Host–Guest Complexation. 49. Cavitands Containing Two Binding Cavities[1]

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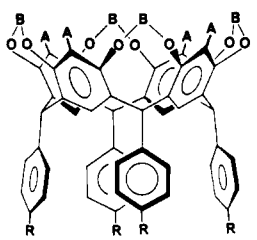
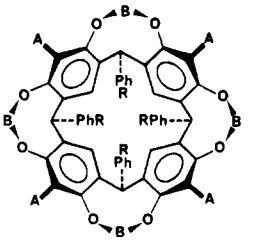
Abstract: Cavitands containing boxlike cavities fused to bowl-like cavities of general structure **1** are reported. They were synthesized from the macrocyclic tetraoligomeric condensation products of 4-RPhCHO and resorcinol. Various combinations of A, B, and R groups were used to control solubility properties and extend the cavities. Bridging groups, B, were either CH_2 or Bu_2Si. Substituents attached to the rim of the bowl-like cavities, A, were H, Br, CO_2CH_3, and CH_2OBu. Substituents attached to the 4-positions of the four phenyl groups defining the sides of the boxlike cavities, R, were H, CH_3, C_2H_5, Br, I, $(CH_3)_3Sn$, and $(CH_3)_3SiC{\equiv}C$. Crystal structures of five caviplexes and one cavitand are reported, all of which possess the box–bowl structures intrinsic to the general structure **1**. The cavitand **1** with A = H, B = $SiBu_2$, and R = $(CH_3)_3Sn$ was free of guest. Cavitand **1** with A = R = H and B = CH_2 crystallized with benzene as guest in stacks, each benzene being half in the box and half in the bowl of two hosts. The same cavitand crystallized from CH_3COCH_3/CH_2Cl_2 provided a caviplex with the $(CH_3)_2CO$ in the bowl and CH_2Cl_2 in the box. Cavitand **1** with A = Br, B = CH_2, and R = CH_3CH_2 crystallized from $CH_3C_6H_5$ gave a caviplex with a $CH_3C_6H_5$ molecule in each of the two kinds of cavities, each $CH_3C_6H_5$ with its methyl facing inward. The same cavitand recrystallized from BrC_6H_5 gave a caviplex isomorphous with that crystallized from $CH_3C_6H_5$. Both bromine atoms face inward. Cavitand **1** with A = CH_3O_2C, B = CH_2, and R = CH_3, when crystallized from CH_3COCH_3, gave a caviplex with one acetone in each kind of cavity. Through ^1H NMR measurements in CCl_4, the binding of CD_3CN by each cavity of **1** with A = $BuOCH_2$, B = CH_2, and R = CH_3CH_2 gave the following thermodynamic parameters: for the bowl, K_a(300 K) = 89 M^{-1}, $\Delta H°$ = −6.2 ± 1.2 kcal mol^{-1}, and $\Delta S°$ = −11.4 ± 4 cal mol^{-1} T^{-1}; for the box, K_a(300 K) = 45 M^{-1}, $\Delta H°$ = −6.4 ± 1.5 kcal mol^{-1}, and $\Delta S°$ = −13.6 ± 5 cal mol^{-1} T^{-1}.

A previous paper in this series[2] describes the preparation and crystal structures of a series of caviplexes based on hosts such as **2–4**. These compounds and others containing CH_3 or Br groups between the oxygens of each resorcinol moiety were too insoluble to carry out binding studies. A different paper[3] reports the synthesis and binding studies between **5–7** and CS_2 in $CDCl_3$, as well as a crystal structure of **5**·CS_2. A third publication describes the ready syntheses of a large number of octols, of which **8–11** (Chart I) are illustrative.[4] The octols were prepared to act as starting materials for the preparation of the new family of cavitands, **1**, containing two fused cavities, one shaped like a box and the other shaped like a bowl.



1 (side view)



1 (face view)

Cavitand systems **1** are particularly attractive for the following reasons. (1) The rims of the bowls can be varied by different choices of substituents A and bridging groups B for shaping the bowl cavity, for manipulating the solubilities of the cavitands, or for introducing potentially cooperating functional groups to act as catalysts. (2) The rims of the box cavity can be independently varied through changes in the R group for shaping the box cavity, for manipulating the solubilities of the cavitands, or for structuring potentially cooperating functional groups to act as catalysts. (3) Compounds **1** are potential starting materials for preparing carcerands (molecular cells).[5] These carcerands can be made in practical quantities from cheap starting materials.

This paper reports the syntheses and characterizations of cavitands **12–30**, six crystal structures, a qualitative survey of the crystalline complexes of **16**, and the binding properties of **26** toward CD_3CN in CCl_4.

Results and Discussion

Synthesis and Characterization. Examination of CPK models of cavitands **16–30** shows that the bowl cavity is derived from four resorcinol units that are rigidly held in place by the four methylene or four silane bridges between the oxygens to provide a 24-membered ring. The bowl is extended and deepened either by the A groups attached at the 2-positions in **16–26** or by the eight butyl groups attached to the silicon bridges in **27–30**.

Four sides of the box cavity are defined by the planes of the four aryl groups attached to the methine carbon originating in the benzaldehyde portion of the cavitands. These four aryl groups are held in their box-forming conformation by nonbonded repulsions between their hydrogens ortho to the methines and the aryls of the resorcinols. The cavity defined by the C_6H_5 or C_6H_4 groups are roughly cubic in shape, and in models they are complementary to a model of ethane. The R groups attached at the 4-positions of the four box aryls extend the depth of the box, and when bulky (i.e., R = $(CH_3)_3Sn$ in **28**), they actually both deepen and close the box.

Octols **8** and **9** were converted by treatment with CH_2ClBr and K_2CO_3 to cavitands **16** and **18** in 5% and 0.9% yields, respectively. These conversions and purifications were greatly hampered by the insolubility of the starting materials, intermediates, and products of the reaction. The physical properties of cavitand **16** are in accord with those expected from its size and shape. It melts at >390 °C, and is most soluble in solvents of moderate polarity and high polarizability (e.g., 1 g dissolves in 35 mL of CH_2Cl_2). Thus it is somewhat soluble in CS_2, CH_2Cl_2, $CHCl_3$, CH_3I, and

(1) We warmly thank the U.S. Public Health Service for Grant No. 12640 and the National Science Foundation for Grant CHE 84-19994, which supported this work. J. A. Tucker is grateful to the W. R. Grace Foundation for a fellowship, 1984–1985.

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(5) Cram, D. J.; Karbach, S.; Kim, Y. H.; Baczynskyj, L.; Marti, K.; Sampson, R. M.; Kalleymeyn, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 2554–2560.

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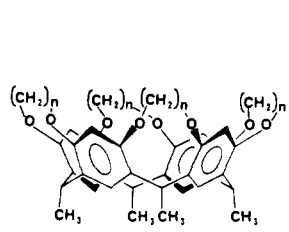
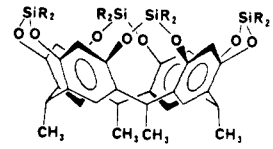
Chart I



2, n = 1

3, n = 2

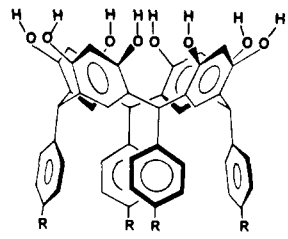
4, n = 3



5, R = CH_3

6, R = CH_3CH_2

7, R_2 = $(CH_2)_4$

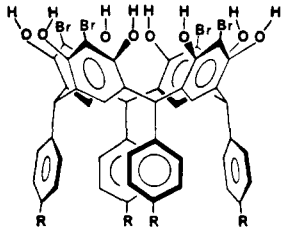


8, R = H

9, R = CH_3

10, R = CH_3CH_2

11, R = Br

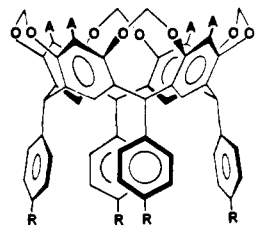


12, R = H

13, R = CH_3

14, R = CH_2CH_3

15, R = Br



16, A = R = H; **17**, A = Br, R = H

18, A = H, R = CH_3

19, A = Br, R = CH_3

20, A = Br, R = CH_2CH_3

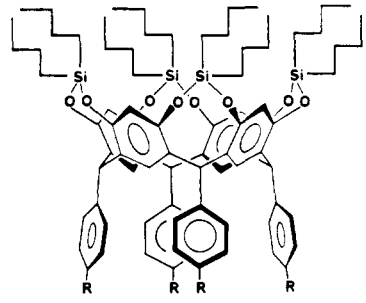
21, A = R = Br; **22**, A = CH_3O_2C, R = H

23, A = CH_3O_2C, R = CH_3

24, A = CH_3O_2C, R = CH_3CH_2

25, A = $CH_3(CH_2)_3OCH_2$, R = H

26, A = $CH_3(CH_2)_3OCH_2$, R = CH_3CH_2



27, R = Br

28, R = $(CH_3)_3Sn$

29, R = I

30, R = $(CH_3)_3SiC{\equiv}C$

$(CH_3)_2S$, is slightly soluble in dioxane, $Cl_2CHCHCl_2$, and pyridine, and is essentially insoluble in C_6H_6, CCl_4, $(CH_2)_6$, $(Cl_3C)_2CO$, $Cl_2C{=}CClCCl{=}CCl_2$, C_6F_6, Et_3N, EtOAc, CH_3CN, $(CH_3)_2SO$, $(CH_3)_2NCHO$, $(CH_3)_2CO$, $(CH_2)_4O$, and Et_2O. In general, **16** is most soluble in those solvents which can effectively solvate the interior surfaces of the two enforced cavities. This generalization also applies to the other cavitands.

Another bulk property exhibited by **16** is its strong tendency to form thermally stable solvates. When a solution of **16** in $CH_2Cl_2/(CH_2)_6$ was allowed to evaporate slowly, the crystalline solvate produced contained 0.75 mol of $(CH_2)_6$ and 0.25 mol of CH_2Cl_2 per mol of host (^1H NMR). The solvent was not removed even after 24 h at 180 °C and 10^{-5} Torr. Replacing the $(CH_2)_6$ in this experiment with EtOAc or C_6H_6 gave one-to-one solvates of **16**, neither of which contained CH_2Cl_2. Crystallization of **16** from CH_2Cl_2 and CH_3CN gave a solvate containing 2 mol of CH_3CN per mol of **16**, and from CH_2Cl_2 and $(CH_3)_2CO$ a mixed solvate containing 1.5 mol of $(CH_3)_2CO$ and 0.5 mol of CH_2Cl_2 per mol of **16** was generated. These results imply that **16** always crystallizes with both of its enforced cavities filled by solvent molecules. Large solvent molecules such as C_6H_6 can be shared by cavities of two molecules to form one-to-one solvates of a polymeric crystalline character. Small solvent molecules such as CH_3CN cannot be shared, and hence form 2:1 guest/host solvates. These ideas find support in the crystal structures of two representative solvates of **16** (vide infra). Although **16** was never freed of solvent (it was analyzed as a EtOAc complex), its mass spectrum gave peaks only for free host, not solvate.

Models of **18** suggest the boxlike cavity to be about 20% deeper than that of **16** and complementary to $CH_3CH_2CH_3$. Although generally less soluble than **16**, **18** showed the same pattern of solubilities as **16**. Ethyl acetate (0.75 mol) of crystallization was not removed after 24 h at 180 °C and 10^{-5} Torr. *Sublimation of* ***18***·*EtOAc at* 10^{-5} *Torr and 450 °C did provide* ***18*** *free of solvent.*

Since **16** and **18** were too insoluble to allow quantitative binding studies to be conducted in solution, the syntheses of cavitands were undertaken that contained conformationally flexible side chains attached to the rims of **16**. Octols **8–11** were brominated with *N*-bromosuccinimide (NBS) to give **12–15**, respectively, in yields ranging from 44 to 59%. These bromooctols when treated with CH_2ClBr/K_2CO_3 in $(CH_3)_2NCHO$ gave **17**, **19–21**, respectively, in yields varying from 5 to 49%. These ring-closing yields are 1 order of magnitude higher than those obtained in the preparation of **16** and **18**, probably because the four bromine atoms on the bowl rims inhibited polymerization rates of the octols more than they did ring closures.

Unlike **16** and **18**, bromocavitands **17**, **19–21** could be crystallized free of solvent or be freed of solvent by heating under vacuum. Host **17** is most soluble in CH_2Cl_2, whereas **19–21** are most soluble in $CHCl_3$. Host **19** is the most insoluble compound obtained in the course of this work. Host **20** is soluble enough in $CH_3C_6H_5$ to be recrystallized from that solvent. Carbon disulfide, one of the best solvents for **16** and **18**, dissolves only very small amounts of **17**, **19**, and **20**.

