

Self-Assembly of Grid and Helical Hydrogen-Bonded Arrays Incorporating Bowl-Shaped Receptor Sites That Bind Globular Molecules

Michaele J. Hardie, Peter D. Godfrey, and Colin L. Raston*^[a]

Abstract: 1,2-Dicarbododecaborane(12) (*o*-carborane) and bowl-shaped cyclotrimeratrylene (CTV) self-assemble through bifurcated C–H_{carborane} ⋯ (O)₂ hydrogen bonds into infinite arrays with two-dimensional (2D) hexagonal grid or helical chain topologies. The in-built shape-specific receptor sites bind *o*-carborane or fullerene C₇₀. The structures of two such supramolecular systems in the solid state were established: (*o*-carborane)₂(CTV) features hydrogen-

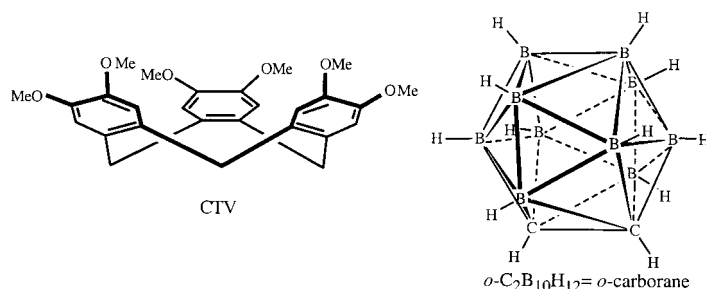
bonded carborane ⋯ CTV hexagonal grids as well as CTV ⋯ carborane host–guest interactions, while a helical hydrogen-bonded carborane ⋯ CTV chain is formed in the quaternary system (C₇₀)(*o*-carborane)(CTV)(1,2-dichlorobenzene) in addition to CTV ⋯ C₇₀

Keywords: ab initio calculations • carboranes • crystal engineering • fullerenes • host–guest chemistry

host–guest interactions. The bifurcated C–H_{carborane} ⋯ (O)₂ hydrogen bonding interaction common to both these structures was studied on the model system (*o*-carborane)(1,2-dimethoxybenzene) using ab initio calculations and found to be energetically favoured by 5.48 kcal mol^{−1}, whereas a B–H_{carborane} ⋯ (O)₂ bifurcated hydrogen bonding was less favoured at 1.13 kcal mol^{−1}.

Introduction

Supramolecular chemistry is concerned with the formation of large arrays stabilised by non-covalent means such as coordinate bonds, π stacking, hydrogen bonds, electrostatic interactions, and van der Waals forces.^[1] It encompasses self-assembly, molecular recognition, and inclusion phenomenon, and the shape complementarity and hydrogen bonding for such processes which are found in molecular biology are among the most valuable tools in devising new supramolecular systems. Bowl-shaped molecules or container molecules such as calixarenes and cyclotrimeratrylene (CTV) can bind globular molecules including C₆₀, C₇₀ and 1,2-dicarbododecaborane(12) (*o*-carborane)^[2–8] resulting in ball-and-socket shaped complexes held together by non-classical hydrogen bonding, C–H_{carborane} ⋯ π (a Coulombic interaction between polarised C–H bond and the basic π electrons of an aromatic ring), and π – π interactions with complementarity of curvature between the host and guest moieties. This chemistry shows considerable potential in the field of separation science and indeed the selective complexation of C₆₀ by *p*-tert-butylcalix[8]arene is a simple and cost efficient means of C₆₀ extraction from a mixture of fullerenes.^[2] The ball-and-socket nanostructures can exist as discrete monomeric species,^[3] or



form aggregates^[4] or polymeric structures^[5, 6] through fullerene–fullerene interactions.^[1–6]

The control of hydrogen bonding interactions to create extended networks in the solid state is one of the central premises of crystal engineering,^[9] and the range of molecular systems employed and structural types obtained are extensive^[10] with considerable advances made in controlling such systems to create nanoporous materials with potential zeolite-like applications.^[11] Herein we show that self-assembly of *o*-carborane and CTV results in infinite hydrogen-bonded networks that incorporate bowl-shaped receptor sites which bind two disparate globular molecules, *o*-carborane or C₇₀. This has implications for building up receptor arrays based on other container molecules and the other isomers of carborane. It is noteworthy that in the absence of carborane, C₇₀ fails to form a complex with CTV, in contrast to C₆₀ which forms two complexes, (C₆₀)(CTV) and (C₆₀)_{1.5}(CTV),^[5] and that C₆₀ and CTV in the presence of *o*-carborane also affords (C₆₀)_{1.5}(CTV).

