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Self-assembly of carborane molecules *via* C–H · · · I hydrogen bonding: the molecular and crystal structures of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$

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The crystal structure of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ reveals that molecules are arranged as infinite head-to-tail zig-zag double chains held together by C–H · · · I hydrogen bonding.

The last two decades have witnessed the emergence of supramolecular chemistry[1] as an area of considerable interest, covering all aspects of the discipline from biochemistry to organic, organometallic, and physical chemistry and encompassing the thriving area of materials. The non-covalent interactions crucial in supramolecular chemistry are most effectively utilised when they are periodic, realising the field of molecular crystal engineering,[2] dependent on appropriate building-block molecules and suitable linking groups.

It has already been pointed out that boron-based clusters can play an important rôle in this field[3] by virtue of their three-dimensional structures and well-developed derivative chemistries. In particular the three isomeric icosahedral carboranes, 1,2-, 1,7- and 1,12-*closo*-$C_2B_{10}H_{12}$ appear to have great potential as building blocks in supramolecular systems which is only now beginning to be explored.[4] Moreover the CH protons of 1,2-carboranes are highly acidic[5] (carrying a charge of +0.30 *cf.* 0.07–0.09 for the hydrogen atoms on boron[6]) and consequently have the potential for hydrogen bonding.[7]

Previously, self-assembly of carboranes *via* C–H · · · X hydrogen bonding has been limited to C–H · · · O interactions, both classical[8] and bifurcated, C–H · · · $(O)_2$,[9] C–H · · · π interactions[10] and, recently, C–H · · · F interactions.[11] Self-assembly of carboranes by weaker C–H · · · I interactions is currently unreported, although intermolecular C–H · · · I–B interactions do exist in a few neutral iodo(hetero)boranes[12] where the source of the C–H unit is a co-crystallising molecule or ion. Crystal structures of four iodo dicarbadodecaboranes, $C_2B_{10}H_{11}I$, have previously been reported, namely 4-I-1,7-*closo*-$C_2B_{10}H_{12}$,[13] 8-I-1,2-*closo*-$C_2B_{10}H_{12}$,[14] 2-I-1,12-*closo*-$C_2B_{10}H_{12}$[15] and 9-I-1,7-*closo*-$C_2B_{10}H_{12}$,[16] but in none of these are there intermolecular C–H · · · I interactions.[17] Here we report the first example of supramolecular self-assembly directed by carborane C–H · · · I interactions.

The carborane 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ was synthesised according to the literature,[18] through {BI} recapitation of [7,8-*nido*-$C_2B_9H_{11}]^{2-}$. The ^1H NMR spectrum of the product reveals a singlet at 3.84 ppm. assigned to the two C-bonded H atoms, *ca.* 0.3 ppm to high frequency relative to that in 1,2-*closo*-$C_2B_{10}H_{12}$, suggesting greater protonic character for these H atoms in the iodo species. Moreover, the solid-state IR spectrum of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ exhibits a C–H stretching frequency at 3052 cm^{-1} measurably lower than that, 3070 cm^{-1}, in the unsubstituted parent. This lower energy stretching mode for C–H is fully consistent with the existence of H-bonding in the solid state, presumably of the C–H · · · I type. To establish the situation unequivocally, a single-crystal X-ray diffraction analysis† of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ was undertaken, colourless crystals having been grown by the slow evaporation of a hexane solution of the compound.

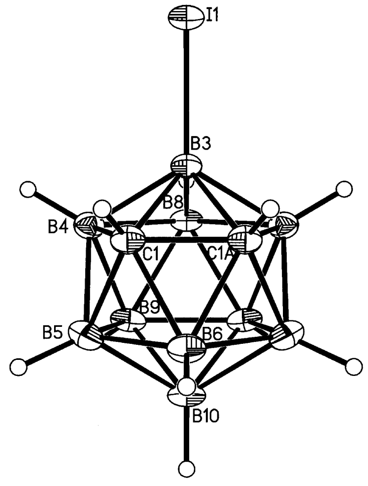

Fig. 1 Perspective view of a single molecule of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$. The plane defined by I1B3B8B6B10 is a crystallographic mirror plane. Atoms reflected across this plane carry the letter A. Atoms are drawn as 50% thermal ellipsoids, except for H atoms. Interatomic distances (Å) and selected angles (°): C1–C1A 1.624(8), C1–B3 1.711(6), C1–B4 1.708(5), C1–B5 1.701(6), C1–B6 1.733(7), B3–I1 2.168(6), B3–B4 1.764(6), B3–B8 1.756(9), B4–B5 1.792(6), B4–B8 1.784(6), B4–B9 1.787(6), B5–B9 1.773(6), B5–B10 1.795(6), B9–B9A 1.789(9), B9–B10 1.791(7), I1–B3–C1 118.9(3), I1–B3–B4 123.1(2), I1–B3–B8 129.1(4).

