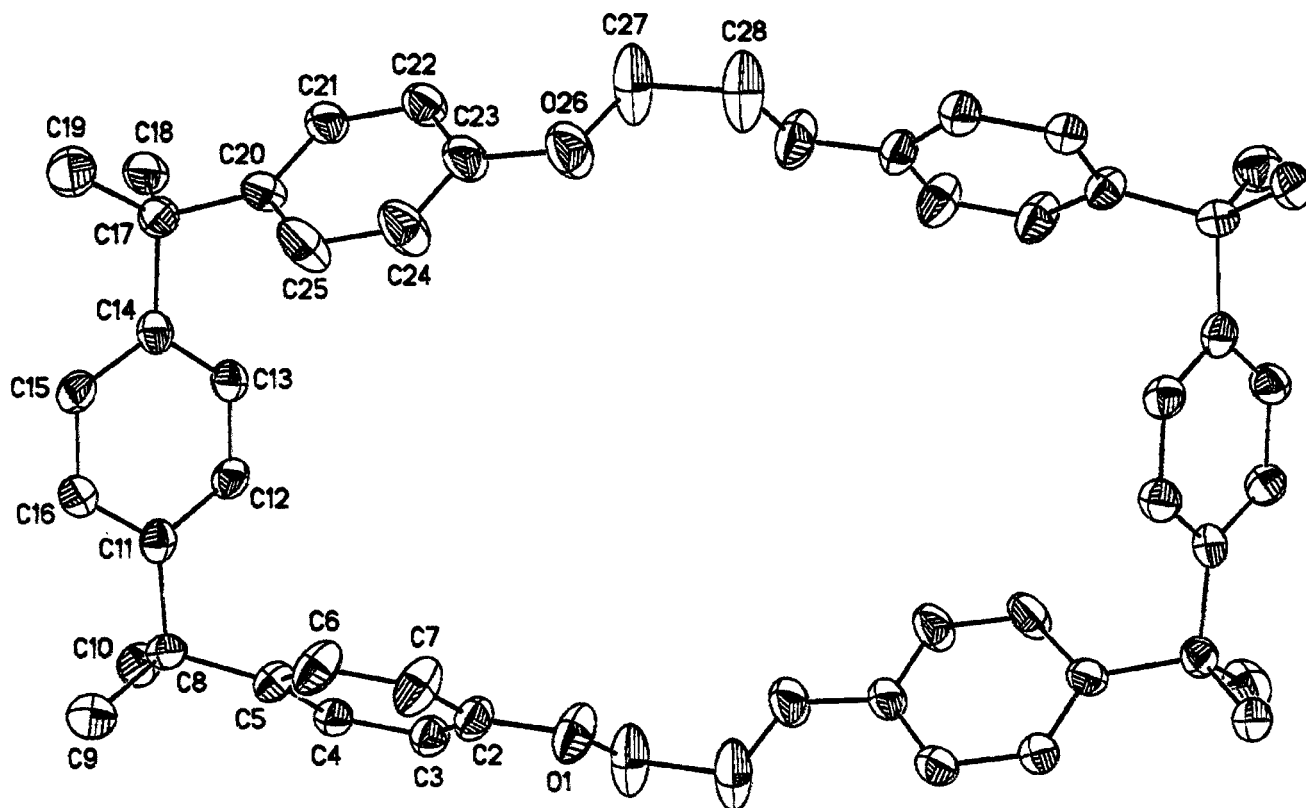


Figure 1. A computer drawing of the crystal structure of 2-HEX with the thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms of the host and the disordered hexane guest are omitted for clarity.

different, disorder of the toluene guest causes it to have the same spatial requirements as *p*-xylene. This is shown in Figures 2–4 and in the space-filling drawings in Figures 6–8. The disorder of both the host and guest in 4-XYL was resolved and conformations I and II are shown in Figures 3 and 4, respectively. It is interesting that in spite of the spatial similarities of the two guests, the disordered methyl groups in 4-TOL point directly toward the middle aromatic rings of the host; whereas the methyl groups in both orientations of 4-XYL point toward the lateral aromatic rings of the host. Such orientation of the methyl groups with respect to the aromatic rings indicates the presence of CH/ π interactions [9, 10].

