Supramolecular Assemblies of 1,2-Dicarbadodecaborane(12) with Bowl-Shaped Calix[5]arene

Michaele J. Hardie[a] **and Colin L. Raston***[a]

Keywords: Calixarene / Carboranes / Host-guest chemistry / Non-classical hydrogen bonding / Supramolecular chemistry

Treatment of globular 1,2-dicarbadodecaborane(12) (*o*-carborane) **1** with the bowl-shaped container molecule calix[5]arene **2** affords either the crystalline 1:1 or 1:2 host-guest complexes (*o*-carborane)(calix[5]arene)(CH_2Cl_2) **3**, (*o*-carborane)(calix[5]arene)(toluene) **4** and (*o*-carborane)-(calix[5]arene)$_2$(CH_2Cl_2)$_{0.5}$ **5**. The three complexes show a remarkable range of different supramolecular interplay beyond the common structural unit, a ball-and-socket nanostructure or supermolecule [(*o*-carborane)∩(calix[5]arene)]. Complex **3** forms dimeric [(*o*-carborane)∩(calix[5]arene)]$_2$ units, and **5** has an additional edge on interaction between the supermolecule and a secondary calix[5]arene host.

Introduction

Carbon-containing polyhedral boranes, the carboranes, are extremely stable cage molecules known for over 30 years. Carboranes and their derivatives have applications in a number of diverse fields such as boron neutron capture therapy, boron carbide-type ceramics, complexing agents for extraction of metal ions, nonlinear optics, conducting polymers and more.[1] The carboranes *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$[1,2-, 1,7-, 1,12-dicarbadodecaborane(12)] (hereafter *o*-, *m*-, and *p*-carborane) are twelve-vertex icosahedral cages whose potential as components or building blocks in supramolecular systems is beginning to be explored.[2−6][9−12] Rigid rod-like and trigonal carborane-based molecular building units have been synthesised,[2] as well as metallodendrimers.[3] A number of carborane derived macrocyles are known, with the clusters linked through their carbon centres by both organic groups[4] and mercury centres.[5] The mercury linked macrocycles show host-guest complexation of halide ions, and the tetrameric macrocycle can complex *closo*-$B_{10}H_{10}^{2-}$.[6]

Carboranes have high C−H acidity[7] and consequently show potential for hydrogen bonding.[8] Supramolecular complexes involving such weak intermolecular interactions are known. The first examples to be reported were the series of inclusion complexes with cyclodextrin host molecules and *o*-carborane as the guest.[9] Thermally stable 1:1 cyclodextrin/carborane complexes were formed with α-, β-, and γ-cyclodextrin, and a 2:1 complex was also found for α-cyclodextrin. More recently the crystal structures of the 1:1 complexes of hexamethylphosphoramide (HMPA) with *o*-, *m*-, and *p*-carboranes have been reported.[10] The three complexes show extensive C−H···O hydrogen bonding and all adopt quite different supramolecular structures, commensurate with their differing arrangement of C−H sites. These complexes represent the first structures of unsubstituted carboranes in a crystal lattice. *o*-Carborane forms 1:1 complexes with diaza-18-crown-6 and aza-18-crown-6 again with distinct supramolecular structures.[11] The (*o*-carborane)(diaza-18-crown-6) complex associates through C−H···O hydrogen bonds at distances similar to those found for the HMPA complexes, whereas the aza-18-crown-6 complex has a layered structure with no close intermolecular contacts. The bowl-shaped container molecule cyclotriveratrylene (CTV) can act as a host for *o*-carborane guest molecules and a 2:1 CTV/*o*-carborane complex is formed.[12] In the solid state one CTV molecule complexes a carborane guest while the other forms a π interaction with the host CTV. Each C−H$_{carborane}$ is directed towards the centroid of an aromatic ring in the cavity of the CTV as a Coulumbic interaction between a polarised C−H bond and the basic π-electrons of an aromatic ring. The energy of such an interaction between benzene with *o*-carborane, shown schematically in Figure 1, is calculated to be energetically favoured by 2.74 kcal mol^{-1},[12] and this type of interaction is usually described as a weak non-classical C−H···π hydrogen bond. NMR studies were uninformative, except to suggest that *o*-carboranes can bind *endo*- and *exo*- to the cavity of the CTV.[12]

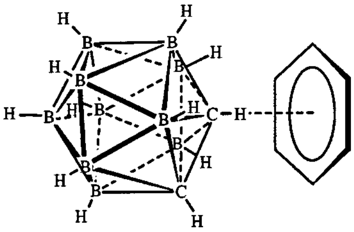


Figure 1. Schematic representation of non-classical hydrogen bonding between *o*-carborane and an aromatic ring