[a] Prof. C. L. Raston, Dr. M. J. Hardie, Dr. P. D. Godfrey
Department of Chemistry, Monash University
Clayton, Melbourne, Victoria 3168 (Australia)
Fax: (+613) 9905-4597
E-mail: c.raston@sci.monash.edu.au

C–H groups of carboranes are acidic [12] and a limited number of supramolecular complexes have been established, notably the 1:1 complexes of *o,m,p*-carborane with hexamethylphosphoramide, [13] 1:1 host–guest complexes of *o*-carborane with α -, β -, γ -cyclodextrins and a 1:2 complex with α -cyclodextrin, [14] 1:1 complexes of *o*-carborane with diaza[18]-crown-6 and aza[18]crown-6, [15] and the 1:2 complex of *o*-carborane with CTV. [7] The latter complex is distinctly different with each C–H_{carborane} directed towards the centroid of an aromatic ring in the cavity of the CTV as a weak non-classical hydrogen bond calculated to be energetically favoured by 2.74 kcal mol⁻¹. Such non-classical hydrogen bonding also features in complexes of *o*-carborane with bowl-shaped calix[5]arene. [16] Supramolecular chemistry of C₇₀ is limited to structurally authenticated complexes available for the 2:1 complex of calix[6]arene, [6] and a hydroquinone enclathrated C₇₀. [17] This is in direct contrast to the lower fullerene C₆₀, which shows a range of supramolecular behaviour. [2–5, 18]

Results and Discussion

Crystals of composition (*o*-carborane)₂(CTV) **1** were obtained from the slow evaporation at room temperature of a solution of CTV and *o*-carborane in a 1:2 ratio in toluene, and crystals of composition (C₇₀)(*o*-carborane)(CTV)(1,2-dichlorobenzene) **2** were obtained from a solution of CTV, *o*-carborane, and C₇₀ in a 1:1:1 ratio in 1,2-dichlorobenzene kept at about 70°C for one week. The solid-state structures were determined by X-ray diffraction techniques.

Structure of (*o*-carborane)₂(CTV) **1:** The crystal structure of (*o*-carborane)₂(CTV) was solved in the trigonal (hexagonal setting) space group *R3m*. There is one type of CTV molecule and two types of carborane molecule in the crystal structure, all of which lie across symmetry elements.

One of the carborane molecules forms three symmetry equivalent bifurcated hydrogen bonds to the methoxy groups of three equivalent CTV molecules (Figure 1); the C/B...O distance is 3.33 Å with the corresponding C/B–H...O

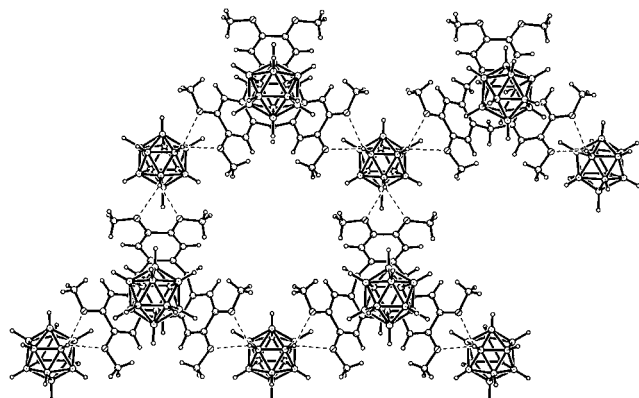


Figure 1. Section of the crystal structure of **1** showing the 2D hexagonal grid of **1** formed through B/C–H...O hydrogen bonding (note that the *o*-carborane is disordered and each icosahedron vertice involved in the hydrogen bonding interaction has 2/3 C and 1/3 B occupancy) and the inclusion of a guest *o*-carborane in the CTV bowl.

