Definitive crystal structures of *ortho*-, *meta*- and *para*-carboranes: supramolecular structures directed solely by C–H···O hydrogen bonding to hmpa (hmpa = hexamethylphosphoramide)

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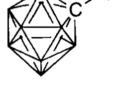
Cocrystallisation of *ortho- meta-* and *para*-carboranes with hmpa (hexamethylphosphoramide) results in the isolation of 1 : 1 carborane:hmpa adducts which provide the first definitive X-ray structures of the unsubstituted carboranes as part of three very different C–H···O hydrogen-bonded supramolecular structures.

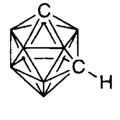
The study of the supramolecular structure of solids is currently an area of intensive research[1] primarily because it is expected that the ability to predict and control the supramolecular structure of organic solids by consideration of the molecular units employed (so-called crystal engineering) will provide the key to the designed synthesis of optically and electronically active organic solids.[2] The major factor that drives the assembly of a particular supramolecular structure in organic compounds is undoubtedly intermolecular hydrogen bonding. One strategy that has been employed to elucidate the molecular factors that govern supramolecular structure is to cocrystallise two components which possess hydrogen-bonding functional groups and to compare structures in which the orientation of these groups has been systematically varied at the molecular level.[3] While this approach has been successful for a number of 'strong' X–H···Y (X, Y = N, O) hydrogen-bonded systems, its application to weaker C–H···X interactions is presently far more limited.[1,2] In recognising the high C–H acidity of carboranes **1**[4] (and therefore their potential for hydrogen bonding[5]) and the ready availability of *ortho* **1a**, *meta* **1b**, and *para* **1c** derivatives, which possess C–H groups in well defined but differing orientations within the same pseudo-spherical molecular framework, we speculated that the $C_2B_{10}H_{12}$ cluster might be a good molecular unit with which to apply this strategy to a system containing *only* C–H···X hydrogen bonds as directors of supramolecular structure; the molecular rigidity and topological versatility of carboranes has already been exploited in other molecular design contexts.[6] An additional incentive for this work was the potential use of a hydrogen bond acceptor to reduce the crystallographically imposed symmetry that, because of disorder of B and C atoms, has frustrated previous attempts to obtain definitive X-ray structures of the parent carboranes **1**.[4b] For this initial study we chose to cocrystallise carboranes with hexamethylphosphoramide (hmpa) **2** as it has been shown to be an excellent acceptor of hydrogen bonds.[7]

Addition of 1 equiv. of hmpa **2** to a suspension of carboranes **1a–c** in toluene caused complete dissolution. Slow evaporation of these solutions yielded crystalline solids which were shown by ^1H NMR to contain carborane and hmpa in a 1 : 1 stoichiometry (the presence of an excess of hmpa in solution was found not to affect the stoichiometry of the isolated solids). Preliminary characterisation (^1H NMR spectroscopy in benzene) suggested that the two components of the cocrystals exist separately in solution. However, a reduction of frequency and a broadening of the carborane C–H stretching signal observed in solid-state IR spectra (KBr disc) indicated that hydrogen bonded adducts $(\mathbf{1}\cdot\mathbf{2})_n$ exist in the solid state.

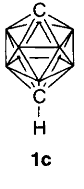
Crystal structures† of the three adducts confirmed the existence of intermolecular C–H···O hydrogen bonding in the solid state, although the three $(\mathbf{1}\cdot\mathbf{2})_n$ adducts adopt quite different supramolecular structures. The *ortho* derivative forms discrete dimers $(\mathbf{1a}\cdot\mathbf{2})_2$ (Fig. 1). Each hmpa molecule bridges two crystallographically independent but similar carborane units *via* two short C–H···O[8] interactions. All four resulting hydrogen bonds are of a similar geometry (see Fig. 1 caption). The P–O bond vectors are almost orthogonal to each other and the HC–CH units within the carboranes are far from coplanar. This unusual geometry [which contrasts with the centrosymmetric and planar $(\cdots HCCH\cdots O)_2$ ring that was previously observed in the crystal structure of a dimeric 1 : 1 decachloro-*ortho*-carborane: Me_2SO adduct] must be a consequence of the need to achieve a close-packed structure. In contrast, both *meta*- and *para*-carboranes form one-dimensional polymeric adducts:



