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Biscavitands II: Self-Inclusion in a Back-to-Back Connected Biscavitand

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Abstract

A foot-to-foot or 'back-to-back' connected biscavitand is prepared directly from a hexadecol resorcinarene precursor. The axial orientation of the biphenyl linker and hence the crown conformation of the hexadecol was established by an X-ray crystal study of the biscavitand. Each cavitand bowl is filled in the crystal by an alkyl 'foot' from the next molecule, a self-inclusion which results in polymeric host–guest chains. The new biscavitand differs from previously prepared Z and C isomers of a bowl-to-bowl or 'front-to-front' connected host, which crystallize as chains of carcerand-like, solvent-filled cages or as distinct molecules of hemicarceplex, respectively.

Introduction

Stable molecular vessels or receptors with defined dimensions are important for the construction of various multidimensional supramolecular systems [1]. Cavitands [2], with rigid bowls, are examples of such receptors. Carcerands [1, 2] and self-assembling molecular capsules [3] are larger molecules, constructed from cavitands, with defined inner cavities and substantial activation barriers for the complexation-decomplexation of guests. Many container hosts are prepared from resorcin[4]arenes, octols formed by the fourfold homogeneous condensations of various aldehydes (RCHO) with resorcinol or 2-substituted resorcinols [4]. The facile functionalization of these octols makes them versatile starting materials for large hosts capable of complexing several molecules [5]. A crown-conformation cavitand made from a resorcin[4]arene has two potential receptor sites, the oxygen-containing 'bowl' and the cavity formed by the 'feet' (R groups of RCHO), which can be rigidified or functionalized [6].

Biscavitands, with four cavities, have previously been prepared by bridging two cavitands 'front-to-front' through their oxygen-containing bowls. Both C and Z isomers were formed. The convergent C isomers bound guests cooperatively in solution, while the Z isomers showed no evidence of binding [7].

The new biscavitands presented here were prepared *directly* from hexadecols. The statistical condensation of resorcinol, octanal and 4,4′-diformylbiphenyl gave hexadecol **1** [8]. When 2-methylresorcinol was substituted for resorcinol, hexadecol **2** was the product. Each hexadecol consists of two octols connected 'back-to-back', through their 'feet,' by biphenyl (Chart 1). The absolute stereochemistry of the methine protons at the bridging carbons, which is critical in determining the geometry of the two bowls and accordingly the binding mode with potential guests, cannot be assigned from ^{1}H NMR in solution.

For hexadecols **1** and **2** the methine protons appeared as singlets at 6.09 and 6.11 ppm in CD_3COCD_3, respectively [8]. If these protons are equatorial and the biphenyl group is axial, the two bowls would face in the opposite direction and be separated as far as possible as shown in Chart 1. Indeed this 'crown' or *rccc* geometry is anticipated from the general tendency of the cyclotetramerization reaction [4]. However, if the biphenyl group were equatorial (Chart 2), as in some octols with aromatic R groups [4], the two bowls need not face in opposite directions. Several *rctt* or chair-conformation cavitands and resorcin[4]arenes have been synthesized [9].

The divergent Z isomer of front-to-front biscavitand **6** (Chart 3), whose preparation and preliminary crystal structure have been reported [7], resembles **5** in its *anti* configuration. In contrast, the convergent C isomer of **6** [7] is a hemicarcerand.

This paper presents the X-ray structural analysis of **5**, with a comparison of the solid-state inclusion properties of biscavitands **5**, **Z-6**, and **C-6**.