distance at 2.53 Å. All three interactions originate from the same triangular face of the carborane icosahedron and, due to symmetry-imposed disorder, each of the three carborane centres involved has 2/3 carbon and 1/3 boron character. A puckered hexagonal two-dimensional (2D) hydrogen-bonded network is formed, shown in Figure 1 projected in the *ab* plane. The formation of infinite 2D hexagonal sheets through hydrogen-bonding interactions has been seen for a number of other systems, the best known are various clathrates of urea. [19] What makes this example more intriguing is the presence of receptor sites within the 2D grid. All CTV molecules within the grid, and indeed throughout the crystal lattice, have their bowl vertices pointing in the same direction with a torsion angle of 75° between adjacent aromatic rings. The second *o*-carborane molecule resides in the receptor sites forming a ball-and-socket (*o*-carborane)C(CTV) nanostructure (Figure 1) throughout the hydrogen-bonded grid.

The host–guest interplay within the supermolecule (*o*-carborane)C(CTV) is remarkably different to that found in (*o*-carborane)(CTV)₂ where the carborane is perched in an unsymmetrical manner in the cavity of the CTV held in place by two non-classical C–H_{carborane}... π hydrogen bonds. The alignment of the carborane within the CTV cavity in the present structure is, in contrast, symmetrical with all carborane C–H vectors directed away from the CTV aromatic rings. However, the difference is consistent with the inherently weak interactions holding the supermolecule together. In an elegant example of symmetry matching, the vertices of one of the triangular faces of the carborane icosahedron lies parallel to the triangle formed by the methylene bridges of the CTV (Figure 1). The three symmetry equivalent icosahedron faces adjacent to this face are arranged nearly parallel to the three aromatic rings of the CTV. The centroid separation between the aromatic ring and triangular face represents the closest contact between the molecules at 3.77 Å and the faces are slightly inclined from each other with a torsion angle of 6.4°. It is notable that this is a considerably longer interaction (by up to about 0.45 Å) than was seen for (*o*-carborane)(CTV)₂. [7]

There are three hydrogen-bonded networks in the crystal lattice shown side-on in Figure 2. The 2D networks pack such that each CTV molecule is surrounded by seven *o*-carboranes. One, which forms part of a second 2D network, sits at the vertex of the CTV bowl, lying directly below the guest carborane along the *c* direction, at a closest contact of 4.30 Å. The other six form a hexagon around the edges of the CTV, three of these are hydrogen-bonded to that CTV and the other three are the guest carboranes of the CTV molecules of a second 2D network. The closest B...C contacts are to the CTV methyls at 4.53 Å. The carboranes within this hexagon are approximately 4.8 Å apart (vertice separation). Carboranes form columns along the *c* direction that alternate between the guest and hydrogen-bonded variety (Figure 2), occurring in pairs 4.09 Å apart on either side of a CTV molecule. Interestingly, the atomic displacement parameters for the carborane included in the CTV cavity are considerably larger than those for the hydrogen-bonded carborane (average U_{iso} 0.098 and 0.050 Å² respectively), indicating greater librational motion for the included carborane, and implying

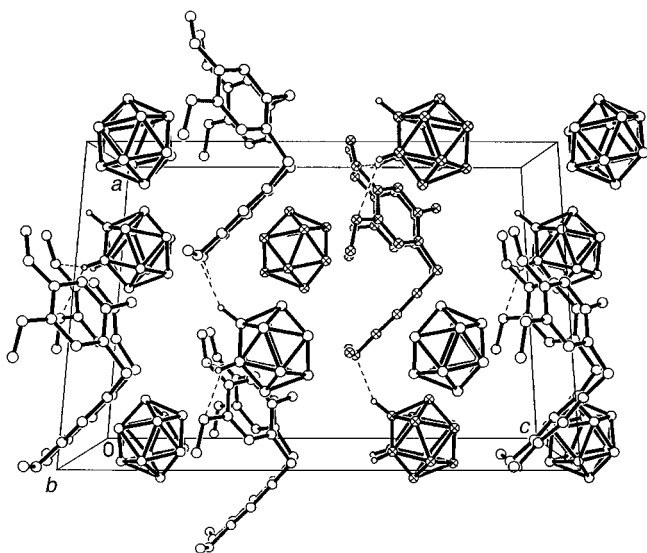


Figure 2. Unit cell of **1** viewed down the *b* axis, showing a side-on view of the packing of three of the hexagonal grids of Figure 1. Atomic positions corresponding to one such grid are shown cross-hatched. Only hydrogens involved in hydrogen bonding are shown for clarity.

that the hydrogen-bonded carborane is more tightly bound within the crystal lattice than is the guest carborane.