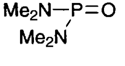
1a



1b



1c


$\begin{array}{l}Me_2N\diagdown\\ Me_2N{-}P{=}O\\ Me_2N\diagup\end{array}$

2

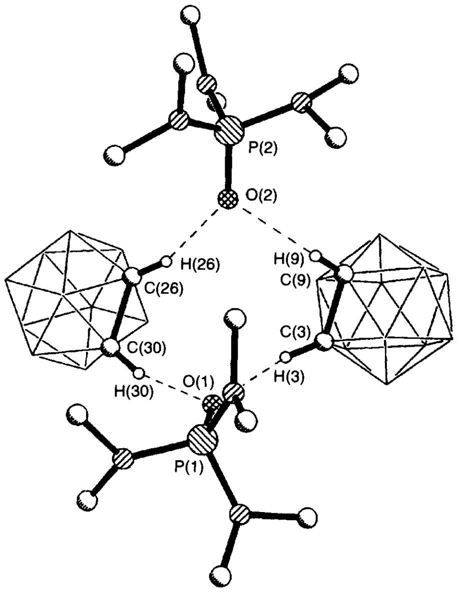


Fig. 1 The discrete, dimeric structure of $(\mathbf{1a}\cdot\mathbf{2})_2$. Selected distances (Å) and angles (°): C(26)–C(30) 1.629(6), C(3)–C(9) 1.630(6), C(3)···O(1) 3.130(5), C(30)···O(1) 3.071(6), C(9)···O(2) 3.050(5), C(26)···O(2) 3.179(6), C(3)–H(3)···O(1) 158(4), C(9)–H(9)···O(2) 154(4), C(26)–H(26)···O(2) 158(4), C(30)–H(30)···O(2) 160(4) (for clarity, only H atoms involved in hydrogen bonding are shown and B_{10} fragments are shown as narrow lines).

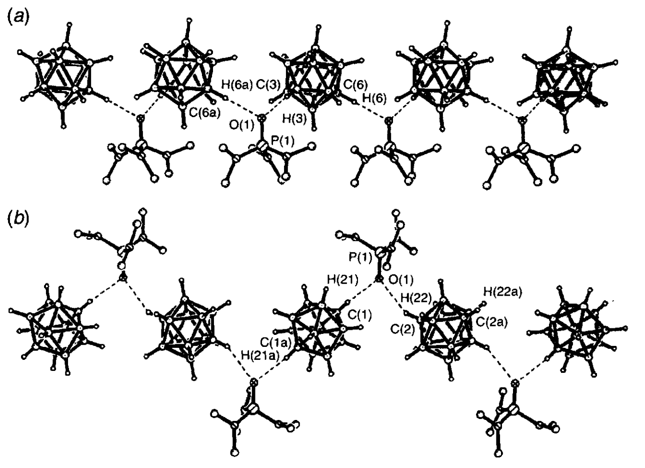


Fig. 2 (*a*) The polymeric structure of $(\mathbf{1b}\cdot\mathbf{2})_\infty$. Selected distances (Å) and angles (°): intracage C(3)···C(6) 2.609(7), C(3)···O(1) 3.328(6), C(6)···O(1) 3.234(5), C(3)–H(3)···O(1) 175(4), C(6)–H(6)···O(1) 164(4). (*b*) The polymeric structure of $(\mathbf{1c}\cdot\mathbf{2})_\infty$. Selected distances (Å) and angles (°): intracage C(1)···C(1a) 3.052(7), intracage C(2)···C(2a) 3.059(8), C(1)···O(1) 3.132(4), C(2)···O(1) 3.378(4), C(1)–H(21)···O(1) 173(2), C(2)–H(22)···O(1) 152(3) (for clarity, only carborane H atoms are shown).

$(\mathbf{1b}\cdot\mathbf{2})_\infty$ and $(\mathbf{1c}\cdot\mathbf{2})_\infty$, respectively (Fig. 2). In both cases carborane molecules are linked by hmpa molecules *via* C–H···O···H–C bridges, but the different molecular orientations of the C–H groups result in correspondingly different supramolecular arrangements of polymers. Surprisingly, in the $(\mathbf{1b}\cdot\mathbf{2})_\infty$ adduct [Fig. 2(*a*)] all hmpa molecules lie on one side of the chain. Also, all carborane molecules are equivalent and contribute one nearly linear and one more acute hydrogen bond (see Fig. 2 caption). The $(\mathbf{1c}\cdot\mathbf{2})_\infty$ adduct [Fig. 2(*b*)], however, consists of zigzag polymeric chains in which the C–H···O···H–C bridges (and therefore the hmpa molecules themselves) alternate from side to side along the chain. Here, though each hmpa is again involved in one nearly linear and one more acute hydrogen bond (see Fig. 2 caption), there are two inequivalent and alternating carborane molecules; one donating only linear hydrogen bonds and the other donating only the more acute hydrogen bonds.

