

Three-in-one: the novel packing and structures of three independent molecules of a tricyclic boron compound

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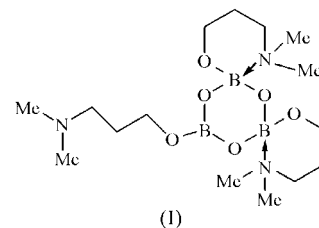
The three independent molecules in a single crystal of the tricyclic compound 15-[3-(dimethylamino)propoxy]-5,5,13,13-tetramethyl-1,7,9,14,16-pentaoxa-5,13-diazonia-15-bora-6,8-diboratadispiro[5.1.5.3]hexadecane, $C_{15}H_{36}B_3N_3O_6$, are bound in dense layers by $C-H \cdots O(B)$ intermolecular interactions. The 3-(dimethylamino)propoxy arms adopt three different conformations with only van der Waals contact distances between the layers. The replicated differences in the B–N bond lengths [mean 1.723 (7) and 1.678 (5) Å] for equivalent geometries are addressed using density functional theory (DFT) calculations.

Comment

This study is part of a programme aimed at investigating boron diolates, aminoalcoholates and alkoxides (Gainsford & Kemmitt, 2005, and references therein). Although borates form a range of diolate complexes (Bachelier & Verchere, 1995; Springsteen & Wang, 2002), structural data are sparse. The Cambridge Structural Database (CSD; Allen, 2002) contains no compounds based on a six-membered B_3O_3 ring with the boron bound to a tertiary amine in a six-membered ring. The closest examples contain an imine function in a BNC_3O ring (CSD refcode DANDEC; Vargas *et al.*, 2004) and a five-membered $BNOBO$ ring [a polycyclic condensate of phenylboronic acid with *N*-hydroxypiperidine (refcode MOXCOR; Kliegel *et al.*, 2002)]. The title compound, (I), is thus quite novel, and the appearance of three independent molecules in the crystal raises some bonding and packing issues, the former through the remarkable internal parameter agreement.

The crystal contains three independent molecules, shown in Figs. 1–3. Fig. 4 further illustrates that the two bis-chelating ligands and the central B_3O_3 rings are essentially superimposable, with the monodentate 3-(dimethylamino)propoxy arm adopting three different conformations (see Table 1). The crystal packing is dense (Fig. 5), with the tricyclic units in close relationships, indicating that intermolecular interactions of the $C-H \cdots O(B)$ type dominate (Table 2). By contrast, the

3-(dimethylamino)propoxy atoms are at non-interacting (van der Waals) distances between the layers containing the tricyclic units (Fig. 5). The $H \cdots O$ distances are only slightly shorter than the van der Waals contact distance (2.72 Å), implying that localized charge may also be enhancing the interactions.



The dimensions of the three tricyclic units are essentially identical and so one set of values is presented here (Fig. 1 labels are used). The central B_3O_3 ring is best described as a flattened boat, with atoms O3, B3, B1 and O2 coplanar [the r.m.s. deviation is 0.003 (2) Å], and atoms B2 and O1 lying 0.128 (5) and 0.191 (5) Å from the plane. The B_3O_3 ring

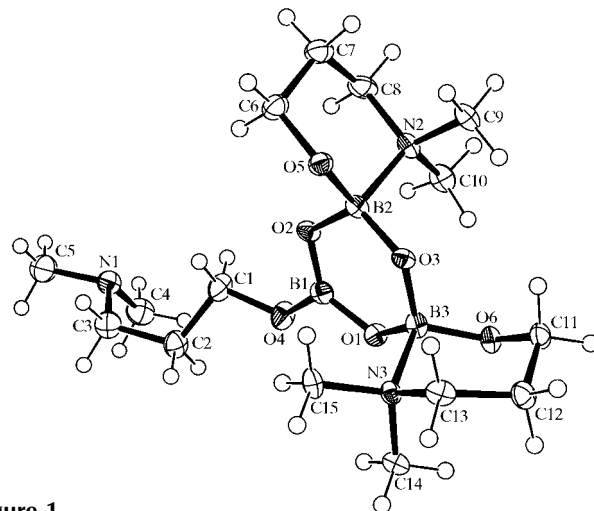


Figure 1
An ORTEP-3 (Farrugia, 1997) view of molecule 1 of (I), shown with 50% probability displacement ellipsoids.

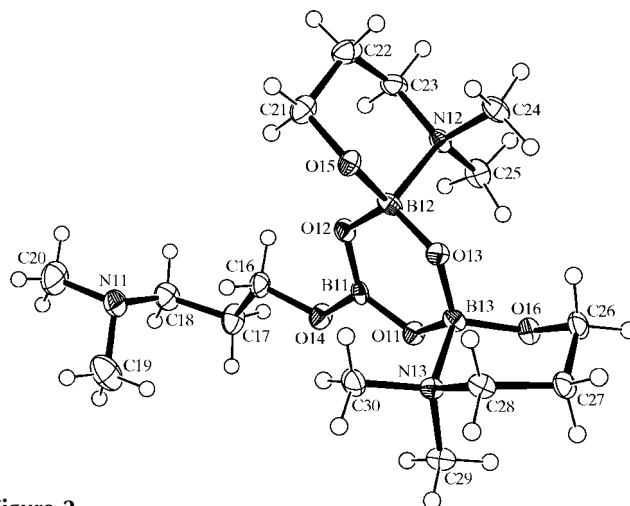


Figure 2
An ORTEP-3 (Farrugia, 1997) view of molecule 2 of (I), shown with 50% probability displacement ellipsoids.

dimensions are remarkably self-consistent [e.g. the mean trigonal in-plane B—O distances are 1.358 (2) Å] and within the ranges noted for a pentaborate (CSPBOR; Frohnecke *et al.*, 1977) and a nonaborate structure (WEHFAQ; Schubert *et al.*, 2000).