Tetrabromides **17**, **19**, and **20** were lithiated with C_6H_5Li in tetrahydrofuran at 25 °C, and the organometallics formed were treated with CH_3O_2CCl to give **22–24**, respectively, in 57–74% yields. Prior to lithiation, the starting tetrabromocavitands were freed of reactive solvent (e.g., CH_2Cl_2) either by heating under vacuum or by guest exchange with an inert solvent such as tetrahydrofuran. The tetraester cavitands were much more soluble

than their bromide precursors. Cavitand **23** proved soluble in $CHCl_3$ but not in CH_2Cl_2 or CS_2.

Tetraesters **22–24** were reduced with $LiAlH_4$ in tetrahydrofuran to their corresponding tetrols (88–92%) which were characterized only by their ^1H NMR spectra. When treated with $CH_3(CH_2)_3I/NaH$, the tetrols from **22** and **24** gave the desired tetraethers **25** (52%) and **26** (15%). Under the same conditions, the tetrol derived from tetraester **23** gave back only starting material, probably due to the insolubility of the alkoxide salt intermediates. Tetraethers **25** and **26** are soluble enough in several nonpolar solvents such as CCl_4, $(Cl_3C)_2CO$, and C_6F_6 to allow high quality ^1H NMR spectra to be determined. In molecular models, these solvents are too large to enter the cavities of **25** in more than a superficial way. Cavitand **25** proved to be more soluble than **26**, probably reflecting the fact that the entrance to the box cavity of **25** is more accessible to atomic parts of these solvents than that of **26**, whose box entrance is blocked by ethyl groups. The melting points of the two cavitands are almost the same (271–273 °C for **25** and 272–274 °C for **26**). The two hosts were fairly soluble in $(CD_3)_2SO$ and $(CD_3)_2CO$, but had no detectable solubility (^1H NMR) in ethanol.

A second synthetic route into soluble rim-functionalized cavitands involved bridging octol **11** with dibutyldichlorosilane[6] to give **27** (63%). The four silicon bridges of **27** and its derivatives were very sensitive to base but only moderately sensitive to acid, whereas the methylene bridges of **16–26** were sensitive to acid but insensitive to base. Host **27** and derivatives **28–30** were found to be soluble in most organic solvents except those that are very polar such as CH_3CN, ROH, and $(CH_3)_2SO$. Among the large number of reactions of **27** that were tried, only its conversion to **28** proved practical. Lithiation of **27** with $(CH_3)_3CLi$ at ~120 °C (−78 °C was less satisfactory) and treatment of the organometallic formed with $(CH_3)_3SnCl$ gave cavitand **28** (66%). When the organometallic was quenched with I_2, product was obtained that resisted purification. However, treatment of cavitand **28** in CH_2Cl_2[7] with I_2 gave **29** (79%). Attempts to convert tetraiodide **29** to aryl carboxylic esters[8] or amides[9] resulted in desilylations and intractable mixtures. Attempts to replace the four iodine atoms in **29** with imidazole groups also failed.[10] The palladium-catalyzed coupling of tetraiodide **29** with (trimethylsilyl)-acetylene[11] gave **30** (53%). In molecular models of this compound, the four trimethylsilyl groups form a roof over the "long box" cavity, whose interior is large enough to encapsulate a model of toluene. Neither the binding properties nor crystal structures of **27**, **29**, or **30** have yet been studied. The crystal structure of **28** is described below.

Crystal Structures. Three different stereoviews of the crystal structure of caviplex **16**·C_6H_6 are shown in Figure 1. This complex crystallizes as polymeric stacks of alternating cavitand hosts and benzene guests. The most important characteristics of these stacks can be seen in the side view (a) of the repeating unit dimer. Each benzene molecule is completely encapsulated within a large void formed by the convergence of the bowl and box cavities of two adjoining cavitand molecules. The methylene carbons of the bowl contact the para carbons of the box phenyls at distances of 3.98–3.99 Å. The benzene molecule arranges itself within this void in a manner which maximizes the effective width of each of the two constituent cavities. This is best seen in views b and c, which show the orientation of the benzene guest in the bowl and box cavities, respectively. There is positional disorder of the benzene molecule with respect to rotation 90° about an axis perpendicular to the plane of the page in views b and c. The benzene guest is nearly "bottomed out" in the bowl cavity with the benzene hydrogens lying as close as 3.14 Å to the four aryl carbons which make up the bottom of the bowl. Further penetration is prevented by other carbon–hydrogen distances of as little as 2.78 Å. The full length of the box cavity is not utilized. This is indicated by the value of 6.85 Å for the closest approach of a benzene hydrogen to the four aryl hydrogens which make up the bottom of the box. Both bowl and box cavities experience many carbon–carbon contacts with the benzene guest of less than 4.0 Å.

Careful examination of the geometry of the host itself provides useful information for predicting the structure and stability of other complexes of **16** and its derivatives. The bowl cavity of **16** is very similar to that of **2**.[2] This may be seen by comparing the crystal structure of **16**·C_6H_6 with that of **2**·CH_2Cl_2. The four resorcinol-derived aryl rings of **16** form angles with the best plane of the methine carbons whose average angle is 59.9°. This value is in good agreement with the value[2,12] of approximately 61° obtained for the analogous angle in **2**·CH_2Cl_2. The upward-pointing aryl hydrogens of **16** in view b that are opposite to each other across the cavity are at an average distance of 9.04 Å from one another. The average value for this distance in **2**·CH_2Cl_2 is also 9.04 Å.

The box cavity of **16** is somewhat larger than one would expect based on molecular model examination. Models predict that the four phenyl rings which compose the sides of the box should lie in planes which intersect the best plane of the methine carbons at angles of about 90°. The observed average value for this angle is 97.6°. The values for individual phenyl rings are 96.2°, 98.9°, 96.2°, and 98.9°. The phenyl rings are pairwise equivalent due to a C_2 axis passing through the two benzene guests in view a. This outward splay of the phenyl rings results from the slight deviation from perpendicularity of the aryl carbon to methine carbon bond to the best plane of the methine carbons by 3.2–6.0° and from the bending of this bond out of the plane of the phenyl ring to which it is attached by 2.3–6.1°. These distortions apparently are caused by unfavorable steric interactions between the substituted carbons of the phenyl rings and the 5-hydrogens of the resorcinol-derived aryl rings. Each of these phenyl carbons has at least one nonbonded carbon–hydrogen distance shorter than 2.75 Å.

A stereoview of the crystal structure of cavitand **16**·CH_3COCH_3·CH_2Cl_2 is shown in Figure 2. These crystals were grown from a mixture of CH_2Cl_2 and CH_3COCH_3 as solvent. The crystallization process randomly deposited either CH_2Cl_2 or CH_3COCH_3 in the box cavity, but only CH_3COCH_3 was entrapped in the bowl. Only the better located CH_2Cl_2 guest of the box cavity is shown in Figure 2.

Acetone rests in the bowl cavity with a methyl group pointed inward. The best plane of the molecule lies 14.0° off of a line connecting a pair of opposing OCH_2O methylenes of the host. Models suggest that an alternative arrangement with the oxygen of acetone pointing into the cavity is disfavored because steric interactions between the acetone methyl groups and OCH_2O methylenes of the host would prevent efficient penetration of the cavity. The inward pointing methyl group of the acetone contacts 25 carbons of the host at distances of less than 4.20 Å. Only two such contacts exist for the sp^2 hybridized carbon of acetone, and the outward pointing methyl group has none. The only close (nonhydrogen) contact between the acetone oxygen and the host is with a single OCH_2O methylene carbon at 3.45 Å. This analysis suggests that in solution only weak complexation is expected between the unsubstituted bowl cavity of **16** and guests significantly larger than methane. The geometry of the bowl cavity in **16**·CH_3COCH_3·CH_2Cl_2 is very similar to that previously described for the bowl cavity of **16**·C_6H_6.

Methylene chloride is almost completely encapsulated by the box cavity of **16**. Examination of molecular models suggests that

(6) The authors warmly thank John C. Sherman for an improved procedure for bridging octols with dialkyldichlorosilanes.
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(12) The angles calculated for this compound were the interplanar angles between the resorcinol-derived aryl rings and the best plane of its four methyl groups.

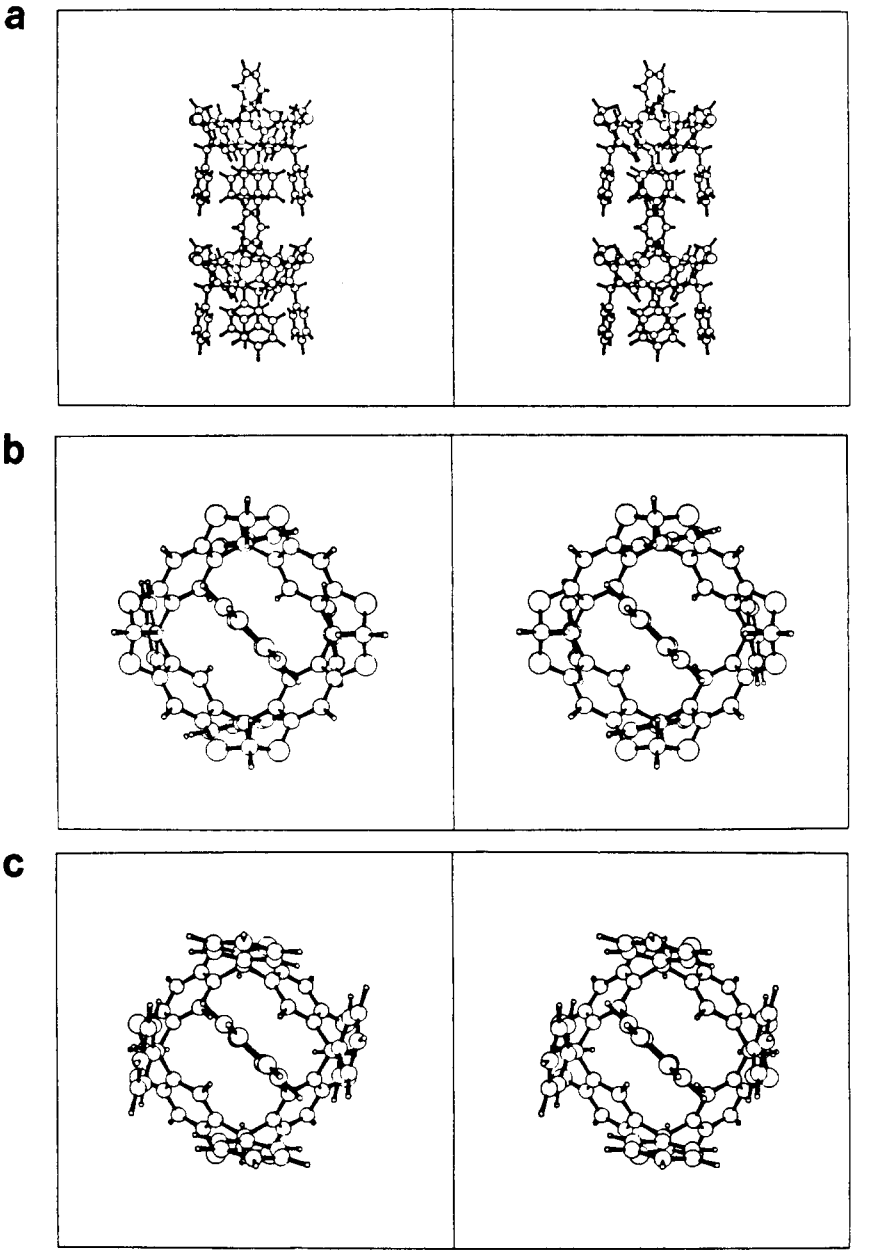


Figure 1. Different stereoviews of crystal structures of $2(\mathbf{16}\cdot C_6H_6)$ and $\mathbf{16}\cdot C_6H_6$: (a) side view of $2(\mathbf{16}\cdot C_6H_6)$, (b) bowl-face view of $\mathbf{16}\cdot C_6H_6$, and (c) box-face view of $16\cdot C_6H_6$.