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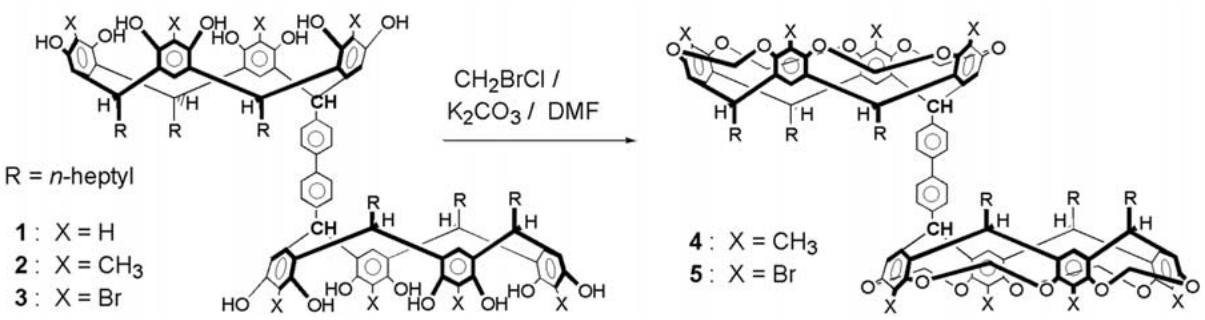

Chart 1. Preparation of back-to-back biscavitands from hexadecols.

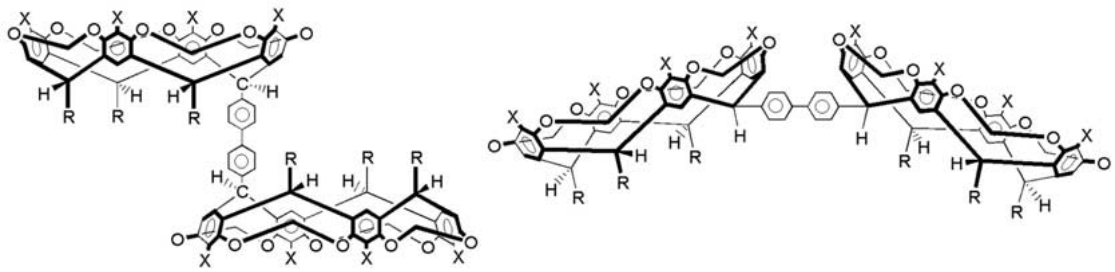

Chart 2. An axially linked (left) and an equatorially linked (right) back-to-back biscavitand.

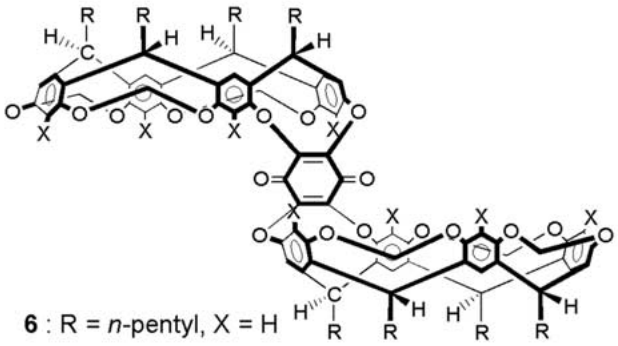

Chart 3. A Z biscavitand joined 'front-to-front' or bowl-to-bowl by a quinone bridge [7].

Experimental

*Preparation and characterization of biscavitands **4** and **5***

Hexadecol **1** was perbrominated with NBS to octabromohexadecol **3**. Compounds **2** and **3** were rigidified to biscavitands **4** and **5** (Chart 1) by spanning adjacent hydroxy groups with methylene units [10]. Compounds **3**, **4** and **5** were prepared in 57.7%, 36.4% and 32.0% yields respectively and were fully characterized by ^{1}H NMR and FAB+ mass spectra as well as by elemental analyses. The bridging methine protons of biscavitands **4** and **5** appear as singlets at 6.46 and 6.56 ppm, respectively, in ^{1}H NMR spectra in $CDCl_3$, from which their absolute stereochemistry cannot be determined. (See the Appendix for details.)

*X-ray analysis of biscavitand **5**·6$C_6H_5NO_2$*

Colorless crystals of **5** were obtained from a nitrobenzene solution and the structure was determined at room temperature. Data collection and refinement parameters appear in Table 1.