To our knowledge, the structures of these adducts represent the first observations of the unsubstituted parent carboranes **1** in a crystal lattice.[10] The C–H···O hydrogen bonds lock the clusters in specific orientations and so allow unambiguous location of the two carbon atoms within the C_2B_{10} clusters. Their location *via* weak intermolecular interactions, rather than by substitution of the carborane at either B or C, causes minimum electronic perturbation of the cluster and one can assume, therefore, that the structural parameters derived from the adducts $(\mathbf{1}\cdot\mathbf{2})_n$ provide a very close approximation to those of the carboranes **1** themselves. As such, these structures provide a useful benchmark from which to judge the effect of substitution on bonding within the cluster. For example, the C–C distances in $(\mathbf{1a}\cdot\mathbf{2})_2$ [1.630(6), 1.629(6) Å for C(3)–C(9), C(26)–C(30), respectively] provide a measure of the electronic effect due to electron-donating C substituents, all structurally characterised examples of which exhibit longer cage C–C distances than are found in $(\mathbf{1a}\cdot\mathbf{2})_2$.[11] Similarly, the cross polyhedral (antipodal) C···C distances in $(\mathbf{1c}\cdot\mathbf{2})_\infty$ [3.052(7), 3.059(8) Å for C(1)···C(1a), C(2)···C(2a), respectively] may be compared with intracage distances ranging between 3.01(3) and 3.22(1) Å for a series of B–iodo derivatives of **1c**.[12]

We are currently further investigating hydrogen bonding in structures containing both parent and substituted carboranes.

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Footnote

† *Crystal data*: $(\mathbf{1a}\cdot\mathbf{2})_2$, $C_8H_{30}B_{10}N_3OP$, M = 323.42, colourless blocks of 0.2 × 0.3 × 0.3 mm size, T = 150(2) K, triclinic, space group $P\bar{1}$, a = 10.662(2), b = 10.890(2), c = 17.078(3) Å, α = 90.59(3), β = 91.97(3), γ = 92.23(3)°, U = 1980.1(6) Å^3, Z = 4, D_c = 1.085 g cm^{-3}, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 1.37 cm^{-1}; data collection on a Siemens three-circle diffractometer with a CCD area detector, ω scan mode, $2\theta < 51°$, 9691 total, 6413 unique, 4636 observed [$I > 2\sigma(I)$] data, R_{int} = 0.043. The structure was solved[13] by direct methods and refined [13] by full-matrix least squares against F^2 (non-H atoms anisotropic, all carborane H atoms isotropic, hmpa H atoms placed in calculated positions, 524 variables/6306 data) to $wR(F^2$, all data) = 0.188, goodness-of-fit 1.22 $R(F$, obs. data) = 0.077; $\Delta\rho_{max}$ = 0.37 e Å^{-3}.

$(\mathbf{1b}\cdot\mathbf{2})_\infty$, $C_8H_{30}B_{10}N_3OP$, M = 323.42, colourless blocks of 0.3 × 0.4 × 0.5 mm size, T = 150(2) K, monoclinic, space group Cc, a = 12.867(4), b = 14.713(8), c = 11.100(2) Å, β = 111.41(3)°, U = 1956.24(6) Å^3, Z = 4, D_c = 1.10 g cm^{-3}, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 1.39 cm^{-1}; data collection on a Siemens three-circle diffractometer with a CCD area detector, ω scan mode, $2\theta < 51°$, 4632 total, 2682 unique, 2367 observed [$I > 2\sigma(I)$] data, R_{int} = 0.033. The structure was solved[13] by direct methods and refined[13] by full-matrix least squares against F^2 (non-H atoms anisotropic, all carborane H atoms isotropic, hmpa H atoms placed in calculated positions, 263 variables/2671 data) to $wR(F^2$, all data) = 0.135, goodness-of-fit 1.20, $R(F$, obs. data) = 0.051; $\Delta\rho_{max}$ = 0.20 e Å^{-3}.

$(\mathbf{1c}\cdot\mathbf{2})_\infty$, $C_8H_{30}B_{10}N_3OP$, M = 323.42, colourless blocks of 0.4 × 0.4 × 0.4 mm size, T = 150(2) K, monoclinic, space group $P2_1/c$, a = 10.234(2), b = 14.338(3), c = 13.531(3) Å, β = 102.81(3)°, U = 1936.1(7) Å^3, Z = 4, D_c = 1.11 g cm^{-3}, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 1.40 cm^{-1}; data collection on a Siemens three-circle diffractometer with a CCD area detector, ω scan mode, $2\theta < 52°$, 8235 total, 3294 unique, 2021 observed [$I > 2\sigma(I)$] data, R_{int} = 0.071. The structure was solved[13] by direct methods and refined[13] by full-matrix least squares against F^2 (non-H atoms anisotropic, all carborane H atoms isotropic, hmpa H atoms placed in calculated positions, 263 variables/3264) to $wR(F^2$, all data) = 0.139, goodness-of-fit 1.08, $R(F$, obs. data) = 0.060; $\Delta\rho_{max}$ = 0.26 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/219.

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