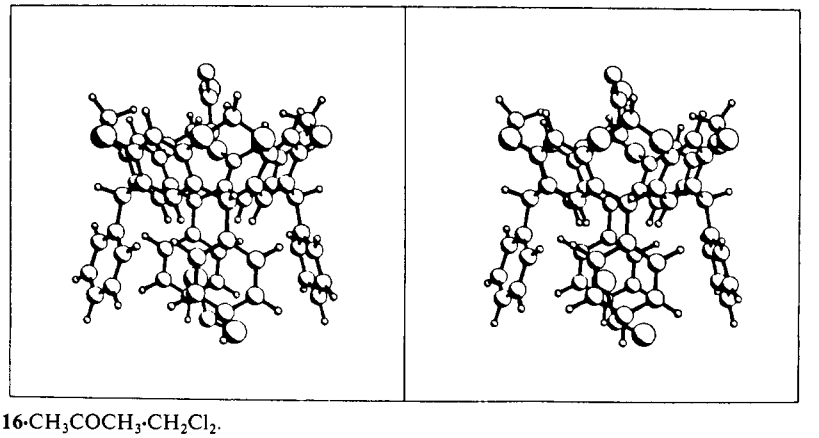


Figure 2. Side stereoview of $\mathbf{16}\cdot CH_3COCH_3\cdot CH_2Cl_2$.

replacement of the para hydrogens of the phenyl groups by methyls would be sufficient to complete the encapsulation of this guest. The entire depth of the box cavity is utilized by the CH_2Cl_2 guest. The inward-pointing chlorine of the caviplex is only 2.98 Å from one of the aryl hydrogens which form the bottom of the cavity and only 2.99 Å from another. The heavier atoms of the CH_2Cl_2 guest lie in a plane almost perpendicular to the best plane of the methine carbons of the host (84.4°) and the outward-pointing chlorine is placed in a "corner" of the box where it contacts two different phenyl rings. The carbon and chlorines of this guest have

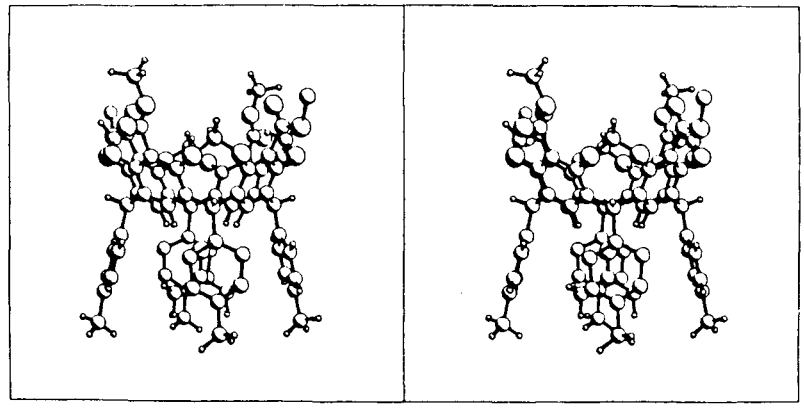


Figure 3. Side stereoview of **23**·CH_3COCH_3.

nine contacts with host carbons shorter than 4.00 Å and 27 contacts with host carbons shorter than 4.20 Å. When this box cavity is occupied by acetone (in this crystal, vide supra), three non-hydrogen atoms of this guest occupy positions similar to those occupied by the carbon and chlorines of CH_2Cl_2 in Figure 2. The remaining non-hydrogen atom points out of the cavity. The average value of the angles between the phenyl groups which make up the sides of the box and the best plane of the methine carbons is 100.2°. One opposing pair of phenyl rings has values of 104.9° and 105.4° for this angle. The other pair has angles of 96.7° and 94.0°. As neither CH_3COCH_3 nor CH_2Cl_2 is tightly restricted within the box cavity, the increase in the average value of this angle relative to that observed for **16**·C_6H_6 is ascribed to differences in crystal-packing forces.

Figure 3 provides a side stereoview of caviplex **23**·$3CH_3COCH_3$·$CHCl_3$ to whose bowl rim are attached four CO_2CH_3 groups and to whose box rims are attached four methyl groups. Crystals were obtained by layering acetone over a $CHCl_3$ solution of **23**. The structure is poorly refined because interstitial cavities between host molecules in the crystal are occupationally disordered between CH_3COCH_3 and $CHCl_3$ (not shown in Figure 3). The two methoxycarbonyl substituents on the rim of the bowl which lack methyl hydrogens are disordered with respect to whether the carbonyl or methoxy group points inward. The single orientation in Figure 3 was chosen arbitrarily for purposes of clarity. The CH_3COCH_3 in the bowl cavity is omitted because it is poorly located.

The acetone guest of the box cavity lies in a plane perpendicular to the best plane of the methine carbons of the host. The carbonyl oxygen rests against the four aryl hydrogens which form the bottom of this cavity (2.43–2.45 Å). The four phenyl rings which form the sides of the box cavity are related pairwise by a C_2 axis which is colinear with the acetone carbon–oxygen bond. One pair of phenyls forms angles of 105.7° with the plane of the methine carbons. The other pair has a value of 95.0° for this angle. The average value for all four is 100.4°. The methyl groups of the acetone lie against the faces of the more outward-bending pair of phenyl rings. These two methyl groups each have 11 carbon–carbon contacts with the host that are shorter than 4.20 Å; the sp^2 hybridized carbon has 10 such contacts. The guest oxygen has four contacts with host carbons shorter than 3.60 Å and four more contacts of 3.60–3.80 Å.

The overall arrangement of acetone within this cavity is correctly predicted by CPK molecular models only if specific account is taken of the models' flexibility regarding the nonperpendicular arrangement of the phenyl rings with respect to the best plane of the methine carbons.

Figure 4 provides three stereoviews of the crystal structure of **20**·$2C_6H_5CH_3$. View a from the side includes both molecules of $C_6H_5CH_3$. In face views b and c, the $C_6H_5CH_3$ guest molecule which is the more distant from the eye of the observer has been deleted for purposes of clarity.

Toluene rests in the bowl cavity of **20**, with its methyl group pointing inward and the plane of its six aryl carbons lying at an angle of 80.0° to the best plane of the host methine carbons. The nonperpendicular angle of approach of the guest to the bowl cavity allows a greater area of contact with the surface of the host because it places a bromine atom of the host against one face of the toluene ring. In spite of this, the overall contact between the host and guest is rather small. Although the methyl carbon of the guest has 24 carbon–carbon contacts with the host that are shorter than 4.20 Å, the aryl carbon to which it is attached has none. The two ortho carbons of the toluene guest each have two carbon–carbon contacts with the host of less than 4.20 Å and one short carbon–bromine contact (3.94 and 3.82 Å). The remaining three carbons of the bowl guest have no close contacts with the surface of the host.

The boxlike cavity of this host also complexes toluene in a "methyl group in" fashion. In this case the plane of the aryl carbons of the guest is very nearly perpendicular (90.5°) to the best plane of the methine carbons of the host. As was observed for complexation of benzene by cavitand **16**, the toluene guest lies along a diagonal of the box. The four ethyl groups of the host wrap around the guest in a way which maximizes the host–guest contact area. The closest approach of the toluene methyl carbon to the four hydrogens that form the bottom of the cavity is 3.62 Å. Closer approach is apparently prohibited by the excessive width of the guest. One ortho carbon of the guest contacts carbons of two different phenyls of the host at distances of 3.67 and 3.54 Å. The other ortho carbon of the guest contacts carbons of the remaining two phenyls of the host at distances of 3.85 and 3.98 Å. Multiple close carbon–carbon contacts (<4.20 Å) with the host are observed for all carbons of the guest except one of the meta carbons (one contact) and the para carbon (no contacts). The angles formed between the phenyl rings which form the sides of the box and the best plane of the methine carbons are 98.6°, 97.7°, 101.2°, and 97.7°. The average value of this angle is 98.8°. Molecular models predict that if these angles were as large as those observed in **23**·$2CH_3COCH_3$ and in **16**·CH_3COCH_3·CH_2Cl_2, nearly complete encapsulation of the $C_6H_5CH_3$ guest would be possible.

When **20** was recrystallized from BrC_6H_5 instead of $CH_3C_6H_5$, crystals of caviplex **20**·$2C_6H_5Br$ were formed whose crystal structure showed the material to be isomorphous to **20**·$2C_6H_5CH_3$. Both the box and the bowl of **20**·$2C_6H_5Br$ were occupied with BrC_6H_5 molecules, with their bromines facing inward.

The crystal structure of tetrakis(trimethylstannyl) cavitand **28** is shown in Figure 5. The crystal used in this structure determination was obtained by slow evaporation of a solution of **28** in diethyl ether. Host **28** crystallized from this solvent without inclusion of solvent molecules and thereby provided the *first crystal structure of a host compound of this series in a noncomplexed state*. Molecular model examination indicates that the bowl cavity of **28** is too narrow to admit diethyl ether due to the intrusiveness of the inward-held alkyl groups attached to silicon. The trimethylstannyl groups create a roof over the top of the box cavity and prevent complexation of guests such as diethyl ether which are too large to be completely encapsulated. Both bowl and box cavities remain organized for complexation in the absence of complexed guest.

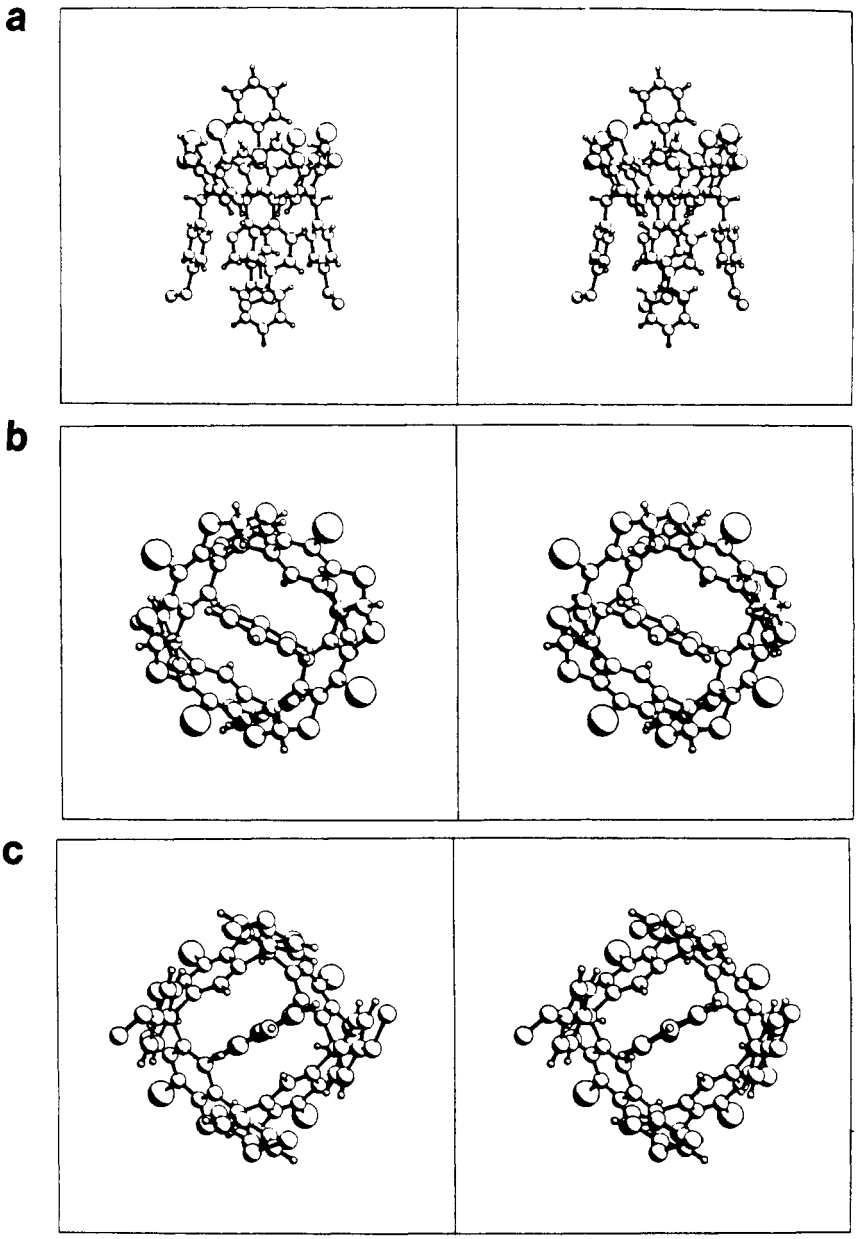


Figure 4. Three stereoviews of the crystal structure of **20**·$2C_6H_5CH_3$: (a) Side view, both guests, (b) bowl-face view, guest in box deleted, (c) box-face view, guest in bowl deleted.

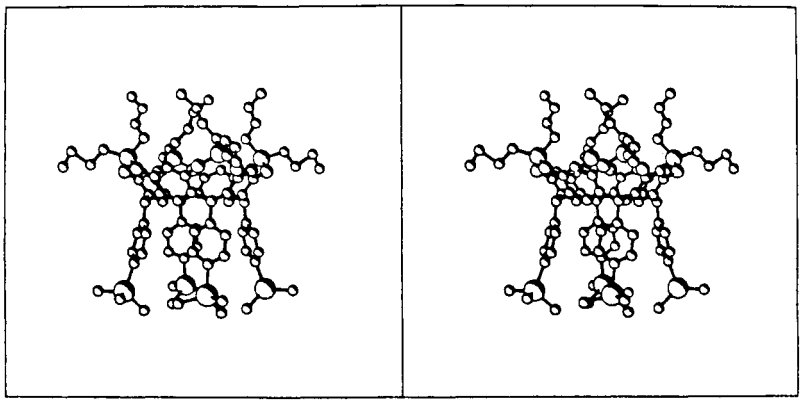


Figure 5. Side stereoview of cavitand **28**.