The structure was solved by direct methods and refined by full-matrix least squares. Bromine and cavitand oxygen atoms and some C atoms in the 'feet' were refined anisotropically; all other non-H atoms were refined isotropically. H atoms were refined with geometric constraints. The nitrobenzene solvent molecules were refined with rigid phenyl groups and with bond length restraints; one of the solvent molecules (N21N–H26P, N21B–H26B) is disordered. Three C atoms (C15–C17) in one of the 'feet' are also disordered. The Crystallographic Information File (CIF) has been deposited with the Cambridge Crystallographic Data Centre (CCDC 161206).

*X-ray analysis of biscavitand Z-**6**·6$C_6H_5NO_2$ and of hemicarceplex C-**6**·5CH_3CN*

The C and Z isomers of **6** were both present in the synthetic product [7]. The isomers were separated by silica gel chromatography and the identity of each was established by x-ray crystallography. Yellow crystals of Z-**6**·6$C_6H_5NO_2$, prepared from nitrobenzene solution, diffracted weakly (Table 1). The structure was solved by direct methods and refined by full-matrix least squares; all non-H atoms were refined isotropically and H atoms were refined with geometric constraints. The three independent nitrobenzene molecules were refined with rigid phenyl groups. One of them is partially disordered, with occupancy 0.70 and 0.30 respectively for the two NO_2 groups. The Crystallographic Information File (CIF) has been deposited with the Cambridge Crystallographic Data Centre (CCDC 182387).

A weakly-diffracting yellow crystalline plate of C-**6**·5CH_3CN obtained from CH_2Cl_2/CH_3CN solution was analyzed at room temperature in a sealed capillary in the

Table 1. Crystal data and parameters of refinement

Compound	**5**·6$C_6H_5NO_2$	Z-**6**·6$C_6H_5NO_2$	C-**6**⊙2CH_3CN·3CH_3CN
Formula	$C_{154}H_{160}Br_8N_6O_{28}$	$C_{144}H_{154}N_6O_{30}$	$C_{118}H_{139}N_5O_{18}$
Formula weight	3182.16	2448.73	1915.34
Space group	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2
Z	1	1	2
Cryst dimen/mm	0.20 × 0.20 × 0.20	0.15 × 0.15 × 0.20	0.08 × 0.15 × 0.35
a/Å	11.9400(9)	12.5480(18)	16.4340(16)
b/Å	13.1043(10)	12.7420(19)	17.4470(15)
c/Å	23.947(2)	20.932(3)	19.8880(18)
α/°	87.489(2)	90.628(4)	82.065(3)
β/°	86.292(2)	104.657(4)	83.242(3)
γ/°	80.794(2)	93.028(4)	80.229(3)
V/Å^3	3688.7(5)	3232.3(8)	5539.8(9)
(h k l) range	0 → 14,	0 → 13,	0 → 16,
	−15 → 15,	−13 → 13,	−16 → 17,
	−28 → 28	−22 → 21	−19 → 19
λ/Å	0.7107, MoK_α	0.7107, MoK_α	1.54180, CuK_α
unique refls	13011	8466	11395
Refls Obs, $I > 2\sigma(I)$	3259	2122	3011
θ_{max}/°	25.00	22.50	50.00
Parameters	510	338	740 (two blocks)
$R(F)_{obs}$	0.070	0.144	0.142
$wR(F^2)$	0.257	0.434	0.421

presence of solvent (Table 1). The structure was solved by direct methods and refined by least squares in two blocks. All O atoms, 6 C atoms in the 'feet,' and two N atoms were refined anisotropically. Hydrogen atoms were refined with geometric constraints. Although it was earlier thought that one bowl cavity contained CH_2Cl_2 [7], the final model includes only acetonitrile molecules, one disordered in each of the bowls, one disordered interstitially, and one ordered acetonitrile nesting in each partially disordered 'foot' cavity. Thus a better formula for the structure is **6**⊙2CH_3CN·3CH_3CN. The Crystallographic Information File (CIF) has been deposited with the Cambridge Crystallographic Data Centre (CCDC 182301).

