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Dihydrobis(methylamine)borate triiodide

Graeme J. Gainsford* and Tim Kemmitt

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
Correspondence e-mail: g.gainsford@irl.cri.nz

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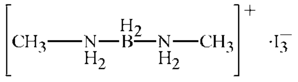
Both cation and anion in the title compound, $C_2H_{12}BN_2^+\cdot I_3^-$, lie on a crystallographic mirror plane and are bound in the lattice by $N—H\cdots I^-$ hydrogen bonds, forming layers. Methyl-H–borane-H dihydride [–C—H(δ^+)$\cdots$(δ^-)H—B–] interactions between molecules crosslink adjacent layers, giving 'sandwich' stacking along the *a* axis.

Comment

During studies investigating the syntheses and structures of ammonia–borane compounds and derivatives, crystals of the title compound, (I), were isolated. Although the reaction sequence is not confirmed, it is likely that the high reactivity of the B—I bond in the intermediate methylamine iodoborane (Nöth & Beyer, 1960) and the primary amine, methylamine borane, in a coordinating solvent (tetrahydrofuran), resulted in the formation of the diamino–borane salt as described by Nöth *et al.* (1964). In the current case, employment of excess iodine led to crystallization of the triiodide salt.



$$\left[CH_3—\underset{H_2}{N}—\overset{H_2}{B}—\underset{H_2}{N}—CH_3\right]^+\cdot I_3^-$$

(I)

Capitalized refcodes hereafter are those of the Cambridge Structural Database (CSD; Version 5.27 with May 2006 updates; Allen, 2002). There are currently three amino–borane compound structures in which both the B and the N atoms are diprotonated as here, namely ethylenediamine-bis(borane) (EDABRO; Ting *et al.*, 1972) and two cyano-boranes (FASJIT and LOYTAU; Vyakaranam, Rana, Zheng *et al.*, 2002; Vyakaranam, Rana, Spielvogel *et al.*, 2002). By contrast there are many in which the B atom is diprotonated and the N atom is singly protonated or present as a dimethylamine, for example, the cyclic borazanes (*e.g.* DUJYOW; Narula *et al.*, 1986) and linear boranes [*e.g.* BATCOO (Nöth & Thomas, 1999) and IRITAE (Jaska *et al.*, 2004)].

The asymmetric unit of (I) contains the independent molecules shown in Fig. 1. Both cation and anion lie on a mirror plane ($y = \frac{1}{4}$) in a neat packing arrangement (discussed below). The B—N and C—N bond lengths (Table 1) are similar to those in EDABRO and the linear boranes but longer, as expected, than those in the cyano and cyclic borazanes. The triiodide anion I—I bond lengths are significantly different, following the trend observed when this anion is involved in $N—H_2^+\cdots I_3^-$ interactions, for example, 3.158 and 2.803 Å in GAFGUQ (Warden *et al.*, 2004). The normal I—I distance in I_3^- (as shown by structures where the molecule has an enforced centre of symmetry) is 2.91–2.92 Å (*e.g.* 2.914 Å in PATVEM02; Konarev *et al.*, 2005). From a cursory study of 188 CSD entries for I_3^-, it appears that the I—I—I bonding

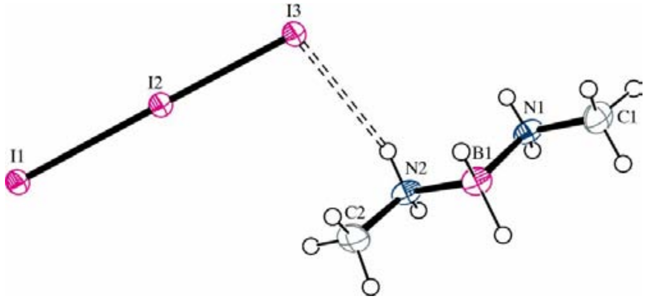


Figure 1
The asymmetric unit of (I), with ellipsoids at the 50% probability level (*ORTEP-3*; Farrugia, 1997). The dashed lines represent a hydrogen bond.

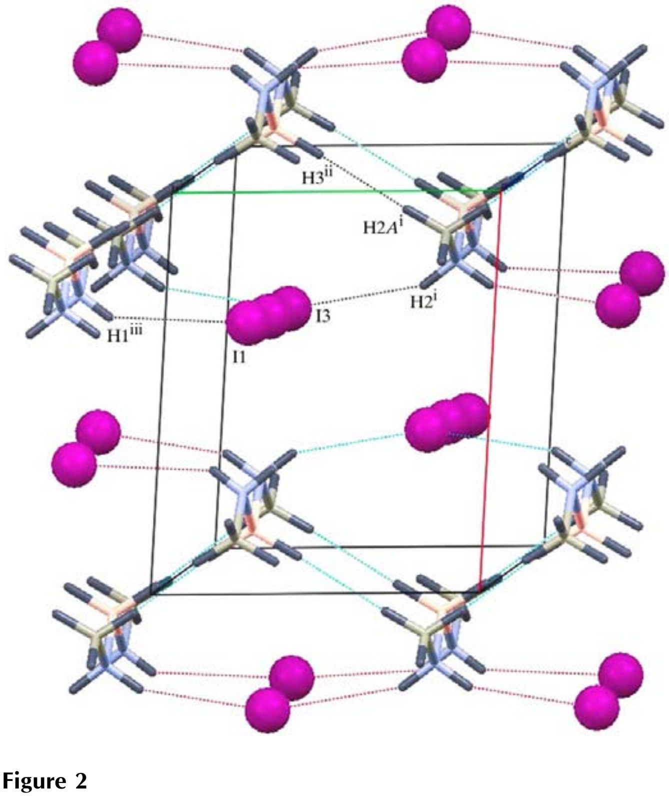


Figure 2
A cell view of (I), approximately down the *c* axis (*MERCURY*; Macrae *et al.*, 2006), showing the 'sandwich' crystal packing along the *a* axis: dotted lines represent hydrogen-bonding interactions. For clarity, only one set of H and I atoms involved in hydrogen bonding is labelled. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z$ (ii) $-x, y + \frac{1}{2}, -z + 1$; (iii) $x, y + 1, -1 + z$.]