The phenyl groups which make up the sides of the box cavity are related pairwise by a C_2 symmetry axis of the molecule. One pair of phenyls forms angles of 99.8° with the best plane of the methine carbons. The other pair of phenyls forms angles of 104.2° with this plane. The average value of this angle is 102.0°. This average value is the largest observed for any of the compounds in this series for which a crystal structure has been solved. The increase in the value of this angle is *not* caused by conformational changes arising from the presence of silylidene bridges in place of the methylene bridges of the previously discussed compounds.

Table I. Chemical Shift Changes in ^1H NMR Spectra Observed upon Addition of Potential Guests (5% by Volume) to a CCl_4 Solution of Host **25**

guest	chemical shift change, ppm[a]			
	H-1	H-2	H-4	H-6 (in)
$CDCl_3$	0.1531	0.0670	0.0564	0.0644
CD_2Cl_2	0.1773	0.0830	0.0752	−0.1170
CD_3CN	0.1666	0.0710	0.0564	−0.0914
$(CD_3)_2CO$	0.1881	0.0870	0.0699	−0.1385
CS_2	0.1720	0.1040	0.0524	−0.0562

[a] See structure **25a** for numbering system.

Table II. Chemical Shift Changes in ^1H NMR Spectra Observed upon Addition of Potential Guests (5% by Volume) to a CCl_4 Solution of Host **26**

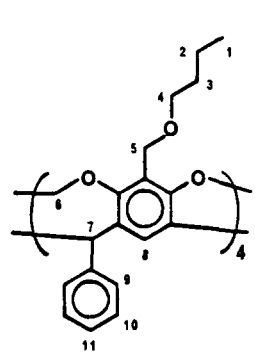
guest	chemical shift change, ppm[a]					
	H-1	H-6 (in)	H-8	H-9	H-11	H-12
CD_2Cl_2	0.2016	−0.1169	−0.1048	0.0484	0.0276	0.0201
CD_3CN	0.1867	−0.0826	−0.2781	0.1020	0.0809	*b*
CS_2	0.1666	−0.0470	−0.1048	0.0081	0.0061	0.0067
CD_3NO_2	0.1881	−0.1142	−0.0161	0.0430	0.0088	−0.0014
$C_6D_5CD_3$	0.0242	−0.0014	*b*	−0.0148	−0.0827	−0.0658

[a] See structure **26a** for numbering system. [b] Not determined due to peak overlap with residual proton resonances of solvent or guest.

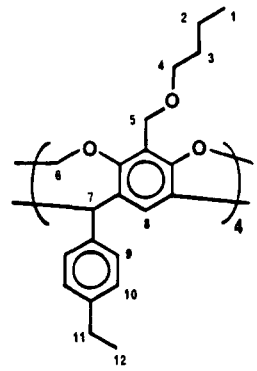
The methine–carbon to phenyl–carbon bonds lie out of the best plane of the methine carbons by an average value of 95.2°. The average value of this angle in **16**·C_6H_6 is 94.6°. The phenyl groups are apparently splayed outward by steric interactions between the bulky trimethylstannyl groups. The aryl carbon–tin bonds are bent out of the three-carbon plane (attached and two ortho carbons) by an average angle of 4.6°. There are two carbon–carbon distances between trimethylstannyl groups of 4.05 Å and two more carbon–carbon distances of 4.49 Å. The four tin atoms lie on the vertices of a parallelogram having sides of 6.52 and 7.77 Å and diagonals of 9.75 and 10.52 Å. Replacement of one methyl group of each trimethylstannyl residue with an electron-withdrawing group such as hydroxyl or chlorine should give a cavity that is both sterically and electronically complimentary to anionic guests such as iodide and perchlorate.

These six crystal structures demonstrate that the four aryl groups originating in the aromatic aldehydes during the syntheses of octols **8–11** form an enforced boxlike cavity of dimensions roughly predictable by CPK molecular model examination. The dimensions adapt within limits to guest shapes or to the steric requirements of bulky substituents in the 4-positions by small deformations of the bond angles involving carbon–carbon bonds in the C-1 and C-4 positions of the four benzene rings defining the box. The bowl-cavity dimensions appear to be nearly independent of the box-cavity dimensions.

Qualitative Binding Studies in Solution. These studies were performed on **25** and **26**, the most soluble cavitands. A small quantity (0.75–2.0 mg) of host was dissolved in 500 μL of a suitable solvent (containing 0.3% v/v tetramethylsilane), and its 200-MHz ^1H NMR spectrum was determined. This spectrum was then compared to that which was obtained when a similar quantity of the same host was dissolved in a 95:5 v/v mixture of the same solvent and a potential guest. The resulting significant chemical shift changes are presented in Tables I and II for several combinations of host, guest, and solvent. The numbering scheme used in these tables to identify the hydrogens are shown in structures **25a** and **26a**. Chemical shift changes for H-3, H-4, H-5, H-6 (out), and H-7 for **25a**, and of H-3, H-4, H-5, H-6 (out), H-10, H-12, and H-13 for **26a** were all less than 0.08 ppm and are omitted. Chemical shift changes were not calculated for H-8, H-9, H-10, and H-11 of host **25a** or for H-2 of host **26a** because of peak overlap and/or ambiguous assignment. The recorded chemical shift changes are interpreted below with the very reasonable assumption that fast exchange occurs between free and complexed host. Binding studies conducted in CCl_4 as solvent were accomplished with an internal coaxial tube containing C_6D_6 or CD_3COCD_3 to provide a deuterium lock signal.



25a



26a

Examination of Table I reveals that when potential guests are added to a CCl_4 solution of host **25**, chemical shift changes occur which range from −0.1385 to 0.1881 ppm. Although these changes are not dramatically greater than those expected to arise from bulk solvent effects, several patterns occur in the data which suggest that a specific host–guest interaction is occurring. Large positive chemical shift changes occur consistently for the H-1 protons, suggesting that a guest is entering the bowl cavity and displacing this methyl group from the shielding cone of the four bowl aryl rings. This notion is further supported by the progressively smaller but still positive chemical shift changes which occur for the H-2 and H-3 protons. When H-4 is reached, relatively larger positive chemical shift changes of 0.052–0.070 ppm are again observed. Molecular model examination suggests that while H-1, H-2, and H-4 may readily be inserted into the shielding cones of the four aryl rings of the bowl, insertion of H-3 is largely inhibited by unfavorable steric interactions with the OCH_2O methylene hydrogens (H-6). The relatively small chemical shift changes (0.019 to −0.011 ppm) observed for the H-5 hydrogens may reflect a preferred conformation for both the free and the complexed host in which these hydrogens are pointing away from the cavity. Models suggest that such a conformation might be enforced by interaction of the benzyl C–O dipole with the dipoles of the two adjacent aryl C–O bonds. The inward-facing hydrogens H-6 undergo chemical shift changes of moderate to large magnitude and of variable direction upon addition of different potential guests. These chemical shift changes may reflect direct anisotropic shielding or deshielding of these protons by an appropriately oriented guest. Molecular model examination suggests that the predicted direction of the chemical shift change is highly dependent on the exact orientations of the guest in the cavity, which are unknown. The outward pointing protons H-6 and the methine protons H-7 undergo chemical shift changes which are usually small.

Table II summarizes the substantive chemical shift changes which occur when potential guests are added to a CCl_4 solution of host **26**. The chemical shift changes for protons H-1 through H-7 generally correspond to the trends discussed for **25** in the same solvent. The four ethyl groups of **26** provide an additional ^1H NMR probe for complexation and simplify the aryl region of the spectrum so that box cavity effects of guests can be observed.

The H-8 proton chemical shift changes of host **26** are susceptible to close contact with guests occupying either of the two cavities of the host. They therefore provide relatively nonspecific information concerning complexation by this host. The relatively large negative chemical shift changes observed for these protons upon addition of CS_2 or CD_3CN to the host solution are in accord with molecular model predictions that these guests enter both bowl and box cavities with their symmetry axes roughly colinear with that of the host.

The aryl protons H-9 and H-10 lie in the corners of the box and in models provide some lining to the cavity. In models some guests (i.e., CD_3CN) appear able to closely approach these protons from within the cavity, while in other cases the chemical shift

Table III. Association Constants for Host **26** Binding CD_3CN in CCl_4 with Five or Six Different Hydrogen Chemical Shifts in **26a** as Probes

	K_a of bowl, M^{-1}				K_a of box, M^{-1}			
T, K	H-1	H-4	H-6 (in)	K_{av} of bowl, M^{-1}	H-9	H-11	H-12	K_{av} of box, M^{-1}
328	54	54	31	47	20	26	21	22
300	109	98	60	89	41	49		45
273	307	320		313	92	169	216	159

changes may result from subtle conformational changes of the host. Small rotations about the bonds connecting the methine carbons and the phenyl rings of the box move the protons of these phenyl rings in and out of each other's shielding cones as well as the shielding cones of the bowl aryl rings.

Protons H-11 and H-12 of **26** show relatively large chemical shift changes upon addition of CD_3CN or $CD_3C_6D_5$ but not upon addition of CS_2, CD_2Cl_2, or CD_3NO_2. The positive chemical shift change observed for H-11 upon addition of CD_3CN is interpreted as due to CD_3CN entering the cavity with its nitrogen innermost. The partial positive charge of the methyl carbon should perturb the nearby H-11 hydrogens. The relatively large negative chemical shift changes observed for H-11 and H-12 upon addition of $C_6D_5CD_3$ are in excellent accord with the mode of complexation of this guest by the box cavity in the crystal structure of host **20**·$2C_6H_5CH_3$ (Figure 4).

Quantitative Binding Studies. Quantitative binding studies were conducted utilizing chemical shift changes in the 200-MHz ^1H NMR spectra of host **26** in CCl_4 induced by incremental guest additions at different temperatures. Table III reports the K_a values derived for each of several protons associated with each cavity of host **26** binding CD_3CN at 328, 300, and 273 K, as well as the K_{av} obtained. The protons whose signals were chosen for K_a determinations exhibited relatively large (>0.0500 ppm) chemical shift changes upon complexation, and were each closely associated with only one of the two cavities of the host. The chemical shift changes undergone by each proton as a function of CD_3CN concentration were used to calculate δ_{HG} for that proton and K_a for the cavity with which it is associated. *These calculations used the assumptions that the chemical shift of each proton is affected only by occupation of the cavity with which it is closely associated and that occupation of one cavity does not affect the complexing properties of the other.* The large dipole moment of acetonitrile and the close proximity of the two cavities suggests that the latter assumption may not be strictly true. Any cooperative or anticooperative binding effects are, however, likely to be small relative to the level of precision of this method of association constant determination.

In the following discussion the symbol H represents the free host, G represents the uncomplexed guest, HG represents a complex in which a guest molecule is bound within the cavity under consideration (without regard for whether the other cavity is occupied), δ represents the chemical shift of a proton closely associated with the same cavity of the host (in its free or complexed state, as specified by subscript), K_a is the equilibrium constant describing the complexation under discussion, and R_{bowl} and R_{box} are the percent occupancies of the bowl and box cavities by guest molecules. The subscripts 0 and obs refer to initial and observed values, respectively. Calculations[13] were based on eq 1, which

$$\frac{1}{K_a(\delta_{HG} - \delta_H)}\frac{1}{[G]} + \frac{1}{(\delta_{HG} - \delta_H)} = \frac{1}{(\delta_{obs} - \delta_H)} \quad (1)$$

predicts that a plot of $1/(\delta_{obs} - \delta_H)$ vs $1/[G]$ should give a straight line with slope $1/K_a(\delta_{HG} - \delta_H)$ and a y intercept equal to $1/(\delta_{HG} - \delta_H)$. In practice, plotting $1/(\delta_{obs} - \delta_H)$ vs $1/[G]_0$ gave approximate values for $\delta_{HG} - \delta_H$ which could be used to estimate R_{bowl} and R_{box} for each point according to eq 2. These values

$$R = (\delta_{obs} - \delta_H)/(\delta_{HG} - \delta_H) \quad (2)$$

were averaged over all appropriate protons and then used to calculate new approximate values of [G] for each point according to eq 3. New plots of $1/(\delta_{obs} - \delta_H)$ vs $1/[G]$ were then made

$$[G] = [G]_0 - (R_{bowl} + R_{box})[H]_0 \quad (3)$$

for each proton with these new approximations of [G] in place of $[G]_0$. This process was repeated until $[G]_{new}/[G]_{old}$ was greater than 0.99. The association constant for each cavity was then calculated by dividing the y intercept of each plot by its slope and averaging over all appropriate protons. All slopes and y intercepts were calculated by means of linear least-squares analysis and gave correlation coefficients of 0.98 or greater. All host–guest association constants were calculated based on binding studies in which R varied over a range of at least 0.25 between minimum and maximum values of 0.20 and 0.92, respectively.