Results

*The structure of biscavitand **5***

Figure 1 provides a stereoview of biscavitand **5**. The molecule is centrosymmetric; the side view (Figure 1) clearly shows the connectivity of the cavitand units through the axial biphenyl linker. The center of symmetry between them requires the two rings of the biphenyl moiety to be parallel. The atoms Br22–Br33–Br39–Br66 are coplanar within 0.035 Å, and the distance between the centroids of the four bromine atoms determining each of the centrosymmetrically related planes in the biscavitand is 18.09 Å.

The cavitand bowls are filled by the terminal propyl group of the C51 foot of the next molecule along the *b* axis. (See *Packing* section below.) Close contacts include H49B···Br22, 3.11 Å, and H50B···Br66, 3.32 Å. The dimensions and conformation of the bowls in the biscavitand resemble those of its monotopic relatives [10].

*The structures of biscavitand Z-**6**·6$C_6H_5NO_2$ and of hemicarcerand C-**6**·5CH_3CN*

A molecule of biscavitand Z-**6** with its guests is shown in a side stereoview in Figure 2. Like **5**, Z-**6** is centrosymmetric, and the bowls face in opposite directions, though the bowl-to-bowl linkage brings the bowls closer to each other in Z-**6** than in **5**. The geometry and conformation of the rest of the bowl remain unchanged after bridging with the quinone moiety. While Z-**6** does not complex $C_6D_5NO_2$ in the presence of solvents such as CCl_4 or CH_2Cl_2 [7], nitrobenzene does perform the role of guest in the crystal. The distance between the centroids of the guest phenyl rings as shown in Figure 2 is 9.52 Å. However, two guests of Z-**6** approach each other much more closely across another center of symmetry; see *Packing* section below.

The molecule of C-**6** in the crystal is shown in Figure 3 with its guests. The approximate two-fold symmetry extends to the incarcerated and nesting acetonitrile guests.

*Packing in **5**·6$C_6H_5NO_2$ and Z-**6**·6$C_6H_5NO_2$*

The three nitrobenzene solvent molecules in the asymmetric unit of **5** perform distinct roles in the packing of the biscavitand in the crystal. Figure 4 is a stereoview showing three of the biscavitands, each bowl connected to the next molecule by the penetration of a foot from above or below. The centrosymmetric biscavitands thus form chains along the *b*

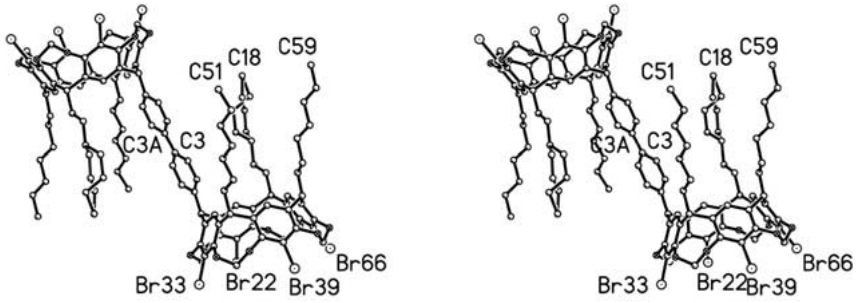

Figure 1. Stereoview of **5**: a biscavitand molecule in the crystal. Hydrogen and solvent atoms have been omitted. The lower right cavitand is related to the upper left cavitand by the center of symmetry in the biphenyl moiety (between C3 and C3A). One 'foot' (terminating in C18) is partially disordered. The 'foot' terminating in C51 fills a neighboring cavitand bowl.