The complexation of *o*-carborane by a bowl-shaped container molecule such as CTV is reminiscent of much of the host-guest chemistry of the fullerene C_{60}[13][14] Both the carboranes and C_{60} are thermally stable, icosahedral clusters with diameters of about 8 and 10 Å respectively. Fullerene C_{60} forms inclusion complexes with the bowl-shaped CTV[13] and a number of calixarenes,[14] indeed the selective

---

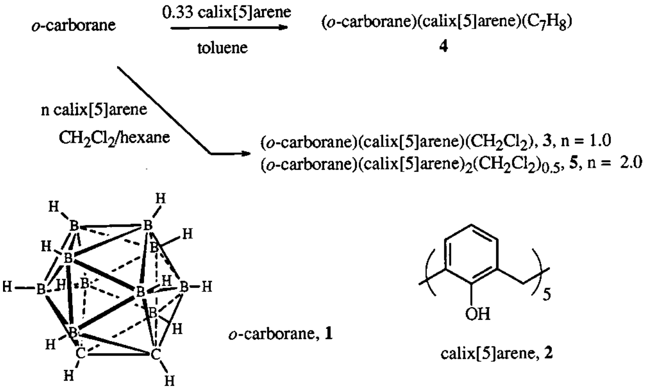
[a] Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3168, Australia

1434−1948/99/0101−0195 $ 17.50+.50/0

complexation of C_{60} by *p*-*t*Bu-calix[8]arene is a simple and efficient means of C_{60} extraction from a mixture of fullerenes. The supramolecular chemistry of carboranes with bowl-shaped potential host molecules is, by comparison, in its infancy and may also lead to simplified separation procedures, currently reliant on chromatographic techniques.[7] The work reported herein further develops host-guest chemistry between carboranes and bowl-shaped molecules with the formation of 1:1 and 1:2 complexes of *o*-carborane with calix[5]arene. The solid state structures have been established from low-temperature X-ray diffraction data. These three complexes show a remarkable range of supramolecular interactions and, despite being constructed from similar or the same supramolecular synthons/molecular building blocks, form different nano-structures. The ability to control weak intermolecular interactions underpins much of the basic aims and ideals of supramolecular chemistry,[15] yet the range of possible interactions is often extensive even for simple systems, illustrated by the quite distinct nano-structures formed here.

Results and Discussion

Slow evaporation of toluene solutions of 1:1, 1:2 mixtures of *o*-carborane **1** and calix[5]arene **2**, and subsequent recrystallisation from dichloromethane/hexane affords the colourless crystalline complexes, (*o*-carborane)(calix[5]arene)(CH_2Cl_2) **3** and (*o*-carborane)(calix[5]arene)$_2$(CH_2Cl_2)$_{0.5}$ **5**, see Scheme 1. Heating a 3:1 mixture of **1** and **2** in toluene at ca. 70 °C for one hour and subsequent cooling gave crystals of the toluene solvated 1:1 complex (*o*-carborane)(calix[5]arene)(C_7H_8) **4**. The complexes were characterised by IR spectroscopy, microanalysis and single crystal X-ray crystallography. The IR showed a clear a shift to lower energy (by 11 cm^{-1}) for ν_{C-H} of the carborane in **5**. Similar shifts in the IR were seen for the previously reported 2:1 complex (*o*-carborane)(CTV)$_2$ where the carborane ν_{C-H} shifts 13.5 cm^{-1} to lower energy.[12] Such an energy shift is indicative of the involvement of the carborane C−H in hydrogen bonding, with dispersal of the extra charge on the carbon resulting in the strengthening of the B−H bonds. Smaller shifts of 6 and 3 cm^{-1} respectively were seen in the 1:1 complexes **3** and **4**.



Scheme 1

(*o*-Carborane)(calix[5]arene)(CH_2Cl_2) 3

X-ray diffraction data was collected for **3** at −123(1) °C. The crystal structure was solved in the monoclinic space group $P2_1/n$. As was seen for (*o*-carborane)(CTV)$_2$,[12] a ball-and-socket supermolecule is formed between the host calix[5]arene and guest *o*-carborane.