A perspective view of a single molecule is shown in Fig. 1. The molecule has C_s symmetry which is crystallographically imposed. The cage has the expected near-icosahedral geometry with the lengths of the differing types of connectivity increasing in the expected sequence C–C < C–B < B–B, the magnitudes of these connectivities standing good comparison with those determined for 1,2-*closo*-$C_2B_{10}H_{12}$.[8] Close inspection of the connectivities involving the substituted B atom, B3, and the otherwise equivalent atom, B6, reveals that iodide substitution has the effect of shrinking the cage connectivities somewhat, since B3–C1, B3–B4 and B3–B8 are all shorter than B6–C1, B6–B5 and B6–B10, respectively, by statistically significant amounts. The B3–I distance is 2.168(6) Å, in excellent agreement with other such distances in the literature.[15,16,19]

The crystal structure of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ reveals two orientations of molecules (head-to-tail) arranged in infinite double zig-zag chains running parallel to the *b* crystallographic axis (Fig. 2). Both carborane C–H vertices participate in C–H · · · I interactions. The chains are held together by I · · · H1 hydrogen bonds, 3.215 Å, involving the protonic C-bound H atom, C(1)–H(1) · · · I 133.5°, and a bifurcated linkage at I, H · · · I–B3 114.6°; H · · · I · · · H 126.6°. Thus the environment at I in the crystal is quasi-planer—the sum of

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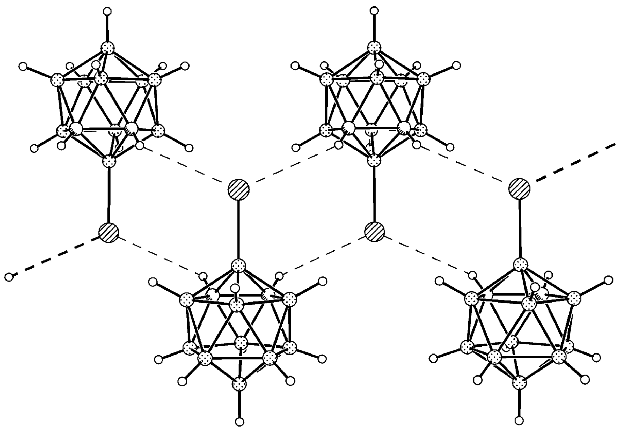

Fig. 2 Crystal structure of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ showing the C–H ··· I hydrogen bonding which results in a head-to-tail arrangement of molecules forming an infinite double zig-zag chain running parallel to the crystallographic *b* axis. I ··· H is 3.215 Å, C–H ··· I is 133.5°, and there is a bifurcated linkage at I, H ··· I–B 114.6° and H ··· I ··· H 126.6°.

angles at I is 355.8°, and I is displaced only 0.33 Å out of the plane defined by B3 and the two adjacent H1 atoms.

Individually these intermolecular C–H ··· I interactions are clearly weak, since the sum of the van der Waals radii of H and I is only 3.35 Å and CH ··· I distances between neutral molecules as small as 2.81 Å are known in the literature.[20] However, the adjacency of the acidic CH groups to the I-substituted boron atom obviously affords a molecule that can maximise its intermolecular C–H ··· I bonding in a very efficient fashion by adopting the double chain shown in Fig. 2. Certainly this is the first reported example of carborane self-assembly *via* C–H ··· I interactions.

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Notes and references

† Colourless single crystals of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ were grown from hexane. Crystal data for $C_2H_{11}B_{10}I$, 160(2) K, $M_r = 270.11$: crystal size 0.36 × 0.68 × 0.42 mm, orthorhombic, *Pnma*, $a = 20.011(3)$, $b = 8.0039(10)$, $c = 6.4946(14)$ Å, $V = 1040.2(3)$ Å^3, $Z = 4$ (C_s symmetry imposed), $D_c = 1.725$ Mg m^{-3}, $F(000) = 504$, $\mu = 3.009$ mm^{-1}. Of 990 unique reflections from 1417 measured ($R_{int} = 0.0480$), 873 were observed [$F_o > 4\sigma(F_o)$]. Refinement of 85 parameters converged at $R_1 = 0.0373$, $wR_2 = 0.0801$ (for all data), $R_1 = 0.0320$, $wR_2 = 0.0773$ (for observed data). $S = 1.045$, max. and min. residual electron density: 0.564 and −1.828 e Å^{-3} (near I1). Intensity data were collected on a Bruker P4 diffractometer, with Mo-Kα radiation ($\lambda = 0.71073$ Å) to $2\theta_{max} = 50°$, ω-scans, corrections for absorption (φ-scans), Lorentz and polarisation effects, and structures were solved by direct methods and refined (against F^2) by full-matrix least-squares refinement.[21] Cage C atoms were unambiguously identified by inspection of *U* values following isotropic refinement of all cage vertices as boron, and confirmed by C–C distances. H atoms treated as riding model. CCDC reference number 154905. See http://www.rsc.org/suppdata/dt/b2/b206892n/ for crystallographic data in CIF or other electronic format.

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