Plots were made of δ_{obs} vs $[CD_3CN]$ at 300 K for each of three types of hydrogens associated with the bowl cavity of **26**. Similar plots were made for the two types of protons associated with the box cavity. All five plots were overlaid with calculated curves[14] of δ vs $[CD_3CN]$ appropriate for a host–guest complexation governed by association constant K_a and having $[H]_0$, δ_H, and δ_{HG} values equal to those measured. The K_a values used to generate the calculated curves are the K_{av} values found in Table III. With the exception of the inward-pointing H-6 proton, the agreement between observed and calculated points is sufficiently good that the latter partially obscure the former. These plots indicate that the raw data fits a model based on a specific host–guest interaction rather than on a general medium effect. These five plots (Figures 6–10) and Table IV (containing the chemical shift data) are supplied as supplementary material.

Three-point van't Hoff plots were made for CD_3CN being bound in the respective bowl and box cavities of **26** (Figures 11 and 12 of supplementary material), from whose least squares straight line were calculated the enthalpy and entropy of binding. For the bowl cavity, $\Delta H_a = -6.2 \pm 1.2$ kcal mol^{-1}, and $\Delta S_a = -11.4 \pm 4$ cal mol^{-1} T^{-1}. For the box cavity, $\Delta H_a = -6.4 \pm 1.5$ kcal mol^{-1}, and $\Delta S_a = -13.6 \pm 5$ cal mol^{-1} T^{-1}. The error limits for these parameters were determined by propagation of an estimated 95% confidence interval for K_a of ±30%. This 95% confidence limit was in turn estimated from the scatter in calculated values of K_a that were based on different protons associated with the same cavity of the host. Although the ΔS_a values obtained from these plots are relatively imprecise, they appear to be in good accord with the values of −11 to −14.5 cal mol^{-1} K^{-1} observed in other systems for this type of complexation.[3,15-17]

These studies taken in sum demonstrate that host compounds having two structurally distinct cavities can be prepared and that the binding ability of each cavity can be individually assessed. The binding by each cavity in the case of at least one guest (CD_3CN) is large enough at 298 K to result in significant concentrations (>0.50 $[H]_0$) of doubly occupied host at relatively low concentrations of host (0.0022 M) and guest (0.052 M). Varying

(13) (a) Hildebrand, J. H.; Benesi, H. A. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. (b) The authors warmly thank Drs. F. A. L. Anet, J. L. Ericson, and Y. S. Xiong for helpful discussions concerning the determination of association constants by ^1H NMR spectroscopy.

(14) These curves were calculated with the equation $\delta_{calc} = ([HG]/[H]_0\delta_{HG} + \{([H]_0 - [HG])/[H]_0\}\delta_H$. A calculator program was used to search by increments of 0.00001 M for the value of [HG] best satisfying the equation $K = [HG]/\{([H]_0 - [HG])([G]_0 - [HG])\}$. This approach neglects the effect of binding by the "other" cavity of the host on [G]. Model calculations suggest that the effect of this neglect on δ_{calc} is small (<0.0020 ppm).

(15) Conceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1986**, *108*, 4230–4232.

(16) Diederich, F.; Dick, K.; Griebel, D. *J. Am. Chem. Soc.* **1986**, *108*, 2273–2286.

(17) Ericson, J. L. Ph.D. dissertation, University of California, Los Angeles, 1987.

the substituents of the cavity rims could in principle lead to bifunctional hosts having even stronger binding and dramatically different guest selectivities for each cavity. Such compounds could be of interest for studying long-range intermolecular forces and/or the binding cooperativity/anticooperativity which might result.

The cavity rims also provide positions potentially capable of substitution by catalytic functional groups that can act cooperatively in catalyzing reactions of bound guests. Such possibilities are being investigated.

Experimental Section

General Procedures. All procedures were performed under a N_2 atmosphere in glassware that was dried 3 h at 220 °C immediately before use. Diethyl ether and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl. Amine solvents and bases were freshly distilled from CaH_2. Dimethyl sulfoxide and $(CH_3)_2NCHO$ were stored 48 h over activated (24 h, 320 °C) 3-Å molecular sieves and degassed at high vacuum immediately before use. NBS was recrystallized according to the procedure given by Perrin.[18] Oil-free NaH was prepared by stirring a 50% dispersion of NaH in mineral oil with hexanes five times in a Büchner funnel (medium glass frit). *All synthesized compounds were dried under the conditions specified for their elemental analyses before use in analytical or further synthetic procedures.*

Melting points (uncorrected) were taken on a Thomas-Hoover or Mel-Temp apparatus; ^1H NMR spectra were recorded on a 200-MHz WP-200 Bruker instrument and are referenced to tetramethylsilane as an internal standard at 0.000 ppm. Electron-impact mass spectra were taken on an AEI Model MS-902 spectrometer. FAB mass spectra were determined on a ZAB SE instrument using the matrix specified for individual compounds. "NOBA" refers to *m*-nitrobenzyl alcohol. E. Merck silica gel (63–200 μm) was used for preparative column chromatography. Thin-layer chromatography was performed with E. Merck aluminum-backed silica gel 0.2-mm plates.

5,11,17,23-Tetrabromo-2,8,14,20-tetraphenylpentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19-(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (Stereoisomer, 12). A solution of 1.00 g (1.26 mmol) of octol **8** in 20 mL of $(CH_3)_2NCHO$ was cooled to 0 °C and *protected from light*. To this solution was added 0.910 g (5.11 mmol) of NBS. This mixture was stirred in the dark at 0 °C for 24 h and then poured into 50 mL of distilled water. The resulting precipitate was collected and dried in a vacuum oven for 20 h at 50 Torr and 65 °C. It was then dissolved in 100 mL of hot acetone and filtered, and the volume was reduced to 5 mL. The precipitate which formed on standing was collected to give 0.65 g (47%) of tetrabromide **12**: mp ca. 270 °C dec; ^1H NMR δ 5.81 (s, Ar_3CH, 4 H), 5.81–6.20 (br s, ArH para to Br, 4 H), 6.68–6.78 (m, ArH, 8 H), 6.92–7.08 (m, ArH, 12 H), 8.27 (s, OH, 8 H); MS (FAB, NOBA) complex envelope of peaks centered near *m/e* 1026 (M^+ – Br, 40). Anal. Sample dried 24 h at 10^{-5} Torr, 70 °C. Calcd for $C_{52}H_{36}Br_4O_8$: C, 56.34; H, 3.27. Found: C, 56.07, H, 3.27.

5,11,17,23-Tetrabromo-2,8,14,20-tetrakis(4-methylphenyl)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19-(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (Stereoisomer, 13). Crude brominated octol **13** was prepared from 40.0 g (47.2 mmol) of octol **9** and 34.3 g (191 mmol) of NBS by using the procedure described above for the preparation of **12**. The crude product was dissolved in 2.5 L of refluxing acetone (a small amount (<25 mL) of $(CH_3)_2NCHO$ was added in some runs to aid dissolution) and filtered while hot. Cyclohexane was added (550 mL), and the volume was reduced to 600 mL to give 24.3 g (44%) of tetrabromide **13** as a pale orange precipitate, which was collected by filtration: mp ca. 270 °C dec; R_f 0.82 (silica gel, 1:1 CH_2Cl_2/EtOAc); ^1H NMR ($(CD_3)_2SO$, 360 K) δ 2.24 (s, CH_3, 12 H), 5.75 (s, Ar_3CH, 4 H), 6.07 (s, ArH para to Br, 4 H), 6.60 (d, J = 8.1 Hz, ArH meta to Me, 8 H), 6.81 (d, J = 8.1 Hz, ArH ortho to Me, 8 H) (at 300 K the singlet at δ 6.07 is very broad); MS (EI, 70 eV) 1:4:6:4:1 Br_4 isotope pattern centered at *m/e* 1164 (M^+ + 4, 100). Anal. Sample dried 24 h at 10^{-5} Torr, 70 °C. Calcd for $C_{56}H_{44}Br_4O_8$: C, 57.76; H, 3.81. Found: C, 57.56; H, 3.94.

5,11,17,23-Tetrabromo-2,8,14,20-tetrakis(4-ethylphenyl)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19-(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (Stereoisomer, 14). Crude brominated octol **14** was prepared from 116.3 g (128 mmol) of octol **10** and 92.6 g (520 mmol) of NBS by using the procedure described above for the preparation of **12**. The crude product was suspended in 3.0 L of refluxing acetone and $(CH_3)_2NCHO$ was slowly added until almost complete dissolution occurred (35 mL). This solution was filtered while hot, 2.0 L of cyclohexane was added, and the volume was reduced to 2.0 L. The orange precipitate which formed was collected. A second crop, which formed on reducing the volume of the mother liquor to 1.0 L, was recrystallized again and combined with the first crop to yield 97.6 g (57%) of tetrabromide **14** as a dark orange powder: mp ca. 270 °C dec; R_f 0.82 (silica gel, 1:1 CH_2Cl_2/EtOAc); ^1H NMR ($(CD_3)_2SO$) δ 1.17 (t, J = 7.5 Hz, CH_3, 12 H), 2.50 (partially obscured by residual proton peak of solvent, q, CH_2 of Et), 5.79 (s, Ar_3CH, 4 H), 7.0–7.4 (br s, ArH para to Br, 4 H), 6.65 (d, J = 8.1 Hz, ArH meta to Et, 8 H), 6.86 (d, J = 8.1 Hz, ArH ortho to Et, 8 H), 8.26 (s, OH, 8 H); MS (FAB, NOBA) 1:4:6:4:1 Br_4 isotope pattern centered at *m/e* 1220 (M^+ + 4, 100). Anal. Sample dried 3 days at 10^{-5} Torr, 190 °C. Calcd for $C_{60}H_{52}Br_4O_8$: C, 59.04; H, 4.29. Found: C, 58.98; H, 4.32.

5,11,17,23-Tetrabromo-2,8,14,20-tetrakis(4-bromophenyl)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19-(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (Stereoisomer, 15). Crude octabromide **15** was prepared from 15.0 g (13.5 mmol) of octol **11** and 9.74 g (54.7 mmol) of NBS by using the procedure described above for the preparation of **12**. Crude **15** was purified by the method described for purification of **14**. This procedure yielded 11.3 g (59%) of octabromide **15** as an orange powder: mp ca. 270 °C dec; R_f 0.69 (silica gel, 1:1 CH_2Cl_2/EtOAc); ^1H NMR ($(CD_3)_2SO$, 360 K) δ 5.78 (s, Ar_3CH, 4 H), 5.92 (br s, ArH para to Br, 4 H), 6.60 (d, J = 8.1 Hz, ArH meta to Br, 8 H), 7.23 (d, J = 8.1 Hz, ArH ortho to Br, 8 H), 8.07 (s, OH, 8 H) (at 300 K the singlet at δ 5.92 is split into 2 equal peaks at δ 5.62 and 6.12); MS (FAB, NOBA) gave a small peak envelope near *m/e* 1424 (M^+ + 8). Anal. Sample dried 24 h at 10^{-5} Torr, 150 °C. Calcd for $C_{52}H_{32}Br_8O_8$: C, 43.86; H, 2.26. Found: C, 43.60; H, 2.33.

1,21,23,25-Tetraphenyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis-[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (Stereoisomer, 16). Bromochloromethane (4.52 mL, 69.4 mmol) and 10.0 g (12.6 mmol) of octol **8** were dissolved in 250 mL of $(CH_3)_2NCHO$. This solution was added dropwise over 3 days to a 45 °C suspension of 26.1 g (189 mmol) of K_2CO_3 in 600 mL of $(CH_3)_2SO$. After stirring an additional 40 h, the reaction mixture was poured into 1 L of 2 M aqueous NaCl solution. The resulting suspension was vacuum filtered through Whatman no. 1 filter paper. The solid was collected and suspended in 500 mL of 9:1 CH_2Cl_2/CH_3COCH_3. After stirring for 2.5 h, this suspension was filtered and the filtrate was dried ($MgSO_4$). The solvent was removed in vacuo. The dark red, solid residue (ca. 3 g) was chromatographed on 30 g of silica gel with $CHCl_3$ as the mobile phase to give a colorless solid. This solid was dissolved in CH_2Cl_2, cyclohexane was added, and the volume was reduced in vacuo until crystallization occurred. This procedure gave 0.53 g (5.0%) of cavitand **16**·$^3/_4C_6H_{12}$·$^1/_4CH_2Cl_2$: mp >390 °C; R_f 0.12 (silica gel, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.54 (s, cyclohexane, 9 H), 4.60 (d, J = 7.0 Hz, OCH_2O, 4 H), 5.30 (s, CH_2Cl_2, $^1/_2$ H), 5.86 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.39 (s, Ar_3CH, 4 H), 6.69 (s, ArH ortho to OR, 4 H), 6.95 (s, ArH meta to OR, 4 H), 7.1–7.4 (m, ArH, 20 H); MS (EI, 70 eV) *m/e* 840 (M^+, 100); a small sample was crystallized by slowly evaporating a solution of **16** in 1:1 CH_2Cl_2/EtOAc, and it was then dried 24 h at 10^{-5} Torr, 100 °C. Anal. Calcd for $C_{56}H_{40}O_8$·$^3/_4$EtOAc: C, 77.91; H, 5.16. Found: C, 78.12; H, 5.12. The presence of $^3/_4$ mol of EtOAc was confirmed by ^1H NMR.