The calix[5]arene adopts a bowl-conformation, with an average torsion angle between an aromatic ring and the plane formed by hydroxy oxygens of around 50°. The ball-and-socket supermolecule is shown in Figure 2. The carborane guest sits close to the middle of the calixarene cavity, with distances from C or B vertices of the carborane to aromatic ring centroids of the calixarene of 3.44, 3.55, 3.78, 3.93, and 4.08 Å. Both C−H vectors of the carborane are directed towards aromatic rings of the host molecule, albeit in an unsymmetrical fashion. As was seen for (*o*-carborane)(CTV)$_2$,[12] this interaction is most likely non-classical C−H···π hydrogen bonding, with the two interactions having $C_{carborane}$···aromatic centroid separations of 3.55 and 3.44 Å, and C−$H_{carborane}$···centroid angles of 11.8 and 24.8° respectively; the closer contact having the lesser C−H···π interaction, indicated by the greater angle at the hydrogen.

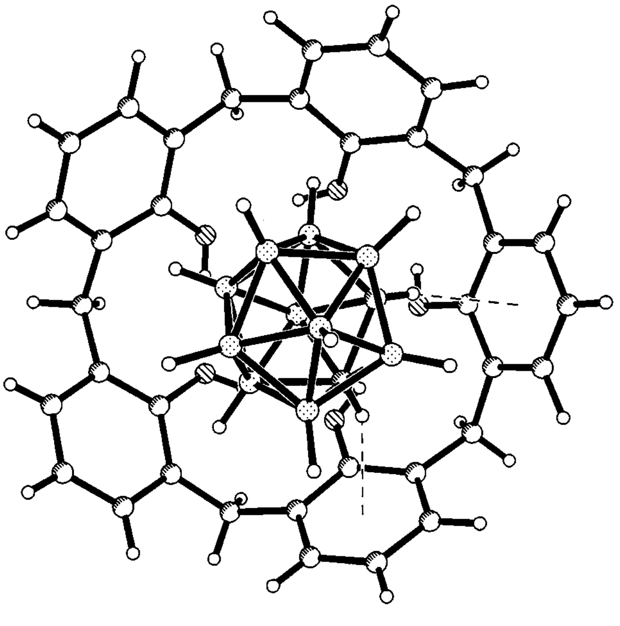


Figure 2. Ball-and-socket (*o*-carborane)∩(calix[5]arene) assembly of (calix[5]arene)(*o*-carborane)(CH_2Cl_2) **3**. Potential non-classical C−H π hydrogen bonds are indicated as dashed lines

The ball-and-socket (*o*-carborane)∩(calix[5]arene) units organise into larger dimeric supramolecules within the crystal lattice. The dimers have the calixarene hydroxy groups facing each other, forming a hydrophilic core shown in Figure 3. The X-ray data obtained did not allow for the location of the hydroxy hydrogens, and those shown in Figures are at calculated positions. This makes it difficult to ascertain the exact hydrogen-bonding pattern. The O···O contacts between the calixarenes are quite close at 2.96, 3.01, 3.09, 3.14, and 3.22 Å. There are no close contacts between dimers within the crystal lattice. The dimers occur in two layers, each running in the *b* direction and alternat-

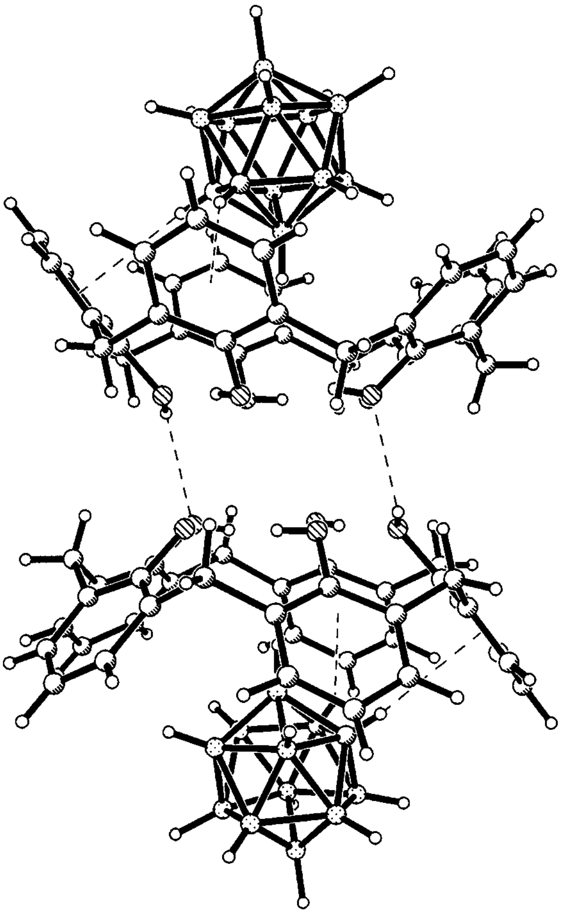


Figure 3. The dimeric [(*o*-carborane)∩(calix[5]arene)]$_2$ nano-structures of **3**. The hydrogen-bonded (calix[5]arene)$_2$ unit can be considered to be acting as a divergent receptor