Structure of $(C_{70})(o\text{-carborane})(CTV)(1,2\text{-dichlorobenzene})$

2: The crystal structure of $(C_{70})(o\text{-carborane})(CTV)(1,2\text{-dichlorobenzene})$ was solved in the orthorhombic space group $P2_12_12_1$. The structure features one type of CTV, *o*-carborane, C_{70} and 1,2-dichlorobenzene molecule in a 1:1:1 ratio.

The carborane molecule in **2** is fully ordered and, as was seen for $(o\text{-carborane})_2(CTV)$ (**1**), each C–H proton is involved in a bifurcated hydrogen bond to adjacent methoxy oxygens of the CTV. Each *o*-carborane interacts with two symmetry-equivalent CTV molecules and in turn, each CTV is hydrogen-bonded to two carboranes forming an infinite helical chain (Figure 3). There are two helices of the same hand in the unit cell, shown schematically in Figure 4, hence the crystal is chiral despite being composed of weakly interacting achiral molecular components. The CTV cavities are directed outwards from the helices, so again an infinite

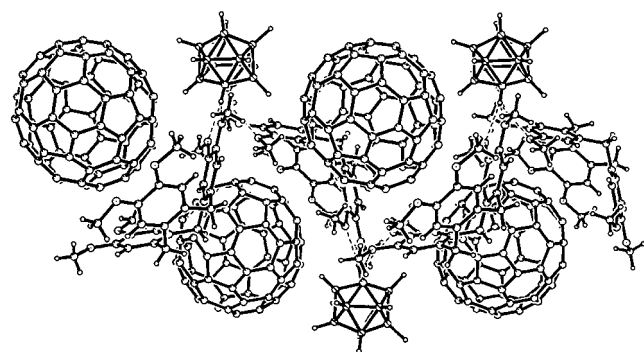


Figure 3. Section of the crystal structure of **2** showing a side-on view of an infinite helical chain formed through hydrogen bonding interactions between *o*-carborane and CTV. Each CTV forms a ball-and-socket type host-guest complex with a C_{70} molecule.

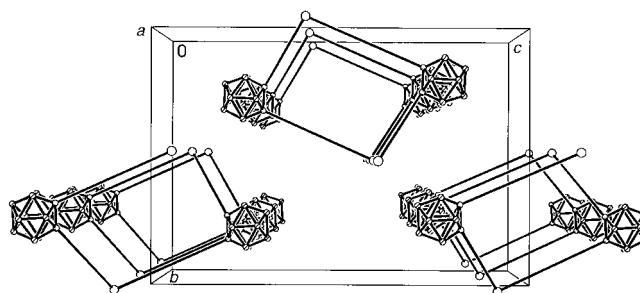


Figure 4. Schematic view of the packing of helices within **2**. Helices as viewed from above and the larger circles represent the centre of the CTV molecules (centroid of CH_2 groups).

hydrogen-bonded array with in-built curved receptor sites has been created. We note that the self-assembly of helices has become a relatively common feature of supramolecular chemistry and can occur through metal templation and hydrogen bonding.^[20]