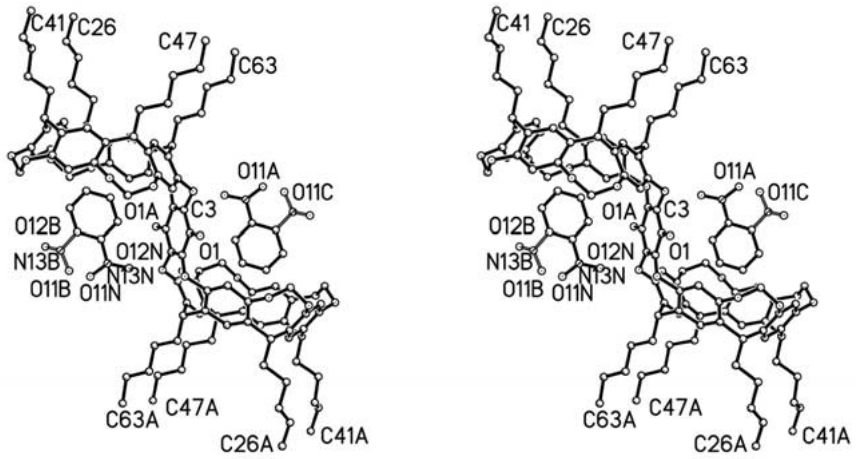

Figure 2. Stereoview of biscavitand Z-**6**. The disordered nitrobenzene molecule that perches in each bowl is shown; H atoms and other solvent molecules have been omitted. The center of symmetry lies between O1 and O1A in the quinone bridge.

axis. Nitrobenzene fits between neighboring bowls along the *c* axis (molecule I), acts as guest in each 'foot' cavity (molecule II), and lies between the feet of neighboring chains (molecule III).

In Z-**6**·6$C_6H_5NO_2$, on the other hand, the bowls of *two* host molecules related by a center of symmetry form a carcerand-resembling cage containing *two* guests. Chains of cages (Figure 5) extend along the *b* axis, while the feet of neighboring chains intertwine along the *c* axis. The distance between the centroids of the two guests' phenyl rings is 5.31 Å, and the closest ring-to-ring distance is 3.68 Å. Solvent molecules in the second and third orientations (not shown in Figure 5) surround the cage.

Discussion

Comparison with other structures

Chain formation by foot-in-bowl interlocking, as in **5**·6$C_6H_5NO_2$, occurs even in solution for a self-complementary deep-bowled crown-conformation cavitand with a single adamantyl-substituted foot [11]. Foot-in-bowl and foot-to-foot interlocking form a two-dimensional network in the crystal of a chair-conformation cavitand made from methyl resorcinarene (Middel *et al.* [9]); the self-inclusion involves the equatorial bromophenyl feet. In contrast, the crystal structure of biscavitand **5**·6$C_6H_5NO_2$ provides foot-in-bowl connections running in two parallel directions (Figure 4).

Self-inclusion may instead produce dimerization, due to the insertion of an upper-rim (or bowl) substituent in the bowl of a neighboring cavitand. One functionalized cavitand dimerizes in solution and in the crystal, each bowl including as guest one $C_6H_4CO_2Me$ from its partner [12]. Another dimer, also formed from two identical cavitands, is held together by hydrogen bonding of amide bowl substituents. Its very large egg-shaped cavity is filled with two alkyl groups, one from each monomer [13]. In still another type of dimerization by self-inclusion, a phenol (upper rim) or a *tert*-butyl group (lower rim) of a thiacalix[4]arene is inserted into the cavity of the partner [14]. Dimerization by guest, rather than self, inclusion is demonstrated in a series of crystalline 2:1 *t*-butylcalix[4]arene clathrates; the size of the 'dimers' can be controlled by the choice of solvent guest [15]. Another cavitand crystallizes in polymeric stacks of cages, each cage enclosing a molecule of guest in an unsymmetrical cavity formed by the bowl of one host and the 'feet' of the next [6].

In **5**·6$C_6H_5NO_2$, the cavitand moiety forms chains by self-inclusion (Figure 4), while in Z-**6**·6$C_6H_5NO_2$ the cavities 'dimerize' to form chains of connected cages filled with guest (Figure 5).