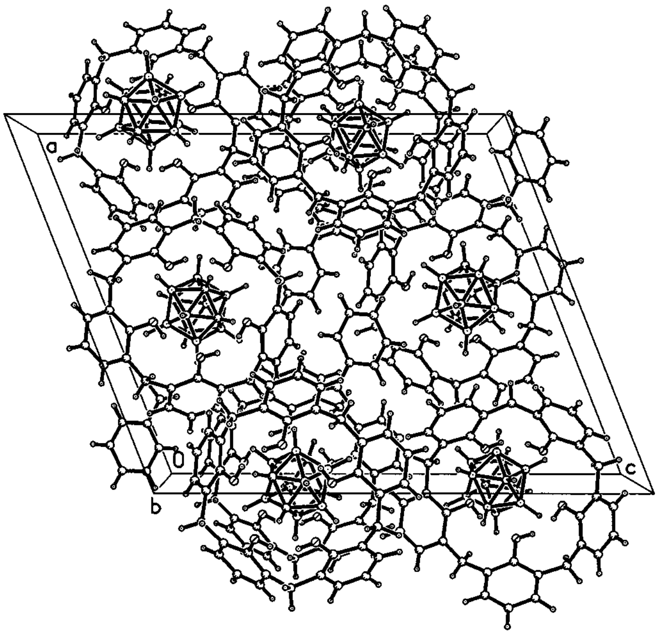


Figure 4. Packing diagram of (calix[5]arene)(*o*-carborane)(C_7H_8) **4** along the *b* axis. Columns of (calix[5]arene)]∩(calix[5]arene) supermolecules are formed along *b*

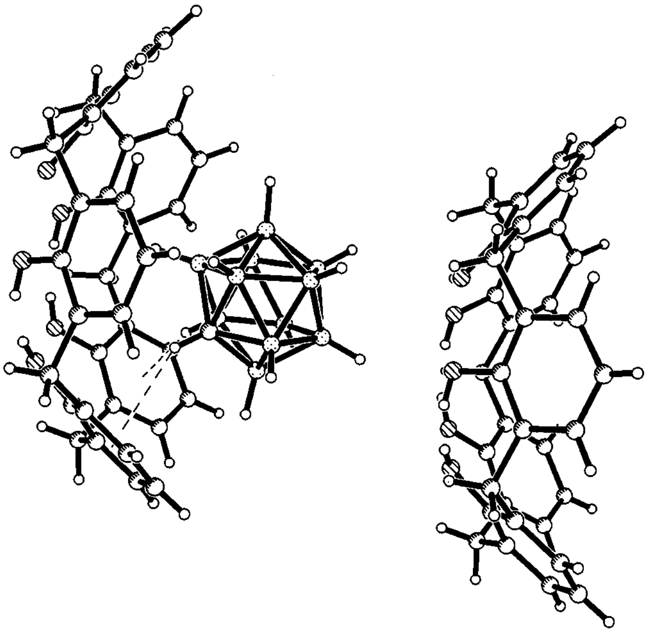


Figure 5. Side view of the ball-and-socket (*o*-carborane)∩(calix[5]arene) supermolecule and calixarene of next supermolecule along *b*, of (calix[5]arene)(*o*-carborane)(C_7H_8) **4**. Potential non-classical C-H π hydrogen bonds are indicated as dashed lines

ing in the *c* direction, with disordered dichloromethane molecules positioned between individual dimers.

(*o*-Carborane)(calix[5]arene)(C_7H_8) 4

X-ray diffraction data was collected for **4** at −150(1)°C. The crystal structure was solved in the monoclinic space group $P2_1/n$. Although the basic structural unit of **4** − a ball-and-socket type (*o*-carborane)∩(calix[5]arene) − is similar to that of **3**, the crystal packing is quite distinct.

