

Bis( $\mu$ -pyrrolidine-*N:N*)bis(dibromoboron), [(Br)<sub>2</sub>B(pyrrolidine)<sub>2</sub>B(Br)<sub>2</sub>]Hijazi Abu Ali,<sup>a</sup> Israel Goldberg<sup>b\*</sup> and Morris Srebnik<sup>a</sup><sup>a</sup>Department of Medicinal Chemistry and Natural Products, School of Pharmacy, Hebrew University in Jerusalem, Jerusalem, Israel, and <sup>b</sup>School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel  
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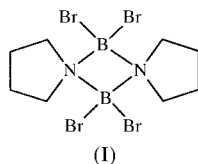
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The B atoms in the title compound, C<sub>8</sub>H<sub>16</sub>B<sub>2</sub>Br<sub>4</sub>N<sub>2</sub>, bridge between the two monomeric moieties, forming a (BN)<sub>2</sub> four-membered ring with partial bond orders of the B–N bonds.

## Comment

The B<sub>2</sub>(NR<sub>2</sub>)<sub>2</sub> compounds are important intermediates in the synthesis of B<sub>2</sub>(OR)<sub>4</sub> compounds, which are very useful in the preparation of boronic acids from alkynes (Ishiyama, Matsuda *et al.*, 1996), 1,3-butadienes (Ishiyama, Yamamoto & Miyaura, 1996),  $\alpha,\beta$ -enones (Lawson *et al.*, 1997), methylenecyclopropanes (Ishiyama *et al.*, 1999) and aromatic compounds (Ishiyama *et al.*, 1995). The preparation of B<sub>2</sub>(NR<sub>2</sub>)<sub>2</sub> involves Wurtz coupling of the dialkylhaloboranes (Brotherton *et al.*, 1960; Nöth & Meister, 1961). Moreover, the structural aspects of diborane chemistry are not well explored and conformational problems are not yet properly understood (Moezzi *et al.*, 1992). It has been shown that the bromides (R<sub>2</sub>N)<sub>2</sub>BBR provide better yields than the chlorides (Brotherton *et al.*, 1960). In addition, the size of the R groups on the nitrogen influences the yields of B<sub>2</sub>(NR<sub>2</sub>)<sub>2</sub>. In an effort to synthesize B<sub>2</sub>(NR<sub>2</sub>)<sub>2</sub> compounds other than the methyl derivative and to explore their structural chemistry, we studied the dehalogenation of bis(pyrrolidino)bromoborane. During the course of this investigation, we isolated an unexpected by-product, *i.e.* the title compound, [(Br)<sub>2</sub>B(pyrrolidine)<sub>2</sub>B(Br)<sub>2</sub>], (I), in low yield. Subsequently, the same product was obtained in 90% yield, as described below.



The molecular structure of (I) is illustrated in Fig. 1. The molecule has three possible directions for a C<sub>2</sub> axis, and it reveals an approximate C<sub>2</sub> symmetry about an axis passing perpendicular to the plane, and through the centre, of the four-membered ring. Its structural features, with relatively

long B–N bonds [mean 1.603 (7) Å], are similar to those observed in closely related aminoboron dichloride and difluoride dimers (Hazell, 1966; Edwards & Stadler, 1970; Jones, 1984; Clegg *et al.*, 1998; Jansen & Jäschke, 1999), as well as in other aminoboron dimers (Metzler & Nöth, 1995). This confirms that the observed elongation of the B–N bond is a genuine feature of the system.

The four-membered (BN)<sub>2</sub> ring in this structure has a distorted tetrahedral geometry. The N5–B7–N6 angle of 92.4 (2)° is significantly less than the ideal tetrahedral value. This results in a corresponding widening of the angles N5–B7–Br2 [113.5 (2)°], N6–B7–Br2 [113.7 (2)°], N5–B7–Br1 [113.9 (2)°] and N6–B7–Br1 [116.0 (2)°], while the Br2–B7–Br1 angle of 107.0 (2)° is relatively close to tetrahedral. The coordination geometry around the N atoms is also distorted from tetrahedral. Although the B7–N5–B8 angle of 86.8 (2)° is significantly less than the ideal tetrahedral value, widening of the C9–N5–C12 angle [100.3 (2)°] is not observed. On the other hand, the angles C9–N5–B7 [117.5 (2)°], C12–N5–B7 [118.0 (3)°], C9–N5–B8 [119.8 (3)°] and C12–N5–B8 [115.7 (2)°] are all expanded. Due to the presence of pseudo-C<sub>2</sub> symmetry, both B8 and N6 are similar to B7 and N5 in terms of geometry. The relatively long B–N bonds may be attributed to the coordination number of four around the B and N atoms, which, due to the bridging manner of the pyrrolidine groups, does not permit B–N  $\pi$ -bonding interactions, giving a bond order of about one. This is in contrast with an average B–N bond length of 1.48 Å observed in compounds having a B–N  $\pi$ -interaction and a bond order of about two (Nöth *et al.*, 1999). In addition, the electronegativity of the heterocyclic pyrrolidine groups also tends to inhibit  $\pi$ -bonding through their N atoms.

