

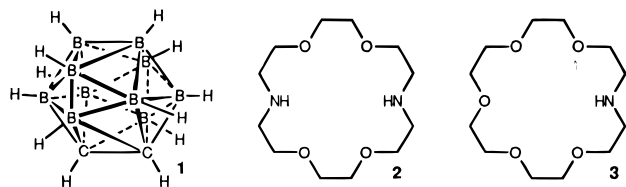
Aza-Crown Ether: 1,2-Dicarbododecaborane(12) Supramolecular Assemblies

Peter D. Godfrey, Warren J. Grigsby, Peter J. Nichols, and
Colin L. Raston*

Department of Chemistry, Monash University
Clayton, Melbourne, Victoria 3168, Australia

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Supramolecular chemistry of the carboranes *o*-, *m*-, and *p*-C₂B₁₀H₁₂ [1,2-, 1,7-, 1,12-dicarbododecaborane(12)] includes the linking of the cages through carbon centers by both organic groups^{1,2} and metal centers,³ as well as the formation of adducts involving inherently weak intermolecular forces. The latter is limited to 1:1 complexes of hexamethylphosphoramide (=HMPA) with the three isomeric carboranes which show C–H_{carborane}···O hydrogen bonding⁴ and host–guest complexes involving container molecules.^{5,6} α -, β -, or γ -cyclodextrins form 2:1 and 1:1 complexes with *o*-C₂B₁₀H₁₂,^{1,5} Cyclotrimeratrylene (=CTV) and **1** interact in toluene, crystallizing as a 2:1 complex with each C–H_{carborane} of the carborane directed toward the centroid of an aromatic ring in the cavity of one CTV, the other CTV forming a π -stacked column. The weak nonclassical hydrogen bond interactions are calculated to be energetically favored by 2.74 kcal mol⁻¹.⁶ We describe herein the novel host–guest/inclusion complexes of *o*-carborane with diaza-18-crown-6, **2** [=1,4,10,13-tetraoxa-7,16-diazacyclooctadecane], and the aza-18-crown-6, **3** [1,4,10,13-tetraoxa-7-azacyclooctadecane].



Slow evaporation of a toluene solution of a 1:1 mixture of **1** and either **2** or **3**⁷ affords the 1:1 complexes [(*o*-C₂B₁₀H₁₂) \cap (diaza-18-crown-6)], **4**, and [(H₂O)_{0.5} \cap (aza-18-crown-6)](*o*-C₂B₁₀H₁₂), **5**, the latter crystallizing with a partial occupancy of water within the aza-18-crown-6. The complexes show two distinct types of inclusion complexes in the solid state, either a hydrogen bonded host–guest complex, **4**,⁸ or alternating layers of carborane and crown ether, **5**,⁹ as established from X-ray diffraction data collected at –100 °C. Examination of the

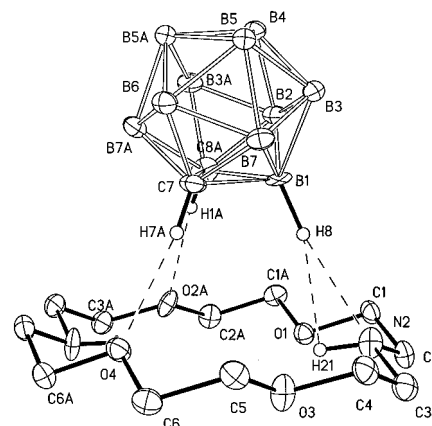


Figure 1. Projection of the host–guest structure of [(*o*-C₂B₁₀H₁₂) \cap (diaza-18-crown-6)], **4**; the nearest contacts are shown as broken lines with O(4)···H(7A) = 2.36 Å, O(2A)···H(1A) = 2.49 Å, and N(2)···H(8) 2.34 Å (corresponding to an N–H···H distance of 2.15 Å).

nonbonded contact distances in these structures reveals in **4** that three H atoms of a triangular face of the *o*-carborane polyhedron bearing the two carbon atoms reside above the diaza-18-crown-6, Figure 1.