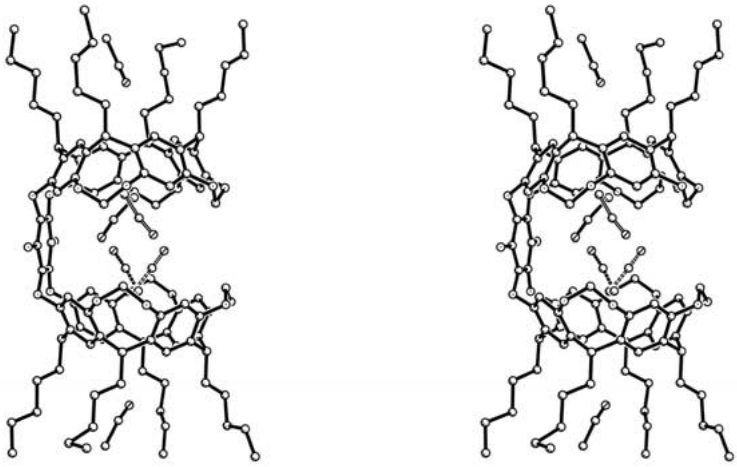

Figure 3. Stereoview of hemicarcerand C-**6**, H atoms omitted; both positions are shown for each of the disordered acetonitrile molecules in the bowl cavities. Disordered interstitial acetonitrile is omitted. See text.

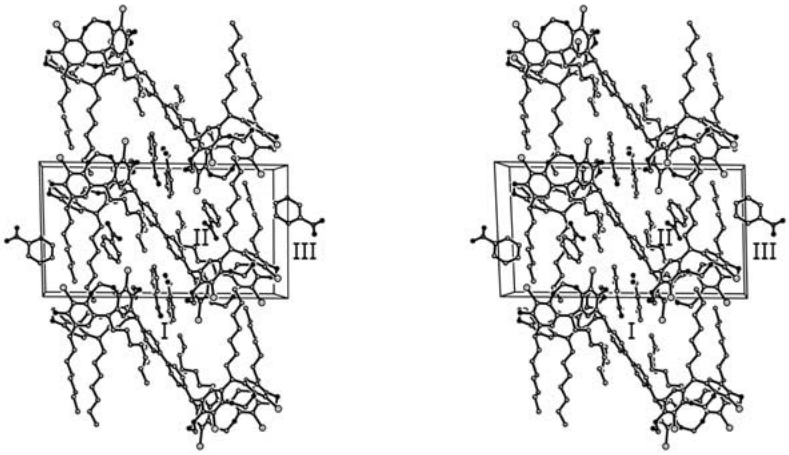

Figure 4. Packing of biscavitand **5** in the crystal, viewed down *a*, *c* horizontal, *b* vertical. The three independent nitrobenzene solvent molecules are labeled I, II and III. Only one of the orientations of disordered molecule I is shown.