Since the occupancies of both disordered complexes of 4-XYL were about 0.5, it was difficult to match a guest with a host using intensity data. The major difference between the host orientations in conformations I (Figure 3) and II (Figure 4) is the dihedral angle between aromatic ring C20–C25 and C20'–C25' with the least-squares plane of the host. The dihedral angles show that benzene C20–C25 is nearly perpendicular to the plane of the host in conformation I, while benzene C20'–C25' is nearly parallel to the host in conformation II. This indicates that the cavity width in conformation I is larger than that of conformation II, and suggests that the guest with the larger dihedral angle between it and the least-squares plane of the host would fit in conformation II. The dihedral angles between the host and the guest C40, C41, C42, and C43 and the guest C40, C41, C42', C43' are 9

and 33°, respectively, so the primed guest matches with the primed host.

The structure of 6-2XYL is shown in Figure 5. Unlike the other reported complexes in which the guest and host lie about the same center of inversion, in this complex there are two *p*-xylene guests, one above and the other below the corral molecule, that are related by the center of inversion of the corral. The dihedral angles between each guest and the host corral is 53°. These observations suggest that the guest molecules are not contained in the host and do not interact with 6 or affect its conformation. This conclusion is supported by a width of 6 that is slightly smaller than that of the smallest corral 2. However, one methyl group of each *p*-xylene guest does approach the central benzene ring of the aromatic unit suggesting CH/ π interaction [9, 10].

Even though these host–guest complexes are present in the solid state, preliminary NMR spectral investigation revealed that they do not exist in solution. Although, it is impossible to assess the strength of intermolecular forces from X-ray data, such data provide conformations and interatomic lengths and angles that may suggest the presence of these forces.

The space-filling drawings of 4-TOL, conformations I and II of 4-XYL, and 6-2XYL shown in Figures 6–9, respectively, suggest the presence of intermolecular forces. The space-filling drawings of the complexes of 4 (Figures 6–8) indicate that the guests do interact with the host. In all three figures, the aromatic guests fit snugly in the cavity of the corral molecule. Also, it is significant that in