The (*o*-carborane)∩(calix[5]arene) supermolecule of **4** is similar to that of **3**, although the *o*-carborane sits slightly closer to the host molecule. The calix[5]arene adopts a bowl-conformation, with an average torsion angle between an aromatic ring and the plane formed by hydroxy oxygens of around 48°. The C−H vectors of the carborane point towards the edges of aromatic rings of the calix[5]arene host at $C_{carborane}\cdots$aromatic centroid separations of 3.40 and 3.49 Å, and $C-H_{carborane}\cdots$centroid angles of 20.2 and 31.4°. The dimeric units evident in **3** are not formed, however, with the (*o*-carborane)∩(calix[5]arene) supermolecules stacking in the same orientation along the *b* direction (Figure 4) to form columns of the supermolecule. The orientation of these columns alternates along the *c* direction. The included *o*-carborane of one supermolecule has contacts to the hydroxy groups of the next (*o*-carborane)∩(calix[5]arene) at a closest B···O distance of 3.55 Å (Figure 5).

Each toluene molecule within the crystal lattice forms close contacts to two calix[5]arene molecules (Figure 6). The plane of the toluene is almost exactly perpendicular to the plane of an aromatic ring of one calix[5]arene (torsion angle 89.1°). An aromatic C−H of the toluene, *ortho* to the methyl group, is directed towards the centre of this arene at a H···centroid distance of 2.6 Å. One of the toluene C-Hs *meta* to the methyl group is directed towards a hydroxy oxygen of the calix[5]arene at an H···O distance of 2.5 Å. The toluenes effectively bridge between the supramolecular columns in the direction of the *c* axis.

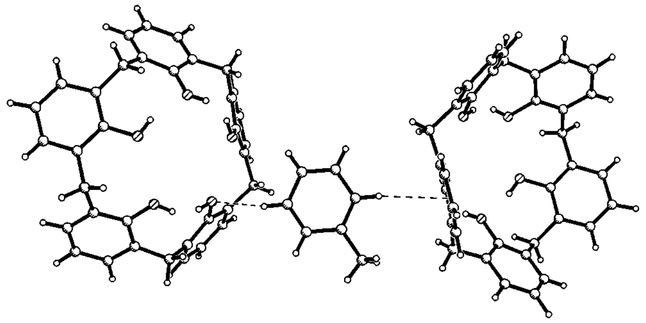


Figure 6. Environment of toluene molecule in (calix[5]arene)(*o*-carborane)(C_7H_8) **4**. Close contacts between the toluene and adjacent calix[5]arene molecules are indicated as dashed lines

(*o*-Carborane)(calix[5]arene)$_2$(CH_2Cl_2)$_{0.5}$ 5

X-ray diffraction data was collected for **5** at room temperature and −100°C. The crystals were observed to undergo a phase change from primitive monoclinic (room temperature, $P2_1/m$: a = 11.679(1), b = 18.128(2), c = 16.394(1) Å, β = 97.12(1)°) to triclinic [−100°C: a = 11.6151(13), b = 16.3617(17), c = 18.014(2) Å, α = 90.699(9), β = 91.612(9), γ = 96.739(9)] on cooling. The room-temperature and low-temperature structures are essentially the same, although the carborane displays some positional disorder in the room temperature structure. Data from the low temperature study is presented here. The structure was solved in space group $P\bar{1}$, and features two types of calixarene molecule and one carborane.

Both calix[5]arene molecules adopt a bowl conformation, and their ability to act as host molecules manifests itself in two distinct manners. The curvature of the two calixarenes is quite different. One calixarene has torsion angle between an aromatic ring and the plane formed by hydroxy oxygens between 46.5 and 49.0° (average 48°). The second calixarene is considerably more puckered with torsion angles between 34.4 and 64.2° (average 49°). The shallower calixarene acts as a host molecule for the *o*-carborane, forming the familar ball-and-socket arrangement seen in **4**. The more puckered calixarene acts as a secondary host for the (*o*-carborane)∩(calix[5]arene) assembly forming the [(*o*-carborane)∩(calix[5]arene)]∩(calix[5]arene) nano-structure illustrated in Figure 7. The complexation of a host-guest species by a secondary host is, to out knowledge, relatively uncommon. Other examples of such supramolecular interactions include the complexation of alkali metal-crown ethers by cyclodextrins.[16] These form entirely different nano-structures to that seen here.