7,11,15,28-Tetrabromo-1,21,23,25-tetraphenyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin (Stereoisomer, 17). A stirred mixture of 30.4 g (27.4 mmol) of octol **12**, 40.0 g (289 mmol) of K_2CO_3, and 2.0 L of $(CH_3)_2NCHO$ was heated to 70 °C, and a solution of 8.92 mL (137 mmol) of CH_2ClBr in 70 mL of $(CH_3)_2NCHO$ was added dropwise over 2 days. After stirring of the solution an additional 36 h, the temperature was raised to 95 °C, and an additional 18.0 g (130 mmol) of K_2CO_3 was added. An additional 30 mL of CH_2ClBr dissolved in 50 mL of $(CH_3)_2NCHO$ was added over the next 40 h. The mixture was stirred an additional 48 h and then cooled to 25 °C and poured into 4.0 L of 2 N aqueous NaCl. The precipitate was collected and suspended in 1.5 L of $CHCl_3$. After stirring 2 h, the suspension was filtered and the solid was stirred 1 h with 1.0 L of 19:1 $CHCl_3/(CH_3)_2CO$. The suspension was again filtered, and the combined filtrates were extracted with 500 mL of distilled water. The organic phase was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. The residue was chromatographed on silica gel with 9:9:2 $CH_2Cl_2/(CH_2)_6/CS_2$ as the mobile phase. The product tended to crystallize on the column and clog it. It was found best to add its CH_2Cl_2 solution to the top of the column in small portions and stir the top of the column with a glass rod if clogging occurred. When the volume of the eluent was reduced in vacuo crystals formed, which were collected by filtration to yield 3.3 g (10.4%) of **17**: mp >360 °C; R_f 0.67 (silica gel, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 4.57 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.08 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.52 (s, Ar_3CH, 4 H), 6.90 (s, ArH para to Br, 4 H), 7.26 (s, ArH, 20 H); MS (EI, 70 eV)

(18) Perrin, D. D.; Perrin, D. R.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd ed.; Permagon Press: New York, 1980; p 141.

1:4:6:4:1 Br_4 isotope pattern centered at *m/e* 1156 ($M^+ + 4$, 100%). Anal. Sample dried 12 h at 10^{-5} Torr, 180 °C. Calcd for $C_{56}H_{36}Br_4O_8$: C, 58.16; H, 3.14. Found: C, 58.08; H, 3.36.

1,21,23,25-Tetrakis(4-methylphenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin (Stereoisomer, 18). Octol **9** (9.0 g, 10.6 mmol) was dissolved in 1 L of hot $(CH_3)_2SO$. The solution was cooled, and 3.80 mL (58.4 mmol) of CH_2ClBr was added. (Note: many difficulties were encountered due to slow precipitation of **9** from this solution.) This solution was added dropwise to a suspension of 43.9 g (318 mmol) of K_2CO_3 in $(CH_3)_2SO$ held at 65 °C. After an additional 36 h, this solution was poured into 2 L of 2.0 N aqueous NaCl. The precipitate was collected, air dried, and suspended in 400 mL of CH_2Cl_2. After stirring 4 h, the suspension was filtered. The solvent was evaporated from the filtrate in vacuo. The dark residue was dissolved in 10 mL of CH_2Cl_2, 10 mL of EtOAc was added, and the volume of the solution was reduced to 10 mL in vacuo. The resulting precipitate (ca. 1 g) was collected by filtration and chromatographed on 10 g of silica gel with $CHCl_3$ as the mobile phase. It was again recrystallized from CH_2Cl_2/EtOAc to give 0.87 g (0.9%) of **18**·EtOAc. Sublimation of this material at 10^{-5} Torr and 400 °C gave free **18** as a white solid: mp >390 °C; R_f 0.12 (silica gel, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.31 (s, $ArCH_3$, 12 H), 4.58 (d, J = 7.0 Hz, OCH_2O, 4 H), 5.84 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.33 (s, Ar_3CH, 4 H), 6.66 (s, ArH ortho to OR, 4 H), 6.98 (s, ArH meta to OR, 4 H), 7.06 (d, J = 8.6 Hz, ArH meta to Me, 8 H), 7.18 (d, J = 8.6 Hz, ArH meta to Me, 8 H); MS (EI, 70 eV) *m/e* 896 (M^+, 100). Anal. Sample sublimed as described above. Calcd for $C_{60}H_{48}O_8$: C, 80.34; H, 5.39. Found: C, 80.38; H, 5.40.

7,11,15,28-Tetrabromo-1,21,23,25-tetrakis(4-methylphenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (Stereoisomer, 19). The procedure described above for the preparation of **17** from **12** was applied to 43.6 g (37.5 mmol) of octol **13**. Similar molar ratios of solvent and reagents were employed. This procedure was departed from only in that the very low solubility of **19** required some changes in the purification procedure. Crude, moisture-free **19** was mixed with an equal volume of sand and placed in a Soxhlet extraction thimble. The solvent reservoir was loaded with 1.0 L of carbon disulfide (**Fire hazard**! we recommend that this solvent be replaced by chloroform for both safety and solubility reasons) and 85 g of silica gel. After extraction of the mixture for 3 days, the solvent was evaporated from the extract in vacuo. The remaining solid was loaded portionwise over 2 h onto a column containing 125 g of silica gel. The column was continuously eluted during this time with 4:1 CH_2Cl_2/CS_2 (we recommend that this solvent mixture be replaced by $CHCl_3$ for solubility reasons). Fractions containing product were combined, and the solvent was evaporated in vacuo. This solid was washed with EtOAc, dried, and suspended in 50 mL of tetrahydrofuran (guest exchange). The mixture was refluxed for three days, the solvent was removed in vacuo, and the resulting solid dried for 48 h at 10^{-1} Torr and 110 °C. This procedure gave 2.38 g (5.3%) of **19** as a white solid: mp >360 °C; R_f 0.76 (silica gel, $CHCl_3$); ^1H NMR (2:1 CS_2/CD_2Cl_2) δ 2.30 (s, $ArCH_3$, 12 H), 4.39 (d, J = 7.0 Hz, OCH_2O, 4 H), 5.97 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.32 (s, Ar_3CH, 4 H), 6.76 (s, ArH para to Br, 4 H), 7.06 (s, ArH, 16 H). MS (FAB, NOBA) 1:4:6:4:1 Br_4 isotope pattern centered at *m/e* 1213 ($M^+ + 5$, 100). Anal. Sample dried 48 h at 10^{-1} Torr, 110 °C. Calcd for $C_{60}H_{44}Br_4O_8$: C, 59.43; H, 3.66. Found: C, 59.41; H, 3.77.

7,11,15,28-Tetrabromo-1,21,23,25-tetrakis(4-ethylphenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (Stereoisomer, 20). A solution of 22.0 g (18.0 mmol) of octol **14** and 6.48 mL (100 mmol) of CH_2ClBr in 400 mL of $(CH_3)_2NCHO$ was added dropwise over 2 days to a stirred (60 °C) suspension of 37.4 g (271 mmol) of K_2CO_3 in 750 mL of $(CH_3)_2N$-CHO. The mixture was stirred at this temperature an additional 48 h, and the temperature was slowly raised to 85 °C over 72 h. An additional 5.0 mL (77.1 mmol) of CH_2ClBr was added. After 48 h at 85 °C and an additional 24 h at 95 °C, the mixture was cooled and poured into 2.0 L of distilled water. The precipitate was collected by filtration and dried in a vacuum oven for 12 h at 80 °C. The dark solid was placed in a Soxhlet extraction thimble. The solvent reservoir was loaded with 100 g of silica gel and 1.0 L of $CHCl_3$. After the solid had been extracted for 3 days, the solvent was removed from the extract in vacuo. The remaining solid was suspended in a minimum amount of 9:1 $CHCl_3/CS_2$ and placed on top of a column containing 500 g of silica gel. Elution of this column with 9:1 $CHCl_3/CS_2$ gave a brown solid, which was stirred with 150 mL of $(CH_3)_2CO$ for 24 h. The suspension was filtered, and the solid was refluxed with 75 mL of tetrahydrofuran for 48 h. The suspension was cooled to 25 °C and filtered. The filtrant was dried 24 h at 10^{-5} Torr and 150 °C to yield 11.3 g (49%) of **20** as off-white crystals: mp >360 °C; R_f 0.67 (silica gel, $CHCl_3$); ^1H NMR (2:1 CS_2/CD_2Cl_2) δ 1.21 (t, J = 8.4 Hz, CH_3, 12 H), 2.59 (q, J = 8.4 Hz, CH_2 of Et, 8 H), 4.41 (d, J = 7.0 Hz, OCH_2O, 4 H), 5.99 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.35 (s, Ar_3CH, 4 H), 6.82 (s, ArH para to Br, 4 H), 7.11 (s, ArH, 16 H); MS (EI, 70 eV) 1:4:6:4:1 Br_4 isotope pattern centered at *m/e* 1268 ($M^+ + 4$, 100). Anal. Sample dried 24 h at 10^{-5} Torr, 150 °C. Calcd for $C_{64}H_{52}Br_4O_8$: C, 60.59; H, 4.13. Found: C, 60.50; H, 4.25.

7,11,15,28-Tetrabromo-1,21,23,25-tetrakis(4-bromophenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]-benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (Stereoisomer, 21). Compound **21** was prepared from octol **15** by using the procedure described above for formation of **20** from **14**. Similar molar ratios of solvent and reagents were employed. The only variation from the procedure was that the crude product/silica gel mixture was added to the top of the chromatography column portionwise. This was necessary because **21** tends to crystallize and clog the column. Application of this procedure to 26.0 g (18.3 mmol) of octol **15** gave 12.3 g (46%) of compound **21** as an off-white powder: mp >360 °C; R_f 0.71 (silica gel, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.53 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.07 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.43 (s, Ar_3CH, 4 H), 6.81 (s, ArH para to Br, 4 H), 7.12 (d, J = 8.5 Hz, ArH meta to Br, 8 H), 7.43 (d, J = 8.5 Hz, ArH ortho to Br, 8 H); MS (FAB, NOBA) complex isotope pattern centered near *m/e* 1472 ($M^+ + 8$, 80). Anal. Sample dried 12 h at 10^{-1} Torr, 110 °C. Calcd for $C_{56}H_{32}Br_8O_8$: C, 45.69; H, 2.19. Found: C, 45.80; H, 2.19.

1,21,23,25-Tetraphenyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis-[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin-7,11,15,28-tetracarboxylic Acid, Tetramethyl Ester (Stereoisomer, 22). To a mixture of 60 mL of tetrahydrofuran and 6.5 mL of 1.8 M (8.65 mmol) phenyllithium was quickly added under a stream of nitrogen 1.00 g (0.865 mmol) of uncomplexed host **17**. This inverse addition helps suppress reduction of the bromide by adventitious water. The solution was stirred for 1 h, cooled to −78 °C, and cannulated into a rapidly stirred solution of 4.0 mL (43.2 mmol) of methyl chloroformate in 75 mL of tetrahydrofuran at −78 °C. The solution was warmed to 25 °C, and the solvent was removed in vacuo. The residue was partitioned between CH_2Cl_2 and water, and the organic phase was dried ($MgSO_4$). The solution was filtered, and the solvent was removed in vacuo. The residue was chromatographed on 250 g of silica gel with a gradient of 4–6% EtOAc in CH_2Cl_2 as the mobile phase. Fractions corresponding to product were combined and the solvent was removed in vacuo. The residue was dissolved in 250 mL of refluxing tetrahydrofuran, and the solvent was evaporated in vacuo (guest exchange). The residue was dried 3 h at 10^{-1} Torr and 145 °C to yield 0.690 g (74%) of **22**·$1.2C_4H_8O$: mp >360 °C; R_f 0.23 (silica gel, 19:1 CH_2Cl_2/EtOAc); ^1H NMR ($CDCl_3$) δ 1.81–1.92 (m, tetrahydrofuran protons β to oxygen, 4.8 H), 3.70–3.80 (m, tetrahydrofuran protons α to oxygen, 4.8 H), 3.92 (s, OCH_3, 12 H), 4.74 (d, J = 7.5 Hz, OCH_2O, 4 H), 5.76 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.41 (s, Ar_3CH, 4 H), 7.02 (s, ArH para to CO_2Me, 4 H), 7.15–7.35 (m, ArH, 20 H); MS (EI, 70 eV) *m/e* 1072 (M^+, 100). Anal. Sample dried 3 h at 10^{-1} Torr, 145 °C. Calcd for $C_{64}H_{48}O_{16}$·$1.2C_4H_8O$·H_2O: C, 70.17; H, 5.10. Found: C, 70.51; H, 5.49.