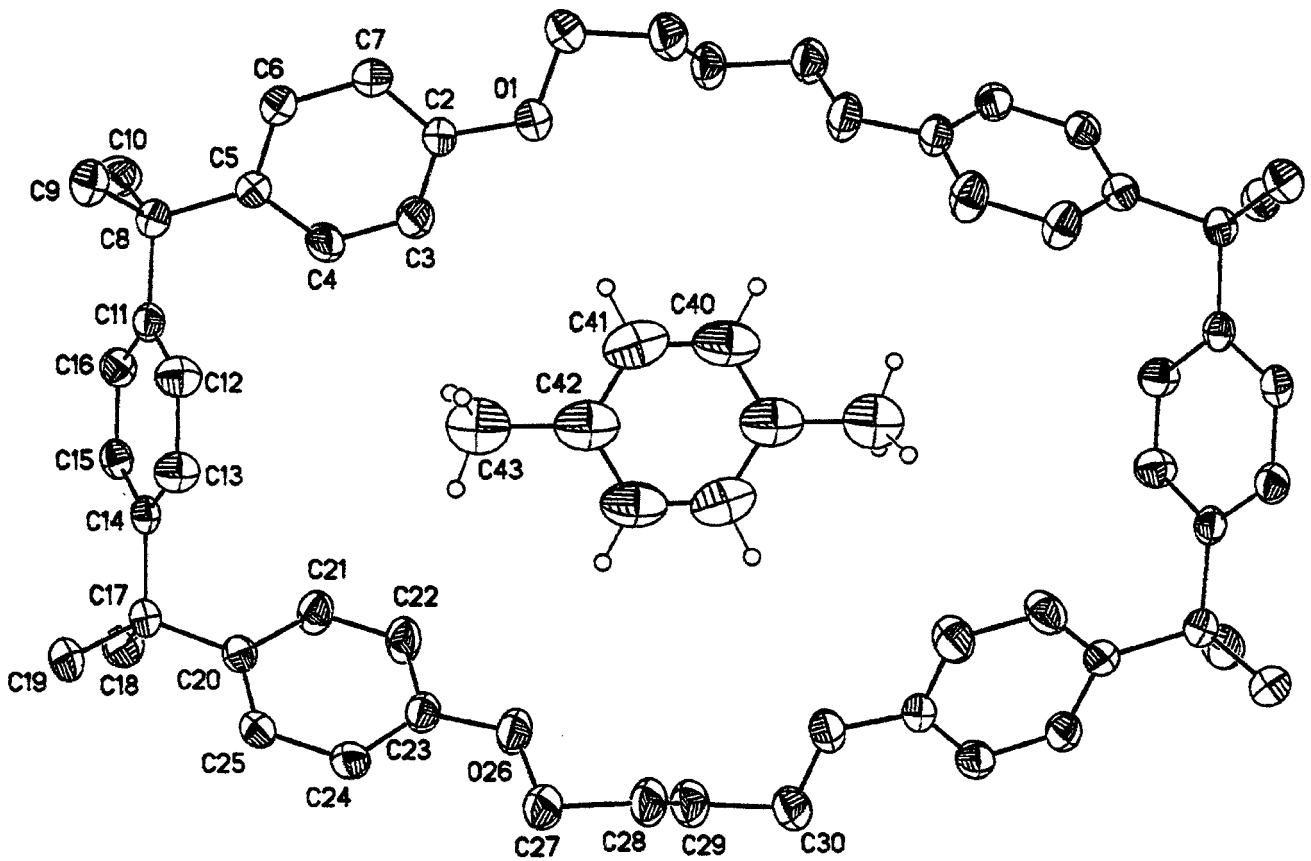


Figure 2. A computer drawing of the crystal structure of 4-2TOL with the thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms of the host and the solvating toluene molecule are omitted for clarity.