Each receptor site within the helices binds a C_{70} molecule (Figure 3) to form the familiar ball-and-socket motif. The C_{70} molecule is bound by π – π stacking associated with size and shape complementarity. One C_6 ring of the fullerene is located almost exactly parallel with an aromatic ring of the CTV, with a centroid separation of 3.69 Å and a torsion angle of 9°. The C_6 rings are slightly displaced from each other and hence do not show exact symmetry matching. The long axis of C_{70} is aligned along the CTV bowl. The C_{70} molecules of adjacent helices within the crystal lattice are separated close to the van der Waals limit with the fullerene–fullerene centroid distance at 10.78 Å, which is comparable to those in $(C_{70})_2(\text{calix}[6]\text{arene})$, 10.53–10.66 Å.^[6] Intra-helix fullerene–fullerene separations are longer at 13.88 Å. The dichlorobenzene molecules within the crystal lattice show two close contacts one involving $Cl \cdots H_3CO_{CTV}$ at 3.46 Å, the other involving $Cl \cdots O$ at 3.69 Å. The plane of the solvent lies normal to the direction of the helices, and the molecules sit between CTV molecules of the spiral. The formation of a bifurcated hydrogen bond in a five-membered ring is not in itself novel, however bifurcated hydrogen bonds from C–H groups are highly unusual and this is, to our knowledge, the first reported example for a carborane.

Quantum chemistry: Calculations were conducted on the model system of *o*-carborane and 1,2-dimethoxybenzene at the ab initio RHF/6-31G(d) level using Gaussian 94.^[21] The optimised structure of $(o\text{-carborane})(1,2\text{-dimethoxybenzene})$ is shown in Figure 5. Starting with an approximately C_s symmetric structure for the adduct with $CH \cdots (O)_2$ hydrogen bonding, the *o*-carborane moiety was found in the optimised structure to be rotated by about 30° about the linking C–H bond. The angle between the plane of the aromatic ring and the closest (CCB) triangular face of the *o*-carborane was about 70°.

The starting structure for the adduct $(o\text{-carborane})(1,2\text{-dimethoxybenzene})$ with $BH \cdots (O)_2$ hydrogen bonding was produced by interchanging a B and C atom on the closest triangular face of the *o*-carborane. The initial structure iterated rapidly (in five optimisation steps) to a quasi-stable

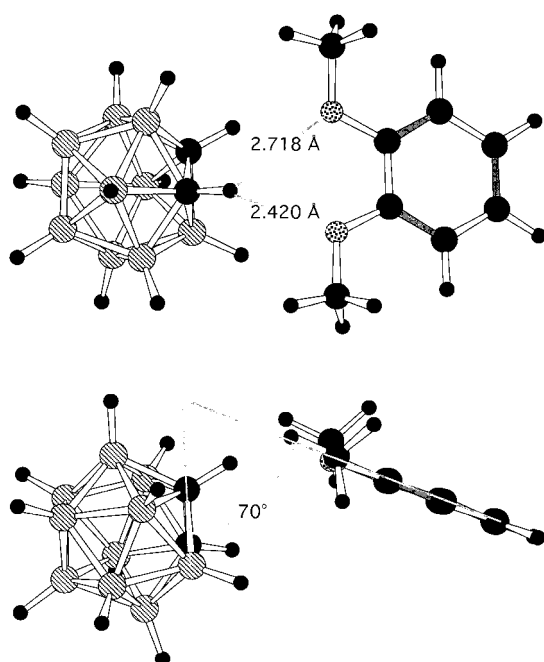


Figure 5. Views of the ab initio optimised structure of the model system of *o*-carborane and 1,2-dimethoxybenzene at the RHF/6–31G(d) level.

structure with a bifurcated hydrogen-bond geometry similar to that for the $\text{CH}\cdots(\text{O})_2$ species, satisfying the usual residual root mean square (rms) force criterion for convergence, at which the binding energy was about $1.13 \text{ kcal mol}^{-1}$. However subsequent iterations resulted in a significant reorientation of the *o*-carborane with the structure eventually transforming to the $\text{CH}\cdots(\text{O})_2$ species. The corresponding evolution of ab initio relative energy is shown in Figure 6, indicating that at this level of calculation the $\text{BH}\cdots(\text{O})_2$ species is not a stable conformer.