Half the supermolecule **4** is the asymmetric unit, the other half being generated by a mirror plane. Disorder across the mirror was resolved showing the carbon atoms (C(7) and C(8A)) and boron atom (B(1)) of the polyhedron are located over the oxygen atoms (O(3A) and O(4)) and the nitrogen atom (N(2)) respectively. The two components are linked through C–H_{carborane}···O H-bonding interactions with O(4)···H(7A) at 2.36 Å and O(2A)···H(1A) at 2.49 Å, coupled with B–H···H–N interplay with H(8)···H(21) at 2.15 Å and H(8)···N(2) at 2.34 Å. The H···H distance is close to the upper limit for unconventional dihydrogen bonds established for B–H···H–N contacts in aminoboranes which lie in the range 1.7 to 2.2 Å,¹⁰ but see further discussion below. The O···H_{carborane} distances are similar to those found in the *o*-, *m*-, and *p*-carborane adducts with HMPA,⁴ and within the crown ether ring the O···H–N distances range from 2.46 to 2.61 Å. There are no short intersupermolecule interactions in **4**. The IR shows a shift for ν_{C-H} of the carborane of 33 cm⁻¹ to lower energy and a shift to higher energy for ν_{B-H} , by 25 cm⁻¹. This is consistent with the presence of C–H···O interactions with dispersal of the extra charge on the carbons resulting in strengthening of the B–H bonds.

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(2) (a) Jiang, W.; Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 4355. (b) Armspach, D.; Cattalini, M.; Constable, E. C.; Housecroft, C. E.; Philips, D., *Chem. Commun.* **1996**, 1823.

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(4) Davidson, M. G.; Hibbert, T. G.; Howard, A. K.; Mackinnon, A.; Wade, K. *Chem. Commun.* **1996**, 2285.

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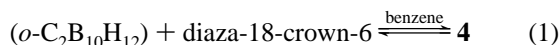
(7) Synthesis of **4**: A solution of *o*-C₂B₁₀H₁₂ (10 mg, 6.94 mmol) in toluene (2 mL) was added to a solution of the diaza-18-crown-6 (18.2 mg, 6.94 mmol) in toluene (2 mL). On evaporation of the solvent over several days the product precipitated as colorless crystals; mp 95.5–96.5 °C. Anal. Calcd for C₁₄H₃₆O₄N₂B₁₀: C, 41.36; H, 9.42; N, 6.89. Found: C, 41.09; H, 10.28; N, 6.55. ν_{CH} (carborane) 3031 cm⁻¹, ν_{BH} 2600 cm⁻¹, ν_{NH} 3433, 3314, 3232 cm⁻¹. ¹H NMR (benzene-*d*₆, 400 MHz, 295 K, 0.07 M) δ 3.5–0.8 (m, BH); 3.38 (m, OCH₂CH₂N); 3.29 (s, OCH₂CH₂O); 2.65 (m, OCH₂CH₂N); 2.53 (s, NH); 2.16 (s, carborane CH). The synthesis of **5** is similar to that of **4**: mp 84–88 °C. Anal. Calcd for C₁₄H₃₅O₅B₁₀(H₂O)_{0.5}: C, 40.37; H, 9.20; N, 3.43. Found: C, 39.56; H, 9.20; N, 3.41. ν_{CH} (carborane) 3037 cm⁻¹, ν_{BH} 2570 cm⁻¹.

(8) **4**: C₁₄H₃₆N₂O₄B₁₀, orthorhombic, *Pnma*, *a* = 9.419(6) Å, *b* = 14.61(1) Å, *c* = 16.82(1) Å, *V* = 2315(3) Å³, *F*(000) = 872, ρ_{calc} = 1.167 g cm⁻³, μ (Mo K α) = 0.73 cm⁻¹(no correction), 0.4 × 0.3 × 0.2 mm³, *Z* = 4, Nicolet R3m/V diffractometer, Mo K α radiation, *T* = 173 K, 2335 unique reflections (2114 observed, *I* > 2.0 σ (*I*)), 2 θ = 50°, refinement on *F*², 193 parameters, *R* = 0.055, *wR* = 0.110 (σ weights). The structure was marred by disorder in both the sites of the nitrogen and oxygen atoms (N2/O2 and N3/O3) in the diaza-18-crown-6 ring and by disorder of the carbon/boron (C8/B1) site in the carborane moiety. A similar disorder was observed for the site occupied by C(8) and B(1). The hydrogen atoms were located in the difference map and refined in *x,y,z,U* except for the H atoms of the methylene groups for which *U* was constrained.