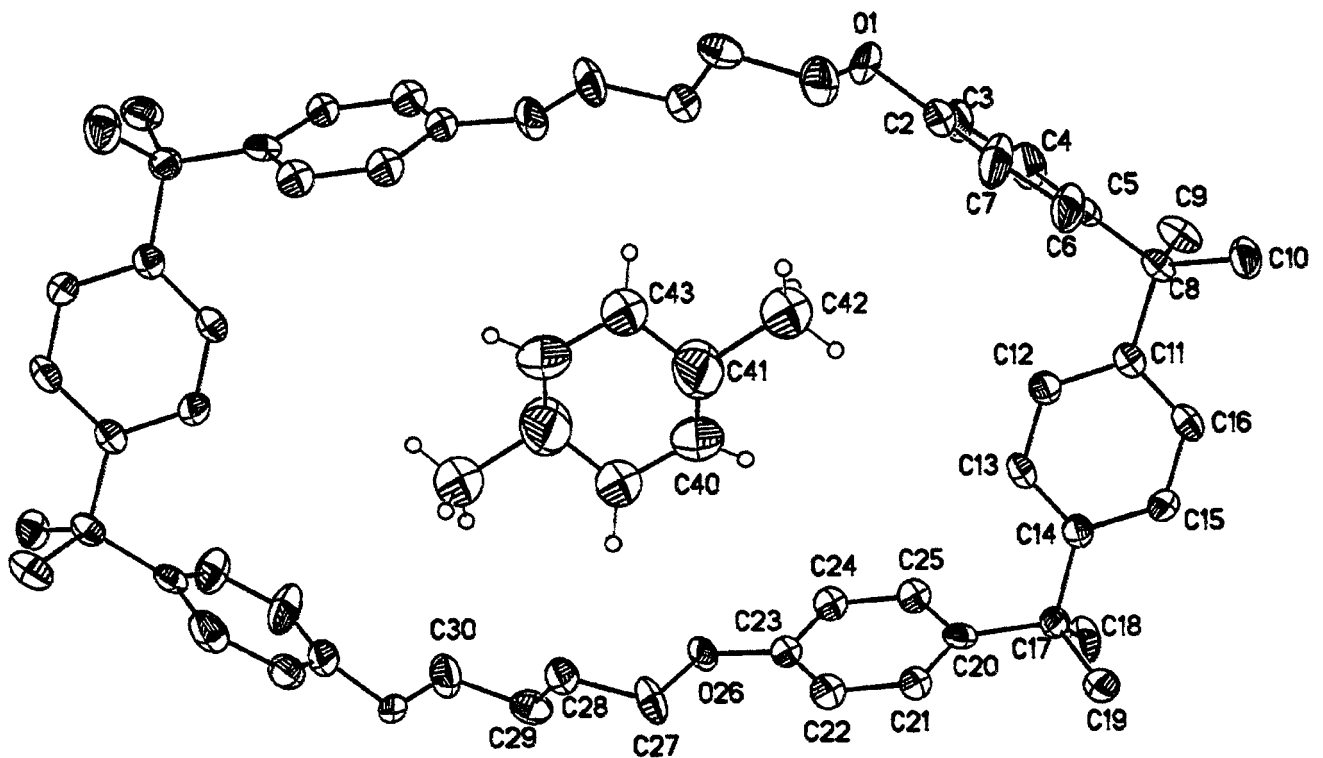


Figure 3. A computer drawing of the crystal structure of 4-XYL (Conformation A) with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms of the host are omitted for clarity.