The (*o*-carborane)∩(calix[5]arene) arrangement in **5** is similar to the analogous supermolecule in **3**, with both C−H vectors of the included *o*-carborane directed towards aromatic rings of the host calix[5]arene to form non-classical hydrogen bonds. In the case of **5**, however, the C−H$_{\text{carborane}}$ vectors point more directly to the centre of the aromatic rings with C···aromatic centroid separations of 3.51 and 3.57 Å, and a C−H$_{\text{carborane}}$···centroid angles of 0.8

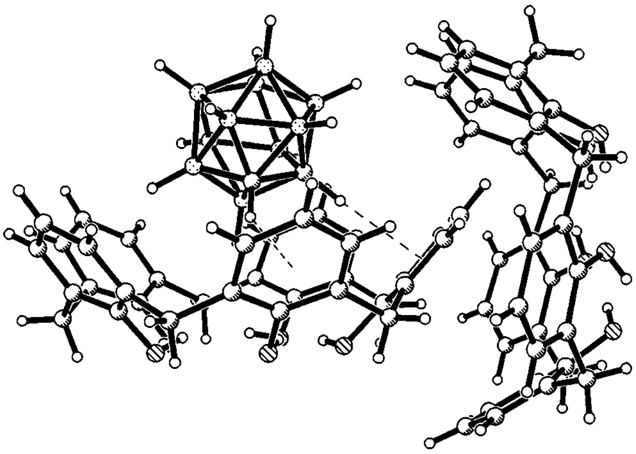


Figure 7. The (*o*-carborane)∩[(calix[5]arene)]∩(calix[5]arene) nano-structure of (calix[5]arene)$_2$(*o*-carborane)(CH_2Cl_2)$_{0.5}$ **5**. Potential non-classical C−H π hydrogen bonds are indicated as dashed lines. The two aromatic rings shown side-on show π-π stacking at a centroid separation of 3.920 Å and torsional angle of 18.8°

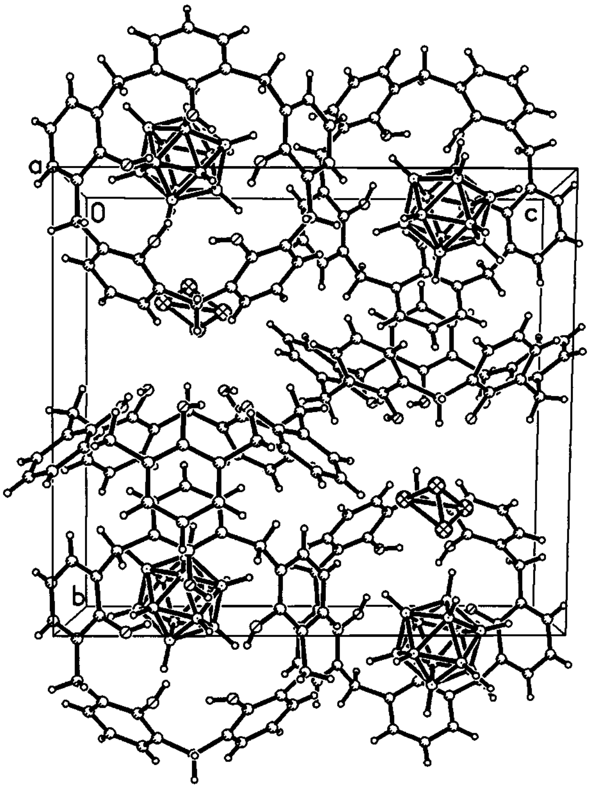


Figure 8. Packing diagram of (calix[5]arene)$_2$(*o*-carborane)(CH_2Cl_2)$_{0.5}$ **5** shown down the *a* axis

and 9.1° (Figure 7). The closest B···aromatic ring centroid distances are 3.80, 3.90, and 4.22 Å. It is evident from this that the carborane is positioned to one side of the calixarene bowl − not surprisingly, the side featuring C-$H_{carborane}\cdots\pi$ interactions (Figure 7). The (*o*-carborane)$\cap$(calix[5]arene) supermolecule.

The presence and identity of solvent molecules also plays a vital role in determining the crystal packing and overall topology of the systems. The crystallisation from CH_2Cl_2 instead of toluene, for instance, results in a dimer of the 1:1 complex being formed. We also note that calixarenes are known to form inclusion complexes with dichloromethane through the formation of non-classical hydrogen bonds.[17] Chlorinated solvents such as chloroform are known to break up analogous fullerene-calixarene complexes through such bonds competing with fullerene-calixarene associations.[14] In the carborane-based supramolecular systems reported here, however, carborane-calixarene and calixarene-calixarene interactions appear to form the preferred interactions.

