

9,12-Diiodo-1,2-dicarba-closo-dodecaborane(12)

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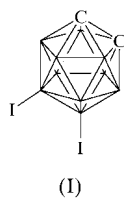
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The title compound, $C_2H_{10}B_{10}I_2$, has a pseudo-icosahedral cluster geometry. The crystal structure features an intermolecular $C-H \cdots I-B$ hydrogen bond with a normalized $H \cdots I$ distance of 3.00 Å.

Comment

Carboranes with I atoms substituted at boron are precursors to a large number of *B*-alkyl-, *B*-allyl-, *B*-aryl- and *B*-ethynyl-carboranes (Zakharkin *et al.*, 1982; Li *et al.*, 1991; Yang *et al.*, 1994; Zheng *et al.*, 1995; Jiang *et al.*, 1995; Harakas *et al.*, 1998; Lee *et al.*, 2000; Fox & Wade, 2002). Some *B*-iodocarboranes have been structurally characterized (Zheng *et al.*, 1995; Jiang *et al.*, 1995; McGrath *et al.*, 2000; Marshall *et al.*, 2001). However, the most widely used precursor, 9,12-diiodo-1,2-dicarba-closo-dodecaborane(12), or 9,12-diiodo-ortho-carborane, (I), has not yet been structurally studied as an individual compound, although the structure of the 1:1 host-guest complex of (I) with the mercuracarborand $(C_2B_{10}H_8Et_2Hg)_4$ has been reported by Yang *et al.* (1994). In this complex, the mercuracarborand host acts as an 'inverse crown-ether', to which (I) is coordinated *via* $Hg \cdots I$ interactions. This nucleophilic role of the iodine substituents is of particular interest since (I) is also a precursor to the mercuracarborand $(C_2B_{10}H_8I_2Hg)_4$, which exhibits remarkable modular self-assembly in the solid state (Lee *et al.*, 2001).



In this paper, we report the structure of (I), which we prepared by reacting 1,2-dicarba-closo-dodecaborane(12) and I_2 in acetic acid with an HNO_3/H_2SO_4 mixture. This method,

developed for the syntheses of several *B*-iodocarboranes by Fox & Wade (1999, 2002) and McGrath *et al.* (2000), is more convenient than those reported earlier by Zakharkin & Kalinin (1966), Stanko *et al.* (1968), Li *et al.* (1991) and Zheng *et al.* (1995).

The molecular geometry of (I) is unremarkable (Fig. 1 and Table 1). The iodine substituents effectively prevent the rotational disorder of the highly symmetrical carborane cage which often hampers crystallographic studies of icosahedral carboranes. The location of the C atoms is not an issue since the spectroscopy data locate them uniquely *para* with respect to the substituted B atoms. An interesting feature of the crystal packing is the $C-H \cdots I$ hydrogen bonding. Covalently bonded I atoms are not known as good acceptors of hydrogen bonds, in contrast to I^- anions (Desiraju & Steiner, 1999). This is not surprising, since the covalent species in question mostly either contained I_2 molecules or were organic molecules with C-I bonds. The electronegativities of iodine and carbon being equal (*ca* 2.5 on Pauling's scale; see Batsanov, 1990, and references therein), the C-I bond is non-polar, as, of course, is the I-I bond. Thus, in either case, the I atom carries no net negative charge. In (I), however, iodine is bonded to an atom with much lower electronegativity (1.9) than itself. Thus, there should be a substantial shift of electron density toward the I atoms, which thus become capable of accepting hydrogen bonds. On the other hand, polarization of the B-I bonds can further enhance the acidity of the carborane CH groups, which, even in unsubstituted carborane, are sufficiently acidic to act as donors of hydrogen bonds.

In fact, the intermolecular contact $C1-H1 \cdots I12(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$ can be regarded as a hydrogen bond; the $H \cdots I$ distance of 3.00 (3) Å, calculated for the corrected C-H bond distance of 1.083 Å (Allen *et al.*, 1987), is shorter than the relevant van der Waals sum of 3.14 Å (Rowland & Taylor, 1996), and the $C-H \cdots I$ angle of 141 (3)° is sufficiently close to 180°.

These bonds link molecules into chains which spiral around 2_1 screw axes parallel to z . However, the other acidic H atom only participates in a much weaker $C2-H2 \cdots I9(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ interaction, with a corrected $H \cdots I$ distance of 3.32 (5) Å. On the other hand, there is a relatively close $B6-H6 \cdots I12(-\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$ contact, with an $H \cdots I$ distance of 3.15 (4) Å (for the B-H bond length corrected to 1.216 Å; see Bohn & Bohn, 1971), which can not be described as a hydrogen bond.

A broadly similar pattern was observed in the crystal of the dibromo analogue of (I), *viz.* 9,12-dibromo-1,2-dicarba-closo-dodecaborane(12) (Potenza & Lipscomb, 1966), although the latter has different symmetry (space group $Pbn2_1$). This structure also contains only one symmetrically independent $C-H \cdots Br$ hydrogen bond, with an $H \cdots Br$ distance of 2.53 Å (relative to the sum of the van der Waals radii for H and Br of 2.99 Å; Rowland & Taylor, 1996), the next shortest $H \cdots Br$ distance being 2.98 Å.