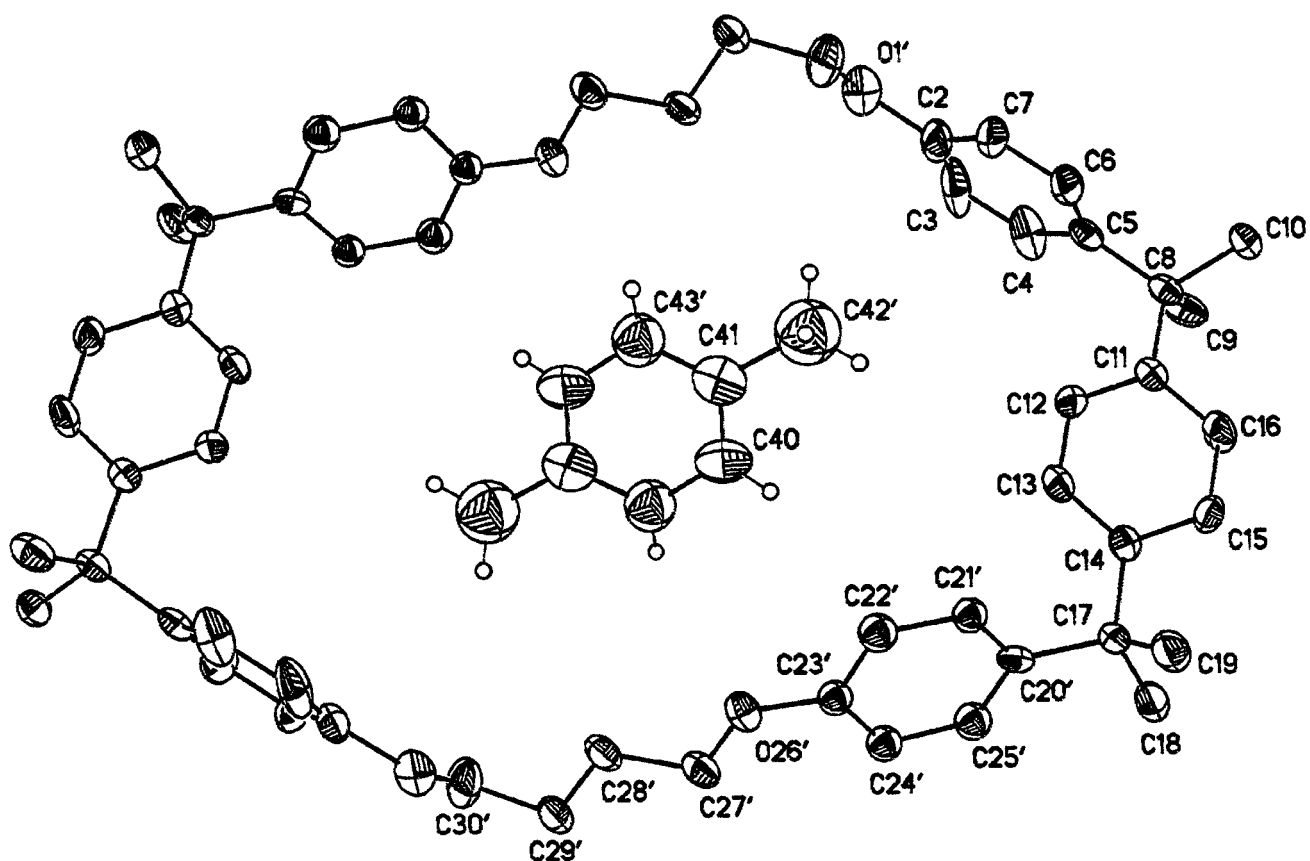


Figure 4. A computer drawing of the crystal structure of 4-XYL (Conformation B) with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms of the host are omitted for clarity.

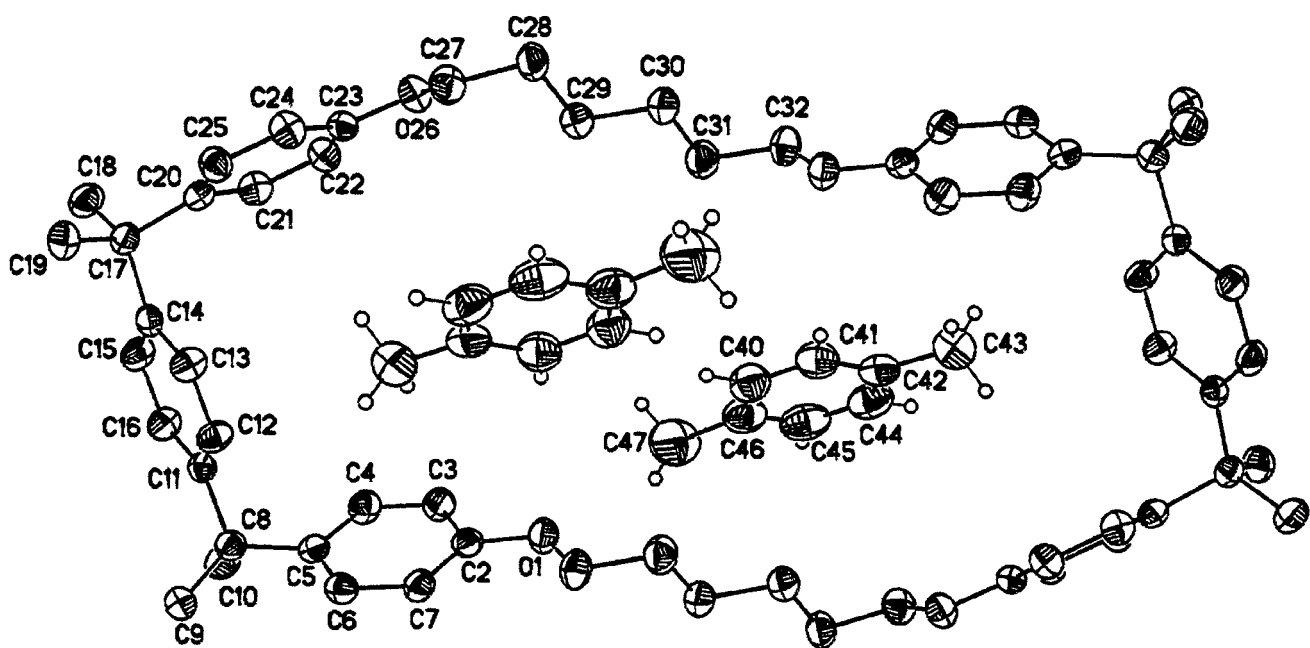


Figure 5. A computer drawing of the crystal structure of 6-2XYL with the thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms of the host are omitted for clarity.