Experimental Section

Synthesis of 3 and 5: Calix[5]arene and *o*-carborane were mixed in toluene in 1:1, 2:1, and 1:3 proportions and the solution slowly evaporated to dryness. The residues were taken up in dichloromethane then hexane vapour was diffused into the solutions to give colourless crystals. (*o*-Carborane)(calix[5]arene)(CH_2Cl_2) **3**; $C_{38}H_{44}B_{10}Cl_2O_5$. − IR 3284, 3061, 2577, 1594, 1489, 1451, 1386, 1245, 1212, 1150, 1089, 1016, 907, 841, 803, 754, 714, 637, 559, 472 cm^{-1}; microanalysis C 60.50% (60.07), H 5.91% (5.83); (*o*-carborane)(calix[5]arene)$_2$(CH_2Cl_2)$_{0.5}$. − **5**; IR 3286, 3059, 2946, 2875, 2556, 2280, 1612, 1468, 1450, 1386, 1244, 1210, 1152, 1086, 906, 841, 803, 755, 698, 639, 558, 486; microanalysis C 69.69% (69.78), H 6.07% (5.90). − **4**: Calix[5]arene and *o*-carborane were mixed in toluene in 1:3 proportions and the solution heated at ca. 70 °C for one hour then cooled to room temperature to give colourless crystals of (*o*-carborane)(calix[5]arene)(C_7H_8); IR 3260, 3066, 2572, 2362, 1611, 1468, 1449, 1398, 1243, 1210, 1151, 1085, 841, 756, 714, 559, 468 cm^{-1}.

X-ray Crystallography: Details of data collections and structure refinements for **3** to **5** are given in Table 1. All data sets were collected on an Enraf-Nonius KappaCCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å). Data was corrected for Lorentzian, polarisation but not absorption. The structures were solved by direct methods using SHELXS-97[18] and refined by full matrix least-squares on $|F^2|$ using SHELXL-97.[19] Carbon atoms within the carborane molecules were assigned by analysis of atomic displacement parameters. As the X-ray scattering factors for B and C are very similar these assignments should be regarded as tentative. Only neutron diffraction data would allow for unequivocal discrimination between C and B. Treatment of hydrogen atoms was mixed. The hydroxy hydrogens for **3** to **5** were fixed at geometrically estimated positions with a riding refinement. The hydrogen positions of the disordered CH_2Cl_2 molecule in **3**, and the toluene molecule of **4** were fixed at geometrically estimated positions with a riding refinement. All other hydrogen atoms were fully refined. The disordered CH_2Cl_2 molecule in **3** was modelled with two carbon positions each with an occupancy of 0.5. The disordered CH_2Cl_2 molecule in **5** was refined with an overall occupancy of 0.5, four disordered chlorine positions (with occupancies of 0.15 or 0.35), forming a rough tetrahedron, were modelled, however the central carbon atom was not located. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101900, CCDC-101901, and CCDC-101902 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk]

Table 1. Crystal structure data and details of structure refinement for **3**

	3	**4**	**5**
Formula	$C_{38}H_{44}B_{10}Cl_2O_5$	$C_{44}H_{50}B_{10}O_5$	$C_{72}H_{72}B_{10}ClO_{10}$
M_r [g mol^{-1}]	759.73	766.94	1240.85
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P1$
a [Å]	12.1605(4)	18.9709(7)	11.6151(13)
b [Å]	12.2485(4)	9.9961(5)	16.3617(17)
c [Å]	27.0023(6)	23.3192(8)	18.014(2)
α [°]	90.0	90.0	90.699(9)
β [°]	100.833(1)	111.369(5)	91.612(9)
γ [°]	90.0	90.0	96.739(9)
V [Å^3], Z	3950.3(2), 4	4118.1(3)	3398.0(7), 2
ρ_{calc} [g cm^{-1}]	1.277	1.237	1.213
crystal size [mm]	0.38 × 0.25 × 0.18	0.38 × 0.35 × 0.25	0.35 × 0.35 × 0.20
μ [mm^{-1}]	0.207	0.074	0.114
T [K]	150(1)	150(1)	173(1)
Scan increment [°], exposure [sec]	1 (ϕ, ω), 40	1 (ϕ, ω), 40	1 (ϕ, ω), 20
2θ range [°]	6.14 to 56.58	5.92 to 56.54	5.82 to 56.36
Reflns collected	21213	25634	24331
Unique reflns	9593	10063	13635
R_{int}	0.049	0.091	0.087
observed refln $I > 2\sigma(I)$	5081	3925	3533
Data/restraints/ parameters	9593/0/653	10063/0/680	13636/0/865
R_1 (obs data)	0.0772	0.0726	0.1082
wR_2 (all data)	0.2398	0.1895	0.3059
weights a[a]	0.1368	0.0866	0.1605
S	1.049	0.945	0.936
max shift/error	0.000	0.000	0.000
$\lvert\Delta\rho\rvert_{max}$ [e Å^3]	0.961	0.331	0.636

[a] $w = 1/[\sigma^2(F_o^2) + aP^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Acknowledgments

This work was supported by the Australian Research Council.