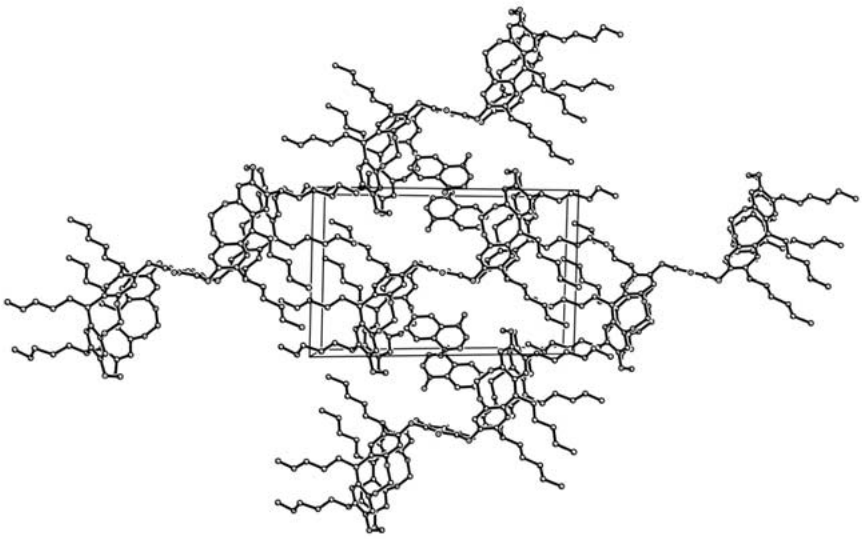

Figure 5. Packing of biscavitand Z-**6** in the crystal, viewed down *a*, *b* vertical, *c* horizontal. Four nitrobenzene guest molecules are included, to show a chain of guest-filled bowls (see Figure 2). Other solvent molecules and H atoms are omitted.

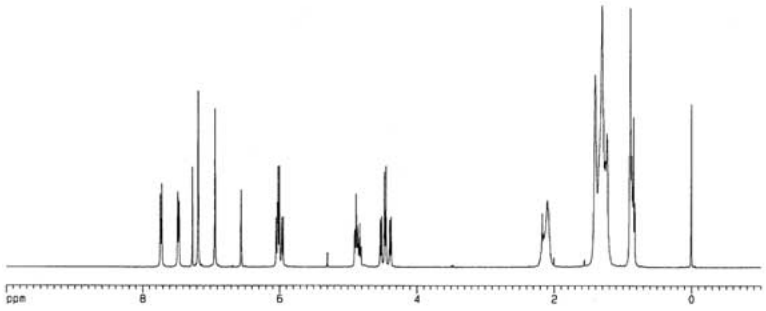

Figure 6. ^{1}H NMR spectrum of **5** in $CDCl_3$.

Conclusions

The rigidity of the bowl architecture and the opposite orientation of the two bowls are common features of biscavitands **5** and Z-**6**. Though neither biscavitand is a good complexing agent in solution, in the solid state the bowls are filled, in **5** by a foot from a neighboring host, and in Z-**6** by a stacked arrangement of solvent molecules. The solvent is the same in both structures, yet the packing is different. In each case the chains of molecules with guests suggest modes of synthesizing polymers held together by non-bonded interactions. Thus the structures indicate straightforward methods for the construction of multidimensional and multifunctional host systems. Future plans include the transformation of divergent ditopic molecular vessels such as **5** into functional multi-container hosts as well as into unprecedented polymers formed not by covalent bonds but by π–π stacking interactions [16], and the development of biscavitands like C-**6** and Z-**6** with non-identical bowls modified by rim substituents.

Acknowledgements

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Appendix

*Synthesis of octabromohexadecol **3***

A mixture of hexadecol **1** (1.9 g, 1.1 mmol), NBS (4.6 g, 25.8 mmol) and MEK (100 mL) was stirred at 25 °C overnight and then concentrated to 40 mL. Acetonitrile (100 mL) was added and the mixture was concentrated to 40 mL, cooled to RT, and then filtered. The filtered precipitate (∼2.09 g) was dissolved in a minimum amount of acetone, acetronitrile (50 mL) was added, and the mixture was concentrated to 30 mL. The precipitate was filtered and dried under high vacuum to give octabromohexadecol **3** (1.5 g, 57.7%): mp > 250 °C (dec.); ^{1}H NMR (CD_3COCD_3, 400 MHz) δ 0.80–0.90 (m, 18H), 1.15–1.35 (m, 60H), 1.95–2.10 (m, 12H), 4.50– 4.70 (m, 6H), 6.95 (s, 2H), 7.63 (s, 4H), 7.75 (s, 4H), 7.49 (d, J = 8.5 Hz, 4H), 7.71 (d, J = 9 Hz, 4H), 7.95 (s, 4H, exchange with D_2O), 8.10 (s, 4H, exchange with D_2O), 8.16 (s, 4H, exchange with D_2O), 8.23 (s, 4H, exchange with D_2O); FAB$^+$ MS (Xenon, NOBA) m/z 2346 (M^+, 80%), 2246 (M^+-$(CH_2)_6CH_3$ + H, 95%); *Anal. Calcd* for $C_{110}H_{130}Br_8O_{16}$: C, 56.28; H, 5.58. *Found:* C, 56.03; H, 5.49.