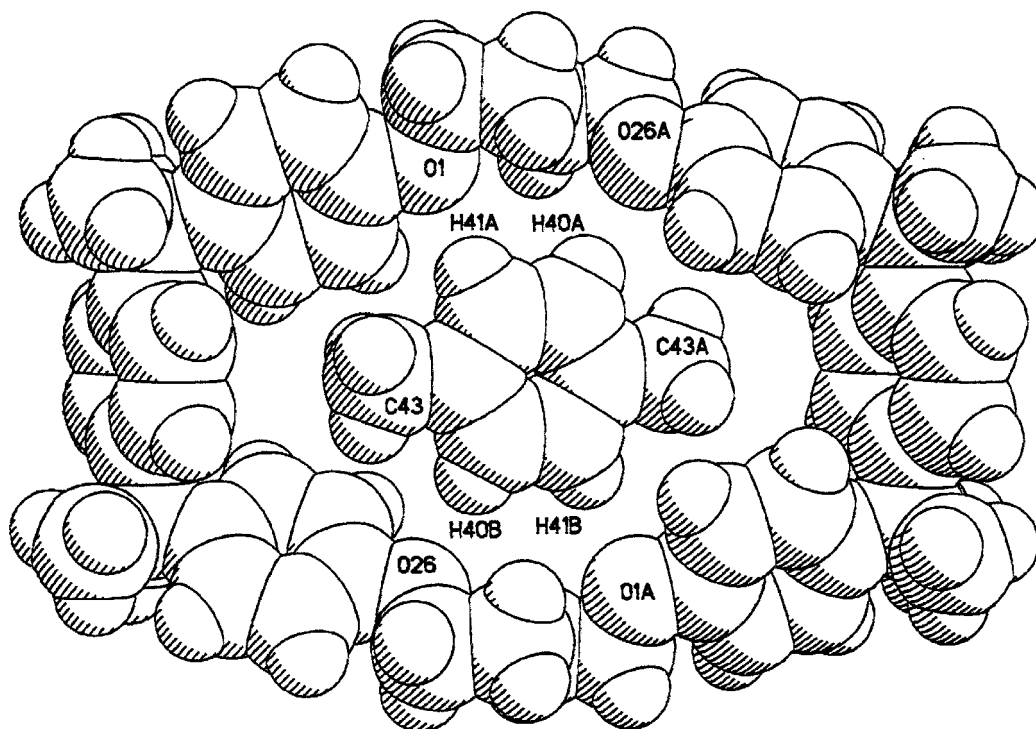


Figure 6. A space-filling model of 4-TOL with the solvating toluene molecule omitted for clarity.