The crystal structure of 3-iodo-1,2-dicarba-closo-dodecaborane(12) has been reported recently (Barberà *et al.*, 2002) and reveals self-assembly of carborane molecules *via* C-

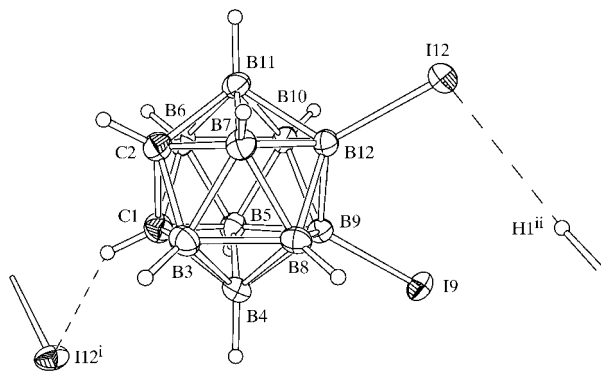


Figure 1

A view of the molecular structure of (I) and the intermolecular hydrogen bonds [symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$]. Displacement ellipsoids are drawn at the 50% probability level.

H...I hydrogen bonds. The C—H...I distance is 3.10 Å, with a C—H...I angle of 131° for a normalized C—H bond distance of 1.083 Å. Unlike in (I), the carbon/boron ordering of the cage in 3-iodo-1,2-dicarba-closo-dodecaborane(12) is directed by these hydrogen bonds.

Experimental

A stirred solution of 1,2-dicarba-closo-dodecaborane(12) (1.44 g, 10 mmol) and iodine (2.54 g, 10 mmol) in glacial acetic acid (40 ml) was heated to 353 K and treated slowly with a mixture of HNO₃ and H₂SO₄ (1:1 v/v, 25 ml). A brown vapour was observed above the solution and within 1 h the solution became colourless. It was poured into distilled water (300 ml) and the precipitate was washed with water and then dissolved in ether. The ether solution was dried and the ether evaporated. The residue was recrystallized from hexane to give 3.25 g (82%) of crude (I), which contained a ca 13% admixture of the 8,9-diiodo isomer, (Ia) [m.p. 463–464 K, cf. 466–467 K for pure (I) (Stanko *et al.*, 1968)]. This product displayed the NMR signals of (I) as reported by Li *et al.* (1991) and Heřmánek (1999) [*viz.* ¹H {¹¹B} (δ in CDCl₃): 4.00 (C1,2H), 2.89 (B8,10H), 2.74 (B4,5,7,11H), 2.49 (B3,6H)], as well as those of (Ia) [*viz.* ¹¹B: −0.8 (B12), −9.4 (B10), −13.2 (B4), −18.8 (B6), −20.9 (B8)]. Further recrystallization from a hexane–acetone (1:1) mixture gave X-ray quality crystals of pure (I).

Crystal data

C₂H₁₀B₁₀I₂
M_r = 396.00
 Orthorhombic, *P*2₁2₁2₁
a = 7.126 (3) Å
b = 12.320 (4) Å
c = 13.905 (5) Å
V = 1220.8 (8) Å³
Z = 4
D_x = 2.155 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 959 reflections
 θ = 11.9–25.9°
 μ = 5.10 mm^{−1}
T = 120 (2) K
 Block, colourless
 0.22 × 0.18 × 0.16 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: by integration (*XPREP*; Bruker, 1998)
T_{min} = 0.391, *T_{max}* = 0.513
 9618 measured reflections

3233 independent reflections
 3133 reflections with *I* > 2σ(*I*)
R_{int} = 0.034
 θ_{max} = 29.1°
h = −9 → 9
k = −11 → 16
l = −18 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.019
wR(*F*²) = 0.047
S = 1.05
 3233 reflections
 127 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 1.295P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.57 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.86 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 1350 Friedel pairs
 Flack parameter = −0.01 (3)

Table 1

Selected geometric parameters (Å, °).

I9—B9	2.183 (3)	B4—B5	1.790 (5)
I12—B12	2.173 (4)	B5—B6	1.773 (6)
C1—C2	1.626 (5)	B5—B10	1.781 (5)
C1—B4	1.693 (5)	B5—B9	1.780 (5)
C1—B5	1.697 (5)	B6—B10	1.757 (5)
C1—B6	1.712 (6)	B6—B11	1.773 (6)
C1—B3	1.723 (5)	B7—B12	1.774 (5)
C2—B11	1.690 (5)	B7—B8	1.785 (5)
C2—B6	1.704 (5)	B7—B11	1.790 (6)
C2—B7	1.708 (5)	B8—B12	1.795 (5)
C2—B3	1.733 (6)	B8—B9	1.795 (5)
B3—B8	1.764 (5)	B9—B12	1.773 (5)
B3—B4	1.781 (6)	B9—B10	1.794 (5)
B3—B7	1.786 (6)	B10—B11	1.780 (5)
B4—B9	1.774 (5)	B10—B12	1.792 (5)
B4—B8	1.789 (5)	B11—B12	1.781 (5)
B12—B9—I9	124.1 (2)	B9—B12—I12	123.3 (2)
B4—B9—I9	119.7 (2)	B7—B12—I12	121.0 (2)
B5—B9—I9	119.2 (2)	B11—B12—I12	119.1 (2)
B10—B9—I9	121.8 (2)	B10—B12—I12	120.1 (2)
B8—B9—I9	122.2 (2)	B8—B12—I12	123.4 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1...I9 ⁱ	1.00	3.37	4.017 (4)	124
C1—H1...I12 ⁱ	1.00	3.05	3.877 (4)	141
C2—H2...I9 ⁱⁱ	1.00	3.37	4.031 (4)	125

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

All H atoms were located in difference Fourier maps. Their geometries were then idealized and they were refined using a riding model, with B—H = 1.12 Å and C—H = 1.00 Å, and with *U_{iso}*(H) values fixed at 1.2*U_{eq}*(B,C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1513). Services for accessing these data are described at the back of the journal.

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