*Synthesis of octamethylbiscavitand **4***

A mixture of octamethylhexadecol **2** (0.5 g, 0.3 mmol), K_2CO_3 (1.0 g), CH_2BrCl (0.3 mL) and DMA (50 mL) was stirred at 65 °C overnight. After addition of CH_2Cl_2 (0.3 mL) the reaction mixture was stirred at 85 °C for 24 h. The reaction mixture was concentrated under reduced pressure and the residue was partitioned between water and CH_2Cl_2. The organic phase was separated, dried over $MgSO_4$, concentrated, and then chromatographed (SiO_2, 2 cm × 20 cm, Hexane : CH_2Cl_2 = 1:1) to give product (183 mg, 35%): mp > 280 °C (dec.); ^{1}H NMR ($CDCl_3$, 400MHz) δ 0.82–0.95 (m, 18H), 1.02–1.70 (m, 60H), 1.98 (s, 12H), 2.05 (s, 12H), 2.00–2.30 (m, 12H), 4.25 (d, J = 7.2 Hz, 4H), 4.32 (d, J = 7.2 Hz, 8H), 4.38 (d, J = 7.2 Hz, 4H), 4.70–4.80 (m, 6H), 5.88 (d, J = 7.2 Hz, 4H), 5.93 (d, J = 7.2 Hz, 8H), 5.96 (d, J = 7.2 Hz, 4H), 6.46 (s, 2H), 6.87 (s, 4H), 7.08 (s, 4H), 7.50 (d, J = 8.2 Hz, 4H), 7.70 (d, J = 8.2 Hz, 4H); FAB$^+$ MS (Xenon, NOBA) m/z 1755 (M + H$^+$, 100%); *Anal. Calcd* for $C_{114}H_{130}O_{16}$ + 0.2 CH_2Cl_2: C, 77.35; H, 7.41. *Found:* C, 77.30; H, 7.53.

*Synthesis of octabromobiscavitand **5***

A mixture of octabromohexadecol **3** (1.5 g, 0.64 mmol), Cs_2CO_3 (3.0 g, 9.2 mmol), CH_2ClBr (0.7 mL, 10.8 mmol) and 100 mL DMA was stirred at 60 °C for 48 h. After addition of CH_2ClBr (0.7 mL) the mixture was stirred at 85 °C overnight and then concentrated. The residue was partitioned between 2N HCl (100mL) and CH_2Cl_2 (150 mL). The organic phase was separated, and the aqueous phase was extracted with 50 mL of CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, concentrated and then chromatographed (SiO_2, 3 cm × 20 cm, hexane : CH_2Cl_2 = 1: 1). The best fractions were collected and concentrated to 50 mL. Acetonitrile (50 mL) was added and slowly concentrated to give precipitate which was filtered to give product (0.5 g, 32%): mp > 290 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.82–0.91 (m, 18H), 1.23–1.40 (m, 60H), 2.05–2.17

(m, 12H), 4.38 (d, J = 7.2 Hz, 4H), 4.46 (d, J = 7.2 Hz, 8H), 4.52 (d, J = 7.2 Hz, 4H), 4.82–4.90 (m, 6H), 5.96 (d, J = 7.2 Hz, 4H), 6.01 (d, J = 7.2 Hz, 8H), 6.04 (d, J = 7.2 Hz, 4H), 6.56 (s, 2H), 6.93 (s, 4H), 7.18 (s, 4H), 7.46 (d, J = 8.2 Hz, 4H), 7.72 (d, J = 8.2 Hz, 4H); FAB^+ MS (Xenon, NOBA) m/z 2445 ($M + H^+$, 100%); *Anal. Calcd* for $C_{118}H_{130}Br_8O_{16}$: C, 58.00; H, 5.36; Br, 26.16. *Found:* C, 58.03; H, 5.32, Br, 26.04.

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