The four-membered heterocyclic ring has a bent nature. The dihedral angles between its N–B–N planes and between its B–N–B planes are 16.2 (3) and 15.4 (3)°, respectively. The pyrrolidine groups are puckered and adopt an envelope conformation with the N atoms at the flaps. The corresponding puckering parameters (Cremer & Pople, 1975) for the two rings are  $q_2 = 0.438$  (4) and 0.435 (3) Å, and  $\varphi_2 = -178.9$  (5) and  $-174.4$  (5)°. The carbon plane of one ring (C13–C16) points up, while the plane of the other ring (C9–C12) points down. The deviations of the N atoms from the respective

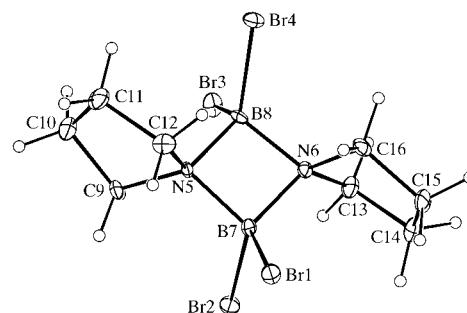


Figure 1

The molecular structure of (I), with displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

carbon planes are 0.665 (3) Å for N5 and 0.655 (3) Å for N6. The H atoms of the pyrrolidine rings are eclipsed. The substituents of the four-membered ring are slightly staggered, with torsion angles of 12.7 (3)° for C16–N6–B8–Br4 and 16.0 (3)° for C13–N6–B8–Br3, to decrease eclipsing interactions between H and Br atoms.

## Experimental

A solution of boron tribromide (9.92 g, 0.04 mol) in pentane (30 ml) was added over a period of 20 min to a vigorously stirred solution of tris(pyrrolidino)borane (4.38 g, 0.20 mol) in pentane (100 ml) at 273 K. After an additional 3 h, the solution was allowed to warm to room temperature. The pentane was then removed by vacuum and the residue was distilled at 1 mm Hg (1 mm Hg = 133.322 Pa) to give the product as a clear liquid which, upon cooling below 273 K, gave colourless crystals of (I) in 90% yield (b.p. 403 K at 0.5 mm Hg). Analysis calculated for C<sub>8</sub>H<sub>16</sub>B<sub>4</sub>Br<sub>4</sub>N<sub>2</sub>: C 19.96, H 3.35, N 5.82, Br 66.38%; found: C 20.00, H 3.67, N 5.79, Br 66.26%. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solution using a Varian Unity (300 or 75 MHz), with Me<sub>4</sub>Si as an internal standard. <sup>11</sup>B NMR spectra were recorded using a Bruker MSL-400 (128 MHz), with BF<sub>3</sub>·OEt<sub>2</sub> as an external standard. Spectroscopic analysis: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, p.p.m.): 1.90 (t, 8H, CH<sub>2</sub>, <sup>3</sup>J<sub>H–H</sub> = 6.9 Hz), 3.45 (t, 8H, CH<sub>2</sub>N, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ, p.p.m.): 26.37 (CH<sub>2</sub>), 51.80 (CH<sub>2</sub>N); <sup>11</sup>B NMR (CDCl<sub>3</sub>, δ, p.p.m.): 23.23.

### Crystal data

C <sub>8</sub> H <sub>16</sub> B <sub>4</sub> Br <sub>4</sub> N <sub>2</sub>	<i>D</i> <sub>x</sub> = 2.316 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 481.49	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Cell parameters from 3271 reflections
<i>a</i> = 12.8750 (2) Å	<i>θ</i> = 2.6–27.9°
<i>b</i> = 6.99600 (10) Å	<i>μ</i> = 11.63 mm <sup>-1</sup>
<i>c</i> = 16.4480 (3) Å	<i>T</i> = 110 (2) K
<i>β</i> = 111.2230 (8)°	Prism, colourless
<i>V</i> = 1381.05 (4) Å <sup>3</sup>	0.20 × 0.15 × 0.10 mm
<i>Z</i> = 4	

### Data collection

Nonius KappaCCD area-detector diffractometer	3271 independent reflections
1° <i>φ</i> scans	2850 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	<i>R</i> <sub>int</sub> = 0.041
<i>T</i> <sub>min</sub> = 0.155, <i>T</i> <sub>max</sub> = 0.341	<i>θ</i> <sub>max</sub> = 27.9°
5628 measured reflections	<i>h</i> = 0 → 16
	<i>k</i> = 0 → 9
	<i>l</i> = -21 → 20

**Table 1**

Selected geometric parameters (Å, °).

Br1–B7	2.014 (4)	N5–B7	1.597 (4)
Br2–B7	1.990 (4)	N5–B8	1.610 (4)
Br3–B8	1.988 (4)	N6–B7	1.601 (4)
Br4–B8	2.006 (4)	N6–B8	1.604 (4)
B7–N5–B8	86.8 (2)	N5–B7–N6	92.4 (2)
B7–N6–B8	86.8 (2)	N6–B8–N5	91.8 (2)
B8–N5–B7–N6	11.2 (2)	B8–N6–B7–N5	-11.2 (2)
B8–N5–B7–Br2	-106.0 (2)	B8–N6–B7–Br2	105.8 (2)
B8–N5–B7–Br1	131.1 (2)	B8–N6–B7–Br1	-129.4 (2)

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 3.5877P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	( $\Delta/\sigma$ ) <sub>max</sub> = 0.019
<i>S</i> = 1.01	$\Delta\rho_{max} = 0.94 \text{ e } \text{Å}^{-3}$
3271 reflections	$\Delta\rho_{min} = -0.81 \text{ e } \text{Å}^{-3}$
145 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.00076 (17)

H atoms were refined as riding, with C–H = 0.99 Å and *U*<sub>iso</sub> = 1.2*U*<sub>eq</sub> of their parent atoms.

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO (Otwinowski, 1985); data reduction: DENZO; program(s) used to solve structure: DIRDIF96 (Beurskens *et al.*, 1996); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPIII (Burnett & Johnson, 1996); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1117). Services for accessing these data are described at the back of the journal.

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