1,21,23,25-Tetrakis(4-methylphenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin-7,11,15,28-tetracarboxylic Acid, Tetramethyl Ester (Stereoisomer, 23). The procedure described above for preparation of tetraester **22** from tetrabromide **17** was applied to 1.00 g (0.824 mmol) of tetrabromide **19**. Similar molar proportions of solvent and reagents were used. Chloroform was used in place of CH_2Cl_2 in the extractive workup because **23** is relatively insoluble in the latter solvent. This compound was triturated to purity without recourse to chromatography. Thus the crude product was stirred for 1 h with 200 mL of 1:1 CH_2Cl_2/CS_2 and filtered. The solid was dissolved in 200 mL of $CHCl_3$ and the solvent was removed in vacuo (guest exchange). The resulting solid was dried for 4 h at 10^{-1} Torr and 110 °C to yield 0.535 g (57%) of **23** as a white powder: mp >360 °C; R_f 0.35 (silica gel, 19:1 CH_2Cl_2/EtOAc); ^1H NMR ($CDCl_3$) δ 2.31 (s, $ArCH_3$, 12 H), 3.90 (s, OCH_3, 12 H), 4.73 (d, J = 7.5 Hz, OCH_2O, 4 H), 5.75 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.34 (s, Ar_3CH, 4 H), 7.05 (s, ArH para to CO_2Me, 4 H), 7.07–7.20 (m, ArH, 16 H). MS (EI, 16 eV) *m/e* 1128 (M^+, 100). Anal. Sample dried 4 h at 10^{-1} Torr, 110 °C. Calcd for $C_{68}H_{56}O_{16}$: C, 72.33; H, 5.00. Found: C, 72.35; H, 5.08.

1,21,23,25-Tetrakis(4-ethylphenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin-7,11,15,28-tetracarboxylic Acid, Tetramethyl Ester (Stereoisomer, 24). The procedure described above for the preparation of cavitand **22** from tetrabromide **17** was applied to 5.00 g (3.94 mmol) of tetrabromide **20**. Similar molar ratios of solvent and reagents were used. This compound could be crystallized to purity without recourse to chromatography. Thus the crude product was dissolved in 100 mL of CH_2Cl_2 and 75 mL of CH_3OH was added. The volume was reduced to

75 mL, and the precipitate was collected by filtration. This solid was then crystallized from a minimum volume of hot CCl_4. The solid was dissolved in 100 mL of tetrahydrofuran which was then removed in vacuo (guest exchange). The residue was dried 6 h at 10^{-2} torr and 110 °C to yield 3.00 g (64%) of **24** as a white powder: mp >360 °C; R_f 0.31 (silica gel, 19:1 CH_2Cl_2/EtOAc); ^1H NMR ($CDCl_3$) δ 1.23 (t, J = 7.5 Hz, CH_3 of ArEt, 12 H), 2.60 (q, J = 7.5 Hz, CH_2 of ArEt, 8 H), 3.91 (s, OCH_3, 12 H), 4.73 (d, J = 7.5 Hz, OCH_2O, 4 H), 5.75 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.36 (s, Ar_3CH, 4 H), 7.09 (s, ArH para to CO_2Me, 4 H), 7.11–7.22 (m, ArH, 16 H); MS (FAB, NOBA) m/e 1185 (M^+ + 1, 88), 1153 ($M^+ - OCH_3$, 100). Anal. Sample dried 6 h at 10^{-2} Torr, 110 °C. Calcd for $C_{72}H_{64}O_{16}$: C, 72.96; H, 5.44. Found: C, 72.99; H, 5.49.

7,11,15,28-Tetrakis(butoxymethyl)-1,21,23,25-tetraphenyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (Stereoisomer, 25). To a suspension of 0.549 g (0.512 mmol) of compound **22** in 150 mL of tetrahydrofuran was added ca. 0.5 g (13 mmol) of $LiAlH_4$. The mixture was stirred for 3 h and quenched by adding water dropwise until gas evolution ceased. An additional 0.2 mL of water was added, and the solvent was removed in vacuo. The residue was placed in a Soxhlet extractor and extracted for 24 h with a 3:1 mixture of $CHCl_3$/$(CH_2)_4O$. Evaporation of the extract in vacuo gave 0.533 g (88%) of the corresponding tetrol as an off-white powder: ^1H NMR (3:1 $CDCl_3$/$(CD_3)_2SO$) δ 4.50–4.60 (overlapping s, OH and $ArCH_2O$, 12 H), 4.78 (d, J = 7.5 Hz, OCH_2O, 4 H), 5.96 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.43 (s, Ar_3CH, 4 H), 7.09 (s, ArH para to hydroxymethyl, 4 H), 7.2–7.4 (m, ArH, 20 H); MS (FAB, NOBA) m/e 961 (M^+ + 1, 3), 913 ($M^+ - CH_2OH - OH$ + 1, 27). The elemental analysis of this compound suggested that it was contaminated with substantial amounts of inorganic material.

A suspension of 0.497 g (0.518 mmol) of this tetrol in 70 mL of tetrahydrofuran was treated with 0.124 g (5.18 mmol) of oil-free NaH and 1.59 mL (14.0 mmol) of 1-iodobutane. After refluxing of the mixture for 48 h, the excess NaH was cautiously quenched with water. The solvent was removed in vacuo, and the residue was partitioned between CH_2Cl_2 and water. The organic extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. The residue was chromatographed on 50 g of silica gel with a gradient elution of 50–70% CH_2Cl_2 in cyclohexane. The product was dissolved in 100 mL of CCl_4, which was then removed in vacuo (guest exchange). This material was dried for 24 h at 10^{-5} torr and 140 °C to give 0.320 g (52%) of **25** as a white solid: mp 271–273 °C; R_f 0.42 (silica gel, 3:1 methylene chloride/hexanes); ^1H NMR (CCl_4, C_6D_6 coaxial tube, TMS in CCl_4) δ 0.73 (t, J = 7.0 Hz, terminal CH_3 of butoxymethyl, 12 H), 1.20–1.37 (m, CH_2, 8 H), 1.37–1.57 (m, CH_2, 8 H), 3.41 (t, J = 6.5 Hz, OCH_2R, 8 H), 4.39 (s, $ArCH_2O$, 8 H), 4.57 (d, J = 7.5 Hz, OCH_2O, 4 H), 5.78 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.39 (s, Ar_3CH, 4 H), 6.93 (s, ArH para to butoxymethyl, partially obscured by residual proton peak of C_6D_6), 7.00–7.37 (m, ArH, 20 H). In $(CD_3)_2SO$ the following spectrum was obtained: δ 0.87 (t, J = 7.0 Hz, terminal CH_3 of butoxymethyl, 12 H), 1.20–1.39 (m, CH_2, 8 H), 1.40–1.55 (m, CH_2, 8 H), 3.47 (t, J = 6.5 Hz, OCH_2R, 8 H), 4.32 (s, $ArCH_2O$, 8 H), 4.52 (d, J = 7.0 Hz, OCH_2O, 4 H), 5.96 (d, J = 7.0 Hz, OCH_2O, 4 H), 6.27 (s, Ar_3CH, 4 H), 7.05–7.39 (m, ArH, 24 H); MS (FAB, NOBA) m/e 1185 (M^+ + 1, 45). Anal. Sample dried 24 h at 10^{-5} Torr, 140 °C. Calcd for $C_{76}H_{80}O_{12}$: C, 77.00; H, 6.80. Found: C, 76.88; H, 6.88.

7,11,15,28-Tetrakis(butoxymethyl)-1,21,23,25-tetrakis(4-ethylphenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (Stereoisomer, 26). Compound **24** was reduced with lithium aluminum hydride under the conditions described for the preparation of **25**. Similar molar ratios of solvent and reagents were used. Application of this procedure to 2.90 g (2.59 mmol) of **24** gave 1.44 g (55%) of the corresponding tetrol as a white powder: ^1H NMR ($(CD_3)_2SO$) δ 1.16 (t, J = 7.5 Hz, CH_3 of ArEt, 12 H), 2.52 (q, J = 7.5 Hz, CH_2 of ArEt, partially obscured by residual proton peak of solvent), 4.44 (d, J = 4.3 Hz, $ArCH_2O$, 8 H), 4.64 (d, J = 7.5 Hz, OCH_2O, 4 H), 4.91 (t, J = 4.3 Hz, OH, 4 H), 5.95 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.25 (s, Ar_3CH, 4 H), 7.16 (overlapping s, ArH, 20 H). The elemental analysis of this compound suggested that it was contaminated with substantial amounts of inorganic material. Alkylation of this material to give **26** was accomplished under the conditions described for the preparation of **25**. From 1.20 g of tetrol was obtained 0.217 g (15%) of **26** as a white powder: mp 272–274 °C; R_f 0.52 (silica gel, CH_2Cl_2); ^1H NMR (CCl_4, $(CD_3)_2CO$ coaxial tube, TMS in CCl_4) δ 0.70 (t, J = 7.0 Hz, terminal CH_3 of butoxymethyl, 12 H), 1.19 (t, J = 8.0 Hz, CH_3 of ArEt, 12 H), 1.19–1.32 (m, butyl CH_2, 8 H), 1.36–1.52 (m, butyl CH_2, 8 H), 2.55 (q, J = 8.0 Hz, CH_2 of ArEt, 8 H), 3.39 (t, J = 6.0 Hz, OCH_2R, 8 H), 4.38 (s, $ArCH_2O$, 8 H), 4.55 (d, J = 7.5 Hz, OCH_2O, 4 H), 5.75 (d, J = 7.5 Hz, OCH_2O, 4 H), 6.35 (s, Ar_3CH, 4 H), 6.95 (d, J = 8.0 Hz, ArH meta to Et, 8 H), 6.99 (s, ArH para to butoxymethyl, 4 H), 7.15 (d, J = 8.0 Hz, ArH ortho to Et, 8 H); MS (FAB, NOBA) m/e 1296 (M^+, 40). Anal. Sample dried 24 h at 10^{-5} Torr, 145 °C. Calcd for $C_{84}H_{96}O_{12}$: C, 77.75; H, 7.48. Found: C, 77.77; H, 7.53.

5,5,9,9,13,13,17,17-Octabutyl-1,21,23,25-tetrakis(4-bromophenyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxasilocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxasilocin (Stereoisomer, 27). A solution of 6.53 mL (30.3 mmol) of dibutyldichlorosilane in 500 mL of tetrahydrofuran was added dropwise over 18 h to a vigorously stirred suspension of 7.00 g (6.31 mmol) of octol **15** and 31.5 mL (227 mmol) of triethylamine in 1.5 L of tetrahydrofuran. The mixture was stirred an additional 24 h and then the solvent was removed in vacuo. This crude mixture was filtered through 150 g of silica gel in a 350-mL fritted-glass funnel with 1.0 L of 35% CH_2Cl_2 in cyclohexane as the mobile phase. The solvent was removed in vacuo. The residue was recrystallized by partial evaporation in vacuo of its solution in 3:1 CH_2Cl_2/CH_3OH. This procedure gave 6.61 g (63%) of compound **27** as a white solid: mp >300 °C; R_f 0.41 (silica gel, 3:1 C_6H_{12}/CH_2Cl_2); ^1H NMR ($CDCl_3$), δ 0.37 (br t, J = 7.5 Hz, $SiCH_2R$ (in), 8 H), 0.58 (t, J = 7.0 Hz, CH_3, 12 H), 0.86–1.05 (m, CH_2, 16 H), 0.91 (t, J = 7.5 Hz, CH_3, 12 H), 1.05–1.27 (m, CH_2, 8 H), 1.27–1.63 (m, CH_2, 16 H), 6.06 (s, Ar_3CH, 4 H), 6.41 (s, ArH ortho to silyloxy, 4 H), 6.80 (s, ArH meta to silyloxy, 4 H), 7.08 (d, J = 8.1 Hz, ArH meta to Br, 8 H), 7.34 (d, J = 8.1 Hz, ArH ortho to Br, 8 H); MS (FAB, NOBA) m/e 1670 (M^+, 100). Anal. Sample dried 3 h at 10^{-2} Torr, 150 °C. Calcd for $C_{84}H_{100}Br_4Si_4O_8$: C, 60.43; H, 6.04. Found: C, 60.50; H, 6.04.