The theoretical calculations on this model system of *o*-carborane and 1,2-dimethoxybenzene gives a $\text{C}-\text{H}_{\text{carborane}}\cdots(\text{O})_2$ interaction energetically favoured by $5.48 \text{ kcal mol}^{-1}$, and a structure with a pseudo mirror plane passing through the supermolecule such that the other C–H group is symmetrically related to a B–H group across the plane. We note that this energy is close to double the calculated energy

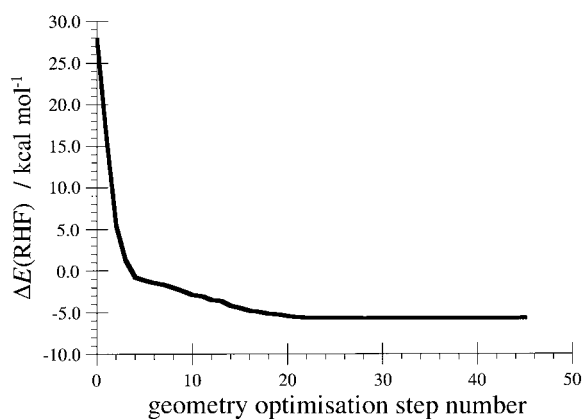


Figure 6. Plot showing the calculated RHF/6–31G(d) energy of the (*o*-carborane)(1,2-dimethoxybenzene) model (relative to the isolated *o*-carborane and 1,2-dimethoxybenzene molecules) during the attempted geometry optimisation of the $\text{BH}\cdots(\text{O})_2$ complex (see text).

($2.74 \text{ kcal mol}^{-1}$) found for a single $\text{C}-\text{H}_{\text{carborane}}\cdots\pi$ non-classical hydrogen bond between *o*-carborane and benzene.^[7] This highlights a delicate balance between the carborane involved in bifurcated hydrogen bonding versus non-classical hydrogen bonding in the cavity of the CTV. The geometry of the bifurcated hydrogen bond is not the same for both complexes. In (*o*-carborane)₂(CTV), where all B/C–H_{carborane}⋯O interactions are symmetry-equivalent, the carborane sits out of the plane of the dimethoxyphenyl moieties of the CTV. The B/C–H_{carborane}⋯O distance is 2.53 \AA .

Ab initio theory on the present model systems gives the B–H_{carborane}⋯(O)₂ less favoured at $1.13 \text{ kcal mol}^{-1}$, as expected by the lower charge on hydrogen atoms attached to boron.^[7] However, this energy does not correspond to a stationary point on the energy hypersurface and it follows that the stabilisation of a B–H_{carborane}⋯(O)₂ interaction requires cooperative forces such as the adjacent C–H groups also being involved in bifurcated hydrogen bonding as found in (*o*-carborane)₂(CTV) (**1**). In (C₇₀)(*o*-carborane)(CTV)(1,2-dichlorobenzene) (**2**), two non-equivalent and unsymmetrical interactions are evident for each of the adjacent C–H groups of the *o*-carborane. These are in and out of the plane of the corresponding dimethoxyphenyl group with C–H_{carborane}⋯O distances of 2.09 and 2.35 \AA , and 2.39 and 2.52 \AA respectively, the later corresponding to a weaker interaction.

Solvent effects: The 2D grid structure of (*o*-carborane)₂(CTV) (**1**) is also obtained when *o*-carborane and CTV are allowed to react in 1,2-dichlorobenzene rather than in toluene. Similarly, a helical structure identical to that of **2** is found when *o*-carborane, C₇₀ and CTV are allowed to react in toluene (crystal composition (C₇₀)(*o*-carborane)(CTV)(toluene), orthorhombic $a = 14.84(9)$, $b = 17.81(9)$, $c = 26.48(13) \text{ \AA}$). It is apparent that the solvent does not dictate which hydrogen-bonded array is formed. It is likely that the nature of the globular guest molecule has far more influence. This is consistent with the template or space-filling role played by solvent in other hydrogen-bonded networks.^[10, 11, 20, 21] The globular molecules here play a considerably larger role than just that of space filling or a template, forming additional supramolecular interactions of fundamental interest. It would be expected that the *m*- and *p*- isomers of *o*-carborane could self-assemble with CTV to form networks of entirely different topologies to those observed in the current study. In this context we note that the *m*-isomer forms a 3:2:2 complex with CTV and C₇₀ but thus far the limited X-ray data has yielded only a partial solution (cell dimensions: hexagonal, $a = b = 14.481(1)$, $c = 76.749(2) \text{ \AA}$). Overall, combining carboranes, or other molecules with acidic X–H groups, with container molecules capable of hydrogen bonding offers scope for swaying the competing energies of interaction in favour of host–guest complexes where the host–guest components otherwise fail to assemble.