---

[1] J. Plesek, *Chem. Rev.* **1992**, *92*, 269.

[2] X. Yang, W. Jiang, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1992**, *114*, 9717; J. Müller, K. Base, T. F. Magnera, J. Michel, *J. Am. Chem. Soc.* **1992**, *114*, 9721; W. Jiang, C. B. Knobler, M. D. Mortimer, M. F. Hawthorne, *Angew. Chem.* **1995**, *107*, 1470; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1332; W. Jiang, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1996**, *35*, 3056; W. Jiang, D. E. Harwell, M. D. Mortimer, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1996**, *35*, 4355.

[3] D. Armspach, M. Cattalini, E. C. Constable, C. E. Housecroft, D. Philips, *Chem. Commun.* **1996**, 1823.

[4] R. N. Grimes, *Angew. Chem.* **1993**, *105*, 1350; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1289; W. Clegg, W. R. Gill, J. A. H. MacBride, K. Wade, *Angew. Chem.* **1993**, *105*, 1402; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1328; I. T. Chizhevsky, S. E. Johnson, C. B. Knobler, F. A. Gomez, M. F. Hawthorne, *J. Am. Chem. Soc.* **1993**, *115*, 6981.

[5] A. A. Zinn, Z. Zheng, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1996**, *118*, 70, references therein.

[6] X. Yang, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1993**, *115*, 4904.

[7] R. N. Grimes, *Carboranes*, Academic Press, New York, **1970**.

[8] L.A. Leites, *Chem. Rev.* **1992**, *92*, 279; G. Harakas, T. Vu, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.*, **1998**, *120*, 6405, references therein.

[9] A. Harada, S. Takahashi, *J. Chem. Soc., Chem. Commun.* **1988**, 1352.

[10] M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, K. Wade, *Chem. Commun.* **1996**, 2285.

[11] P. D. Godfrey, W. J. Grigsby, P. J. Nichols, C. L. Raston, *J. Am. Chem. Soc.* **1997**, *119*, 9283.

[12] R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kaddour, C. L. Raston, *Angew. Chem.* **1997**, *109*, 520; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 504.

[13] J. L. Atwood, M. J. Barnes, R. S. Burkhalter, P. C. Junk, J. W. Steed, C. L. Raston, *J. Am. Chem. Soc.* **1994**, *116*, 10346; J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.*. **1996**, 1449.

[14] R. M. Williams, J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 531; J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, *368*, 229; R. M. Williams, J. M. Zwier, J. W. Verhoeven, *J. Am. Chem. Soc.* **1994**, *116*, 6965; T. Suzuki, K. Nakashima, S. Shinkai, *Chem. Lett.* **1994**, 699; T. Suzuki, K. Nakashima, S. Shinkai, *Tetrahedron Lett.* **1995**, *36*, 249; C. L. Raston, J. L. Atwood, P. J. Nichols, I.B. N. Sudria, *Chem. Commun.* **1996**, 2615; K. Araki, K. Akao, T. Suzuki, S. Shinkai, *Tetrahedron Lett.* **1996**, *37*, 73; A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713; T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1997**, *109*, 288; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 259; T. Haino, M. Yanase, Y. Fukazawa, *Tetrahedron Lett.* **1997**, *38*, 3739; K. Tsubaki, K. Tanaka, T.Kinoshita, K. Fuji, *Chem. Commun.* **1998**, 8955. J. L. Atwood, L. J. Barbour, C. L. Raston, I. B. N. Sudria, *Angew. Chem.* **1998**, *110*, 1028; *Angew. Chem., Int, Ed, Engl.*, **1998**, *37*, 981.

[15] J.-M. Lehn, *Supramolecular Chemistry, Concepts, Perspectives* **1995**,VCH, Weinham.

[16] S. Kamitori, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1987**, *109*, 2409; S. Kamitori, K. Hirotsu, T. Higuchi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3825.

[17] J. L. Atwood, S. G. Bott, C. Jones, C. L. Raston, *J. Chem. Soc., Chem. Commun.* **1992**, 1349.

[18] G. M. Sheldrick, *SHELXS97. Program for the Solution of Crystal Structures*, **1997**, University of Göttingen, Germany.

[19] G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, **1997**, University of Göttingen, Germany.

Received August 20, 1998
[I98287]