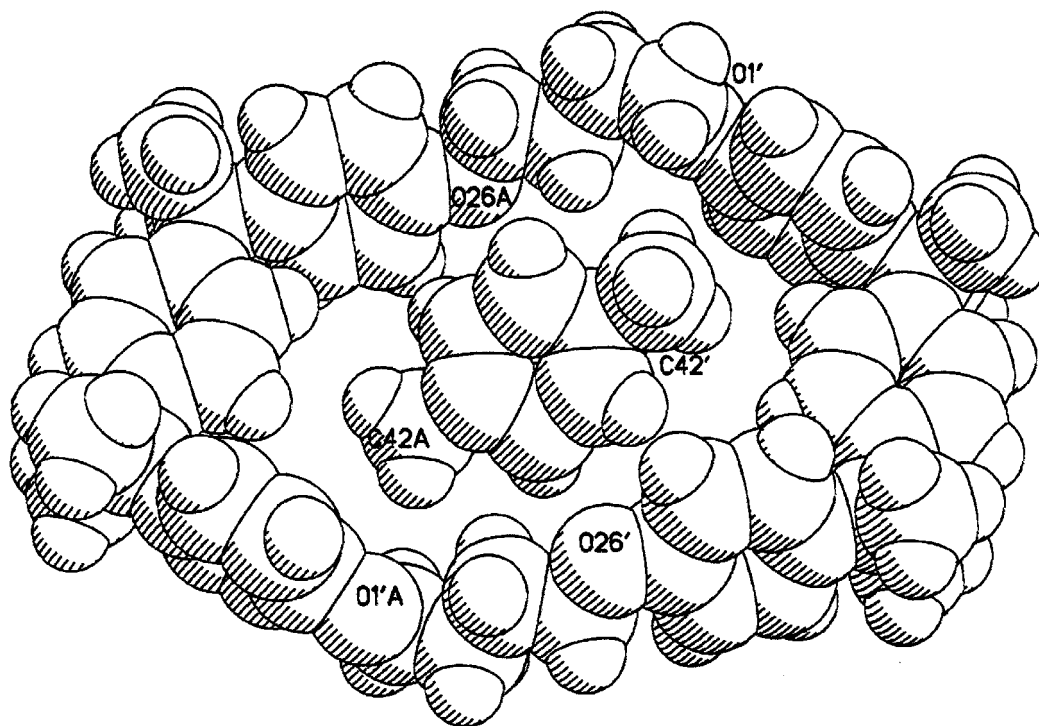


Figure 7. A space-filling model of 4-XYL (Conformation I).

all three complexes a methyl group of the guest points toward benzene rings of the host that are nearly perpendicular to the least-squares planes of the guests and that at least one other benzene ring of the host is close to the methyl group. This not only suggests the presence of packing forces, but also indicates CH/π interactions [9, 10] between the slightly positive hydrogen atoms of the methyl groups and the electron-rich benzene rings. These forces are not strong

since the distances between the hydrogen atoms and the center of the benzene rings are over 3 Å. Surprisingly, one methyl group of each guest molecule in 6-2XYL is also directed towards a benzene ring, even though the guests are not in the cavity (Figure 9).

Another indication of intermolecular attractive forces is present in 4-TOL. Figure 6 suggests that there are polar interactions between H40 and O26', H41 and O1, and their

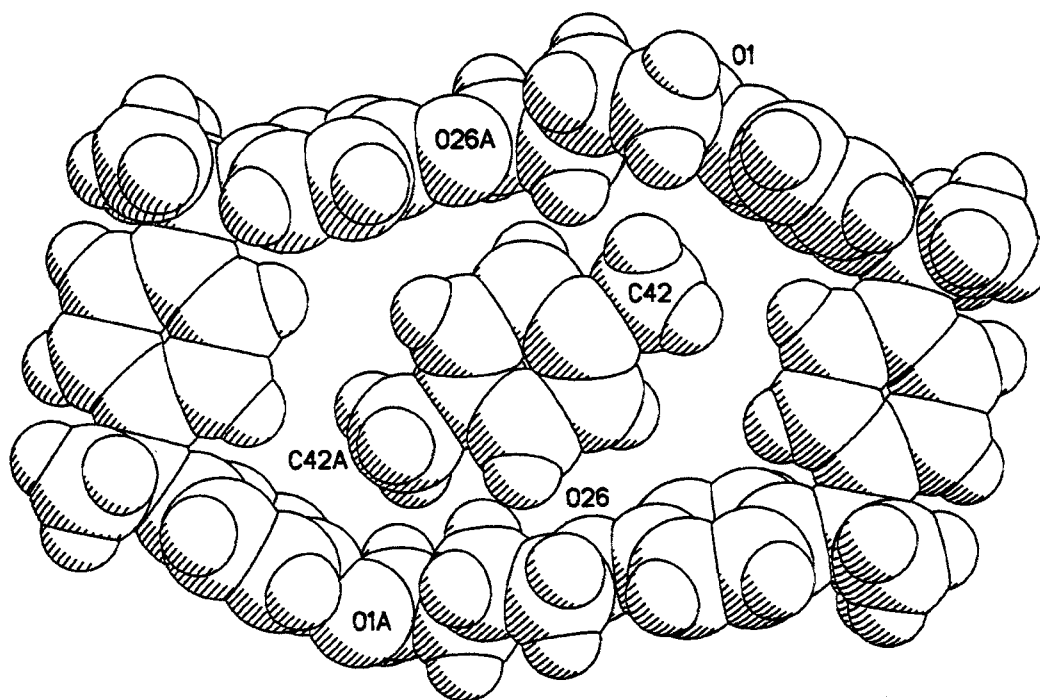


Figure 8. A space-filling model of 4-XYL (Conformation II).