5,5,9,9,13,13,17,17-Octabutyl-1,21,23,25-tetrakis[4-(trimethylstannyl)phenyl]-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxasilocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxasilocin (Stereoisomer, 28). A solution of 0.700 g (0.420 mmol) of tetrabromide **27** in 30 mL of 2:1 diethyl ether/tetrahydrofuran was cooled to −120 °C in a liquid nitrogen/absolute ethanol slush bath. To this mixture was added 1.97 mL (3.36 mmol) of 1.7 M *tert*-butyllithium. After an additional 6 min at −120 °C, a solution of 0.811 g (4.03 mmol) of trimethyltin chloride (**highly toxic and volatile**) in 7 mL of diethyl ether was added over 3 min. The mixture was allowed to warm to 25 °C over 2 h. The excess trimethyltin chloride was destroyed by adding 10 mL of 3 M monosodium phosphate solution and stirring for 20 min. Methylene chloride (80 mL) was then added, and the phases were separated. The organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo. The residue was eluted through a 1-in. pad of silica gel in a 30-mL fritted funnel with 3:1 C_6H_{12}/CH_2Cl_2. The solvent was removed in vacuo and the residue was recrystallized by partial evaporation in vacuo of its solution in 2:1 CH_2Cl_2/CH_3COCH_3. This procedure gave 0.56 g (66%) of **28** as a white powder: mp ca. 250 °C dec; R_f 0.61 (silica gel, 7:3 C_6H_{12}/CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.25 (s, Me_3Sn, 36 H), 0.36 (br t, J indet., $SiCH_2R$ (in), 8 H), 0.58 (t, J = 7.0 Hz, CH_3, 12 H), 0.86–1.05 (m, CH_2, 16 H), 0.91 (t, J = 7.0 Hz, CH_3, 12 H), 1.07–1.30 (m, CH_2, 8 H), 1.27–1.60 (m, CH_2, 16 H), 6.17 (s, Ar_3CH, 4 H), 6.41 (s, ArH ortho to silyloxy, 4 H), 7.01 (s, ArH meta to silyloxy, 4 H), 7.23 (d, J = 8.0 Hz, ArH meta to Me_3Sn, 8 H), 7.34 (d, J = 8.0 Hz, ArH ortho to Me_3Sn, 8 H). In addition to these peaks, small satellite peaks were visible at δ 0.12 and 0.39 due to $^{117}Sn/^{119}Sn$ geminal coupling and at δ 7.39–7.48 due to $^{117}Sn/^{119}Sn$ ortho coupling. Each satellite peak taken individually had about 10% the intensity of its parent peak.[19] Anal. Sample dried 12 h at 10^{-1} Torr, 80 °C. Calcd for $C_{96}H_{136}O_8Si_4Sn_4$: C, 57.50; H, 6.81. Found: C, 57.56; H, 6.77.

5,5,9,9,13,13,17,17-Octabutyl-1,21,23,25-tetrakis[4-iodophenyl]-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxasilocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxasilocin (Stereoisomer, 29). A solution of 0.300 g (150 mmol) of tetrakis(trimethylstannyl) cavitand **28** in 10 mL of CH_2Cl_2 was treated with 0.157 g (0.615 mmol) of iodine. This mixture was stirred at 25 °C for 2 h. The excess iodine was then quenched by addition of sodium thiosulfate solution, and the phases were separated. The aqueous phase was washed twice with 5 mL of CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$). The solution was filtered, 5 mL of acetonitrile was added, and the volume was reduced in vacuo to 7 mL. The resulting white precipitate was collected by filtration (The mother liquor contains a highly volatile and malodorous substance. **Inhalation and skin contact should be avoided** as this is probably a organotin residue.[20]) In some cases a minor impurity was observed in the ^1H NMR spectrum at δ 7.25–7.30. This impurity could be removed by crystallization from hot 2-butanone (15 mL/g compound, allowed to stand 2–3 days). This procedure gave 0.220 g (79%) of tetraiodide **29** as white crystals: mp 326–327 °C dec; R_f 0.45 (silica gel, 7:3 C_6H_{12}/CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.37 (br t, J = 8.0 Hz, $SiCH_2R$ (in), 8

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H), 0.57 (t, J = 7.0 Hz, CH_3, 12 H), 0.80-1.08 (m, CH_2 and CH_3, 28 H), 1.10-1.33 (m, CH_2, 8 H), 1.35-1.62 (m, CH_2, 16 H), 6.06 (s, Ar_3CH, 4 H), 6.41 (s, ArH ortho to silyloxy, 4 H), 6.80 (s, ArH meta to silyloxy, 4 H), 6.94 (d, J = 7.0 Hz, ArH meta to I, 8 H), 7.54 (d, J = 7.0 Hz, ArH ortho to I, 8 H); MS (FAB, NOBA) m/e 1857 (M^+ + 1, 100). Anal. Sample dried 12 h at 10^{-1} Torr, 65 °C. Calcd for $C_{84}H_{100}I_4Si_4O_8$: C, 54.31; H, 5.43. Found: C, 54.48; H, 5.50.

5,5,9,9,13,13,17,17-Octabutyl-1,21,23,25-tetrakis[4-[(trimethylsilyl)-ethynyl]phenyl]-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxa-silocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxasilocin (Stereoisomer, 30). To a suspension of 0.743 g (0.400 mmol) of tetraiodide **29** in 50 mL of triethylamine were added 0.48 mL (3.42 mmol) of (trimethylsilyl)acetylene, 0.041 g (0.214 mmol) of copper(I) iodide, and 0.125 g (0.175 mmol) of bis(triphenylphosphine)palladium(II) dichloride. The mixture slowly turned green and then black. After 18 h the mixture was diluted with 50 mL of CH_2Cl_2 (to dissolve the product) and filtered, and the solvent was removed in vacuo. The residue was partitioned between CH_2Cl_2 and distilled water. The organic phase was dried ($MgSO_4$) and filtered. The solvent was removed in vacuo. The residue was chromatographed on 15 g of silica gel with 7:3 C_6H_{12}/CH_2Cl_2. Fractions corresponding to product were combined, and the solvent was removed in vacuo. The residue was dissolved in 80 mL of $(CH_3)_2NCHO$. The solution was allowed to cool very slowly to -10 °C. The precipitate was collected by filtration to give 0.367 g (53%) of compound **30** as a white powder: mp 349-350 °C; R_f 0.80 (silica gel, 3:2 C_6H_{12}/CH_2Cl_2); ^1H NMR ($CDCl_3$), δ 0.25 (s, Me_3Si, 36 H), 0.33 (br t, J indet, $SiCH_2R$ (in), 8 H), 0.57 (t, J = 7.0 Hz, CH_3, 12 H), 0.90-1.05 (m, CH_2, 16 H), 0.92 (t, J = 7.0 Hz, CH_3, 12 H), 1.08-1.30 (m, CH_2, 8 H), 1.32-1.61 (m, CH_2, 16 H), 6.09 (s, Ar_3CH, 4 H), 6.41 (s, ArH ortho to silyloxy, 4 H), 6.74 (s, ArH meta to silyloxy, 4 H), 7.13 (d, J = 8.0 Hz, ArH meta to ethynyl, 8 H), 7.34 (d, J = 8.0 Hz, ArH ortho to ethynyl, 8 H); MS (FAB, NOBA) m/e 1736 (M^+, 100). Anal. Sample dried 12 h at 10^{-1} Torr, 110 °C. Calcd for $C_{104}H_{136}O_8Si_8$: C, 71.83; H, 7.88. Found: C, 71.74; H, 7.90.

Crystal Structure Data. Compound **16**·C_6H_6 crystallizes from CH_2Cl_2 as colorless parallelepipeds in the orthorhombic system $P2_12_12$. Unit-cell dimensions are as follows: a = 11.969 (4) Å, b = 16.858 (5) Å, c = 11.410 (4) Å, V = 2302 Å^3, Z = 2 (four half molecules, related by a two-fold axis). The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by direct methods. Refinement of 308 parameters (2020 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.068.

Compound **16**·CH_2Cl_2·$(CH_3)_2C{=}O$ crystallizes from CH_2Cl_2/$(CH_3)_2C{=}O$ as large colorless, irregular fragments in the triclinic system $P\bar{1}$. Unit-cell dimensions are as follows: a = 10.836 (2) Å, b = 12.356 (2) Å, c = 20.057 (4) Å, α = 90.597 (5)°, β = 80.509 (6)°, γ = 114.290 (5)°, V = 2404 Å^3, Z = 2. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by direct methods. Refinement of 103 parameters (5826 reflections with $I > 3\sigma(I)$) has an R currently at 0.09.

Compound **20**·$2C_6H_5CH_3$ crystallizes from $C_6H_5CH_3$ as colorless fragments in the rhombohedral system $R3$. Unit-cell dimensions are as follows: a = 18.52 Å, γ = 109.60°, V = 4880 Å^3, Z = 3. Hexagonal indices are a = 30.298 (3) Å, c = 18.422 (2) Å, V = 14645 Å^3, Z = 9. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by heavy-atom methods. Refinement of 348 parameters (2656 reflections with $I > 3\sigma(I)$) has an R currently at 0.10.

Compound **20**·$2C_6H_5Br$ crystallizes from C_6H_5Br as colorless multi-faceted crystals in the rhombohedral system $R3$. Unit cell dimensions are as follows: a = 18.777 (2) Å, γ = 109.81 (2), V = 5030 Å^3, Z = 3. Hexagonal indices are a = 30.749 (3) Å, c = 18.459 (2) Å, V = 15097 Å^3, Z = 9. The crystal was examined on a Huber diffractometer, with Mo Kα radiation, at 298 K. The structure was determined by heavy-atom methods. Refinement of 305 parameters (2790 reflections with $I > 3\sigma(I)$) has an R currently at 0.10.

Compound **23**·$3(CH_3)_2C{=}O{\cdot}CHCl_3$ crystallizes from CH_2Cl_2 as colorless parallelepipeds in the orthorhombic system $Pbnn$ (standard setting $Pnna$). Unit-cell dimensions are as follows: a = 12.772 (10) Å, b = 24.284 (18) Å, c = 22.276 (17) Å, V = 6950 Å^3, Z = 4. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 128 K. The structure was determined by direct methods. Refinement of 225 parameters (2880 reflections with $I > 3\sigma(I)$) has an R currently at 0.18.

Compound **28** crystallizes from $(C_2H_5)_2O$ as colorless needles in the monoclinic system $C2/c$. Unit-cell dimensions are as follows: a = 29.561 (2) Å, b = 18.486 (1) Å, c = 22.594 (2) Å, β = 119.745 (2)°, V = 10725 Å^3, Z = 4 (eight half molecules related by a two-fold axis). The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 305 parameters (3342 reflections with $I > 3\sigma(I)$ has an R currently at 0.089.

Further crystallographic details will be published elsewhere.

Quantitative Binding of CD_3CN by 26. These studies were conducted by utilizing chemical shift changes in the 200-MHz ^1H NMR spectra of 0.0016-0.0035 M **26** in CCl_4 (containing 0.3% by volume of $(CH_3)_4Si$) induced by incremental guest additions at three different temperatures. An internal coaxial tube containing C_6D_6 or $(CD_3)_2CO$ was employed to provide a deuterium lock signal. A small quantity (2-10 μL) of a 1-100% v/v solution of the guest in CCl_4 was then added via a syringe and the ^1H NMR spectrum of the solution was redetermined. If the experiment was conducted at a temperature other than 298 K, the sample was equilibrated in the spectrometer probe 10 min before determination of the spectrum. This process was repeated until a minimum of five points were obtained which appeared to be reasonably well spaced with regard to the chemical shift changes occurring in the host. Table IV of the supplemental material tabulates the resulting chemical shift changes.

Supplementary Material Available: Table of chemical shifts (Table IV), plots of chemical shift vs concentration of CH_3CN (Figures 6-10), van't Hoff plots (Figures 11 and 12) (4 pages). Ordering information is given on any current masthead page.

Bilayer-Type Crystal Structure of 4-(2-Anthryl)-1-butanoic Acid

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Abstract: 4-(2-Anthryl)-1-butanoic acid crystallizes in the centrosymmetric, monoclinic space group $C2/c$; a = 51.337 (9) Å, b = 6.022 (2) Å, c = 8.969 (2) Å, β = 92.68 (2)°, Z = 8. This crystal has a bilayer structure with two bilayers per unit cell. The packing of the anthracene moieties is quite similar to that of unsubstituted anthracene. Neighboring anthracene bilayers are separated by hydrogen-bonded butanoic acid chains.

Truly crystalline molecular two-dimensional systems of molecular chromophores are of considerable interest since unusual properties are expected for coherent electronic excited states[1,2] and for incoherent exciton and charge-carrier transport.[3,4] A

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