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asymmetry generally reflects strong $H^{+}\cdots I^{-}$ interactions in the lattice; there are exceptions, however, such as the values of 3.086 and 2.797 Å in HILLUJ (Grafe-Kavoosian *et al.*, 1998). The intermolecular interaction distance between anions here is 3.5895 (7) Å compared with the expected 3.96 Å van der Waals distance. However, this interaction distance is typical and close to the minimum value reported so far in the CSD for this anion (3.55 Å in GUFNEA; Chandrasekaran *et al.*, 2000).

Conventional N—H···I hydrogen bonds (Table 2 and Fig. 2) provide the main packing forces in the cell, building two-dimensional layers in the *bc* plane. Typical $N—H\cdots I_3^{-}$ hydrogen bonds have H···I distances and N—H···I angles ranging from 2.52 Å and 171° (RACNOY; Robertson *et al.*, 1996) to 2.85 Å and 139° (GAFGUQ; Warden *et al.*, 2004). In addition, dihydride methyl C—H···H-borane interactions (Table 2) crosslink adjacent layers to form a 'sandwich stack' along the *a* axis (Fig. 2). The existence of intramolecular C—H···H—B close contacts, leading to stabilization against disproportionation, has been noted before by Custelcean & Jackson (2001). There are other crystallographic examples of such interactions; most commonly these involve ammonia–borane (BH_3–NH_3) in compounds such as GIJPAC (Pears *et al.*, 1988), with H···H distances of 2.21 and 2.25 Å, or with the adjacent N atom singly protonated (*e.g.* LOKFAS; Amezcua *et al.*, 1999; H···H = 2.26 Å). A CSD search with the B atom bound to a C rather than the N atom shows that the H···H distance is usually longer and that the B atom is bonded to an electron-withdrawing group or atom, *e.g.* a metal atom such as Rh in MADMEK (Londesborough *et al.*, 2004), with H···H distances of 2.38 and 2.35 Å. In our case, the elegant N—H···I hydrogen binding, whereby both ends of the I_3^{-} ion bind to different amine H atoms in the molecules, permits the dihydridic interactions to be available from both distance and steric points of view (as shown in Fig. 2).

Experimental

Iodine (16.75 g, 0.066 mol) was added in small aliquots to an ice-cooled solution of methylamine borane (2.94 g, 0.066 mol) in tetrahydrofuran (100 ml). After stirring for 2 h, the solution was warmed to room temperature and stirred for a further 4 h. On removal of most of the solvent, needles of the title compound precipitated.

Crystal data

$C_2H_{12}BN_2^{+}\cdot I_3^{-}$
$M_r = 455.64$
Monoclinic, $P2_1/m$
$a = 9.3387\ (11)$ Å
$b = 7.1393\ (8)$ Å
$c = 9.4837\ (10)$ Å
$\beta = 118.495\ (5)^\circ$
$V = 555.70\ (11)$ Å^3
$Z = 2$
$D_x = 2.723$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 8.37$ mm^{-1}
$T = 93\ (2)$ K
Needle, red–purple
0.58 × 0.13 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 1996)
$T_{min} = 0.241$, $T_{max} = 0.606$
6410 measured reflections
2067 independent reflections
1745 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 33.7^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.100$
$S = 1.10$
2067 reflections
72 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.986P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.82$ e Å^{-3}
$\Delta\rho_{min} = -1.97$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—I2	3.0592 (6)	N1—B1	1.606 (9)
I2—I3	2.8581 (6)	N2—C2	1.476 (9)
N1—C1	1.504 (8)	B1—H3	1.12 (6)
I3—I2—I1	179.232 (15)	C2—N2—B1	112.5 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···I1^{iv}	0.80 (6)	2.99 (6)	3.6651 (15)	144 (6)
N2—H2···I3	0.89 (6)	2.94 (6)	3.7320 (19)	149 (5)
C2—H2*A*···H3^{v}	0.98 (5)	2.28 (9)	3.25 (6)	171 (6)

Symmetry codes: (iv) $x, y-1, z+1$; (v) $-x, -y, -z+1$.

The H atoms on N1, N2 and B1 were positionally refined with U_{iso}(H) values of $1.2U_{eq}$(parent atom). Methyl atoms H1*A* and H2*A* were constrained to the mirror plane ($y = \frac{1}{4}$); the C—H distances of all the methyl H atoms were restrained to 0.98 (1) Å, with refined isotropic displacement parameters. An alternative model [using the density setting AFIX 137 (*SHELXL97*; Sheldrick, 1997) for the methyl H atoms] placed one H atom just off the mirror plane, indicating possible minor disorder across the plane. As both gave identical final agreement parameters, the simpler model above was used.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3034). Services for accessing these data are described at the back of the journal.

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