Experimental Section

Synthesis of (*o*-carborane)₂(CTV) (1**):** Solutions of *o*-carborane and CTV in a 2:1 ratio in toluene were mixed at room temperature and allowed to

slowly evaporate to complete dryness. After several days crystals of **1** were recovered.

Synthesis of (C₇₀)(*o*-carborane)(CTV)(1,2-dichlorobenzene) (2**):** Solutions of *o*-carborane, CTV and C₇₀ in a 1:1:1 ratio in 1,2-dichlorobenzene were mixed at about 70°C and maintained at that temperature for a week, after which dark crystals of **2** were obtained. Using two equivalents or an excess of *o*-carborane also affords crystals of **2**.

Crystal structure determinations: X-ray data for **1** and **2** were collected at 123(1) K on an Enraf-Nonius KappaCCD single-crystal diffractometer with MoK α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentzian and polarisation effects but not absorption. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on $|F^2|$ using SHELXL-97. Carbon positions within carboranes were assigned by an analysis of anisotropic displacement parameters. Hydrogen atoms of the guest *o*-carborane were fixed at geometrically estimated positions with a riding refinement for **1** and hydrogen atoms of the CTV and dichlorobenzene were fixed at geometrically estimated positions with a riding refinement for **2**. All other hydrogen atoms were fully refined. Summaries of crystal data and refinements are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102410 and CCDC-102411. 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).

Quantum chemistry: Calculations were conducted on the model system of *o*-carborane and 1,2-dimethoxybenzene at the ab initio RHF/6-31G(d) level using Gaussian 94.^[21] Calculated geometries were fully optimised subject to the standard Gaussian 94 convergence criteria that all residual forces on the nuclei were less than 0.00045 atomic units, that the maximum nuclear displacement since the previous iteration step was less than 0.0018 atomic units and that a threshold value 2/3 of this size applied to each of the corresponding the rms values. The geometries for the model adducts (*o*-carborane)(1,2-dimethoxybenzene) with either CH \cdots (O)₂ or BH \cdots (O)₂ hydrogen bonding were optimised without any constraints as were the structures of the isolated components (*o*-carborane) and the CTV model (1,2-dimethoxybenzene). Initial structures for geometry optimisation of the model adducts were established by the Gaussian 94 graphic interface option GaussView.

Table 1. Crystal structure data and details of structure refinements for **1** and **2**.

	1	2
formula	C ₃₁ H ₅₄ B ₂₀ O ₆	C ₁₀₅ H ₄₆ B ₁₀ Cl ₂ O ₆
M_r [g mol ⁻¹]	738.94	1582.42
crystal system	trigonal (hexagonal)	orthorhombic
space group	$R\bar{3}m$	$P2_12_12_1$
a [Å]	13.9478(3)	14.7493(5)
b [Å]	13.9478(3)	17.7715(5)
c [Å]	18.0887(3)	26.3542(7)
V [Å ³], Z	3047.5(1), 3	6907.9(4), 4
ρ_{calc} [g cm ⁻³]	1.208	1.522
crystal description	block, colourless	irregular, dark red
crystal size [mm]	0.35 × 0.30 × 0.28	0.40 × 0.25 × 0.13
μ [mm ⁻¹]	0.071	0.165
$F(000)$	1164	3232
T [K]	123(1)	123(1)
2θ range [°]	5.8 to 56.5	5.86 to 52
reflections collected	7408	37483
unique reflections	1651	13535
R_{int}	0.028	0.097
observed reflections $I > 2\sigma(I)$	1445	6746
data/restraints/parameters	1651/1/135	13535/0/1156
R_1 (obs data)	0.0607	0.0939
wR_2 (all data)	0.1647	0.1786
S	1.040	1.129
Flack parameter	0(2)	0.1(1)
max shift/error	0.000	0.001
$ \Delta\rho _{\text{max}}$ [e Å ⁻³]	1.08	0.31

Acknowledgments

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