(9) **5**: C₁₄H₃₅N₂O₅B₁₀(H₂O)_{0.5}, orthorhombic, *Pbam*, *a* = 9.176(7) Å, *b* = 9.502(6) Å, *c* = 14.012(7) Å, *V* = 1222(1) Å³, *F*(000) = 436, ρ_{calc} = 1.108 g cm⁻³, μ (Mo K α) = 0.71 cm⁻¹(no correction), 0.35 × 0.25 × 0.25 mm³, *Z* = 2, Nicolet R3m/V diffractometer, Mo K α radiation, *T* = 173 K, 998 unique reflections (840 observed, *I* > 2.0 σ (*I*)), 2 θ = 45°, refinement on *F*², 97 parameters, *R* = 0.0994, *wR* = 0.2976 (σ weights). The carbon atoms of the carborane were disordered over all sites, and the N and O atoms over the aza-18-crown-6 were similarly disordered. In addition, the aza-18-crown-6 ring is disordered equally over two sites, and a water molecule in the cavity is disordered over two sites with total occupancy close to 0.5. H atoms were calculated and included in the refinement as invariants.

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^1H NMR in benzene- d_6 at 25 °C for a range of concentration of **2** (0.0–0.14 M) for a fixed *o*-carborane concentration (0.07 M) resulted in shifts in the *o*-carborane C–H resonance from 2.05 ppm to 2.20 ppm and N–H resonance for **2** from 2.26 ppm to 2.85 ppm. A near linear relationship indicates a low equilibrium constant ($<5\text{ M}^{-1}$), eq 1.



For *m*-carborane small differences in the chemical shift for C–H (25 °C, δ 1.94; –75 °C, δ 1.43) relative to a 1:1 mixture of the carborane and **2** (0.07 M; 25 °C, δ 1.98; –75 °C, δ 1.51) in benzene- d_6 indicate little or no complexation. In support of this there was no evidence of complex formation in the solid state with the crystallization of separate components. Presumably the ability for *m*-carborane to form two C–H \cdots O interactions within the same supermolecule while maintaining the crown conformation of the host is lost. The different binding prowess of *o*- and *m*-carborane with **2** suggests that separation of isomeric carboranes *via* selective binding is possible rather than using conventional chromatography.¹¹ Interestingly, ^1H NMR data show the corresponding *N,N'*-dibenzylidiazia-18-crown-6 forms a complex with *o*-carborane in benzene. However, attempts to isolate this complex were unsuccessful.

Alignment of the carborane with the diaza-18-crown-6 is consistent with the acidic nature of the protons attached to the carbon centers of the carborane. This is supported by theoretical studies which give the protons on carbon a residual charge of +0.299 e, *cf.* +0.068 e to +0.091 e for the hydrogen atoms on boron.⁶ Calculations¹² in the present study give the docking of the carborane with **2** to be favored by 9.32 kcal mol^{–1}. The optimized C–H \cdots O distances at 2.471 Å compare well with experimental values at 2.49 Å, whereas optimized B–H \cdots N and B–H \cdots H–N at 2.924 and 2.721 Å, respectively, are much longer than experimental values at 2.34 and 2.15 Å, and analogous distances in aminoboranes.¹⁰ The reason for this is unclear, but we note the high error in the position of the H-atom attached to nitrogen in **4**, and that the short B–H \cdots H–N contacts for aminoboranes¹⁰ arise from residual negative charge on the H atoms attached to boron, *cf.* positive charge in **4**.

In separate calculations, the single C–H_{carborane} \cdots O interaction for a carborane dimethyl ether complex is favored by 3.73 kcal mol^{–1}, and the associated intermolecular distance optimized at 2.28 Å. In contrast, the optimized binding energy of the carborane with dimethylamine was much less at 0.89 kcal mol^{–1}, with B–H \cdots N at 3.09 Å and B–H \cdots H–N at 3.85 Å. Thus the H atom attached to the nitrogen is remote to the borane. Overall the binding in **4** is driven by the two adjacent C–H \cdots O interactions with the interaction to the nitrogen being less important. In principle a second *o*-carborane could bind to the other face of the crown ether in the same way, albeit rotated by 180°, Figure 1. Nevertheless, even in the presence of excess carborane only the 1:1 complex is formed in the solid state.