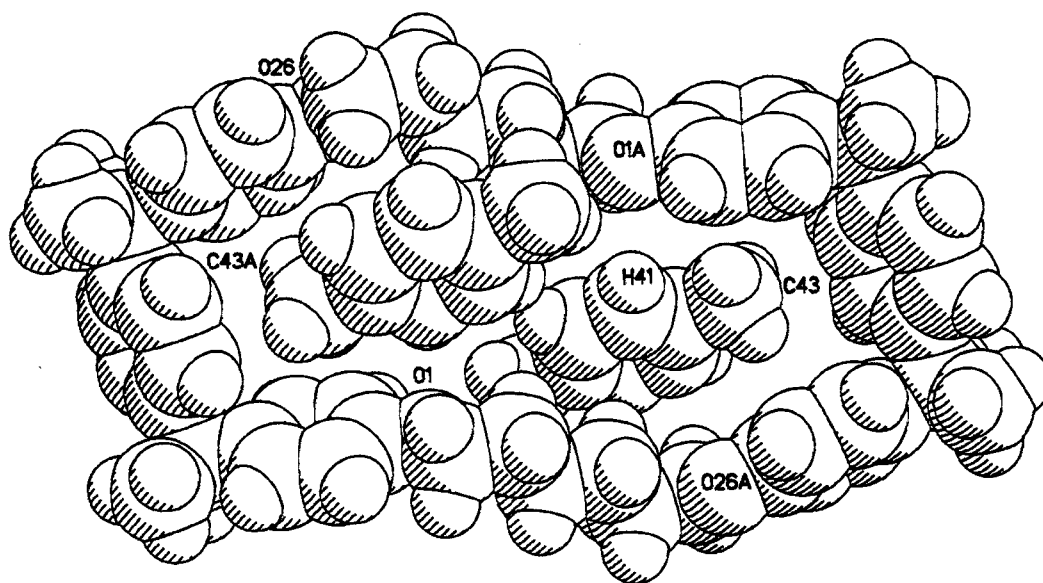


Figure 9. A space-filling model of 6-2XYL.

symmetry equivalents. The interatomic distances between the hydrogen atom of the guest and the oxygen atom of the host are too long for a hydrogen bond ($H41 \cdots O1 = 2.80 \text{ \AA}$ and $H40 \cdots O26' = 2.79 \text{ \AA}$), but the fact that the hydrogen atoms point directly at the oxygen atoms (the $C41-H41-O1$ and $C40-H40-O26'$ bond angles are 152 and 172° , respectively) suggests some attractive forces.

Some other van der Waals forces in 4-XYL are likely, but the disorder of the guest in this structure makes intermolecular distances involving hydrogen atoms uncertain. In 6-2XYL, the major part of the guest is not in the cavity of the corral, so there is no additional information beyond that mentioned above to suggest host-guest interaction.

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References

1. F. Diederich: *Cyclophanes*, Royal Society of Chemistry, Cambridge, UK (1991).
2. F. Vögtle: *Cyclophane Chemistry*, Wiley and Sons, New York, NY, Chapter 12 (1993).
3. G.F. Broderick, B.C. Oxenrider and J. Vitrone: *U.S. Patent 3,393,244*, July 16 (1968).

4. N.K. Dalley, X. Kou, R.A. Bartsch, B. Czech and P. Kus: *J. Inclusion Phenom.* **29**, 323–334 (1997).
5. R.A. Bartsch, P. Kus, N.K. Dalley and X. Kou: *Tetrahedron Lett.* **43**, 5017–5019 (2002).
6. G.M. Sheldrick: SHEXTL-PLUSTM, Siemens Analytical X-ray Instruments, Inc., Madison, WI (1990).
7. G.M. Sheldrick: SHELXTL-PC, version 5.03, Bruker Analytical X-ray Systems, Madison, WI (1994).
8. The deposited structure numbers are: CCDC 182202 for **2-HEX**; CCDC 182203 for **4-2TOL**; CCDC 182204 for **4-XYL**; and CCDC 182205 for **6-XYL**.
9. M. Nishio and M. Hirota: *Tetrahedron* **45**, 7201-7245 (1989).
10. M. Nishio, M. Hirota and Y. Umezawa: *The CH/ π Interaction. Evidence, Nature, and Consequences*, Wiley-VCH, New York, NY (1998).