The most striking structural feature of **5** is the intercalation of layers of **1** and **3**, and the partial inclusion of water in the aza-18-crown-6, Figure 2. The structure represents an ordering of a ternary supramolecular system, *viz* the interplay of the supermolecules [(H₂O)_{0.5}C(aza-18-crown-6)] with *o*-carborane.

(11) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.

(12) Calculations were at the RHF/6-31G(d) level with Gaussian 94 (Revision D.3, Gaussian, Inc.: Pittsburgh, PA, 1995). For **4** the geometry was optimized with the parameters of the carborane frozen at optimized values and subject to the constraint that the complex possessed a mirror plane bisecting the C–C bond of the carborane and an N-center of the diaza-18-crown-6. For [(**2**)(OMe₂)] and [(**2**)(HNMe₂)] the carborane was treated similarly with the mirror bisecting the dimethyl ether and dimethylamine.

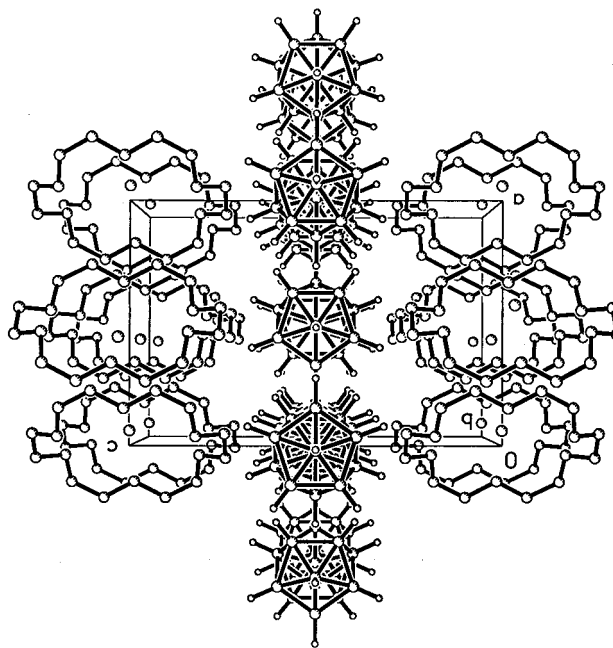


Figure 2. Projection of [(H₂O)_{0.5}C(aza-18-crown-6)](*o*-C₂B₁₀H₁₂), **5**.

There is only 50% occupancy of the water molecule in the cavity of the aza-18-crown-6 (disordered equally over two sites) with the occluded water arising from adventitious water during crystallization. Unfortunately the solid is highly disordered with the crown ether and carborane residing over sites of 2/*m* symmetry such that there is no distinction between the carbon and boron atoms in the cluster, and between the oxygen and nitrogen atoms of the crown ether. Moreover, the carbon skeleton of the crown ether is also disordered. This aside the structure clearly shows the absence of any close intermolecular contacts like those observed in **4**. Rather the polarized clusters form a two-dimensional sheet, the nearest inter-carborane contacts, C/B–H \cdots H–B/C at 2.41 Å and the packing of **3** involves C–H \cdots H–C interactions, the nearest contacts, 2.72 Å. Nearest interlayer contacts are 2.33 Å. A 1:1 mixture of **1** and **3** in toluene- d_8 (0.14 M) gave ^1H NMR (400 MHz) chemical shift changes for the *o*-carborane C–H and N–H for **3** of 2.35 to 2.38 and 2.27 to 2.75 ppm, respectively. This suggests intimate contact of the two components in solution, but in this case host–host and guest–guest interactions win out over host–guest interactions in the solid state. A similar effect is observed in the absence of moisture but in this case no host–guest or intercalation complex could be isolated. While the IR of **5** shows a large $\nu_{\text{C–H}}$ shift of 30 cm^{–1} to higher energy which is similar to that of **4** at 33 cm^{–1}, the shift in $\nu_{\text{B–H}}$ is small at 8 cm^{–1} to lower energy rather than a large shift of 25 cm^{–1} to higher energy for **4**.

The difference in structure between the two complexes is striking and reflects the balance between weak intermolecular interactions, host–host, host–guest, and guest–guest, which are within the realms of crystal packing forces.

Acknowledgment. Support from the Australian Research Council is gratefully appreciated.

Supporting Information Available: Tables of X-ray data, positional and thermal parameters, and distances and angles for **4** and **5** and optimized geometries and thermochemistry data for **4** (13 pages). See any current masthead page for ordering and Internet access instructions.