The BOC₃N rings are in normal chair conformations; atoms B2, N2, C6 and C7 average 0.010 (2) Å from the plane, with atoms O5 and C8 lying 0.645 (4) and 0.635 (4) Å, respectively, from opposite sides of the plane. The B—N lengths found here are within the ranges observed previously for four-coordinate B, for example 1.732 Å within an O₂BCN ring (CANXOE; Yalpani & Boese, 1983) and 1.693 Å in WOLLOY (Rico *et al.*, 1999); other longer interaction distances can involve the fused-ring linking bonds [e.g. 1.736 and 1.761 Å in a boratabicyclo[3.3.0]octane structure (YAPGAX; Kliegel *et al.*, 1992)]. Shorter distances are commonly observed in six-membered rings [e.g. in a 1,3,2-oxazaborinane (1.640 Å; Ferguson *et al.*, 1991)] and in non-ring systems [e.g. 1.619 and 1.627 Å in an isobutylamine compound (CEZHUK; Beckett *et al.*, 1999)]. The two B—N lengths in each molecule are consistently different, even though their chemical environ-

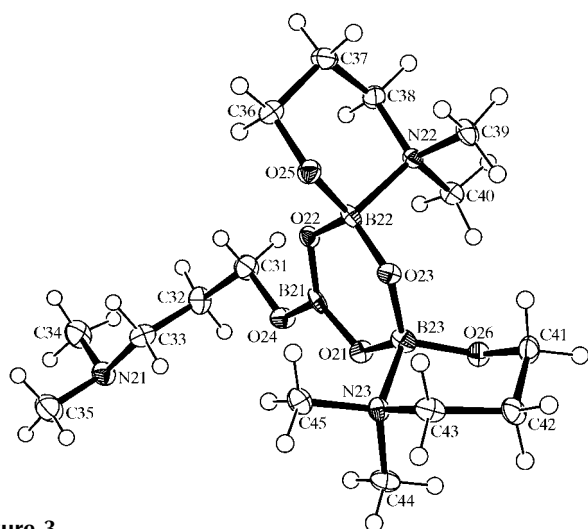


Figure 3
An ORTEP-3 (Farrugia, 1997) view of molecule 3 of (I), shown with 50% probability displacement ellipsoids.

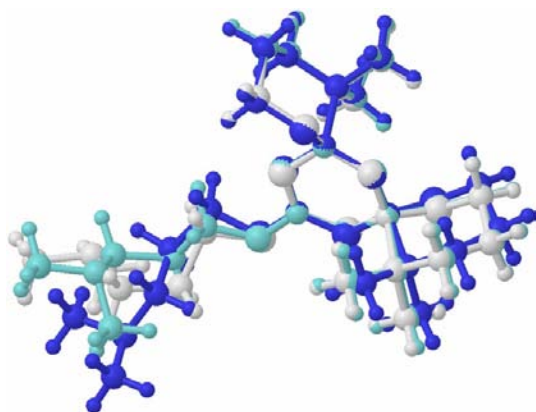


Figure 4
A CrystMol overlap view (Duchamp, 2005) of the three independent molecules in (I).

ments appear identical; the statistical averages (Fig. 1 labels) are 1.723 (7) and 1.678 (5) Å for N2—B2 and N3—B3, respectively. One can have confidence in the B—N difference because of other self-consistencies in the parameters; for example, the equivalent B—O bonds O1—B1 and O2—B1 both average (statistically) as 1.358 (2) Å (with X-ray derived errors of 0.003 Å). As such a difference is statistically significant [being 0.045 (9) Å, compared with refinement standard uncertainties for the difference of 0.006 Å], we attempted to determine its source. In structural terms, the B2—O3 and B3—O3 bonds are also different, with statistical averages of 1.400 (5) and 1.426 (3) Å; these lengths ensure that the O3···N2 and O3···N3 distances are similar.

We determined the relative electronic energies (gas phase) using the Amsterdam Density Function programs (SCM, 2005), starting initially using the X-ray coordinates. As expected, the B—N distances moved to longer gas-phase values (around 1.75 Å), but the refined models also retained somewhat reduced but significant B—N length differences (around 0.02–0.03 Å). Using the restraint feature (on the B—N distances only), we also forced the inversion of the B—N distances and refinement to a mean distance with subsequent release from these states. All calculated relative energies were within 1 kcal mol⁻¹ (the initial values for molecules 2 and 3 were within 0.1 kcal mol⁻¹). Our conclusions are that the observed X-ray differences reflect small energy changes (much less than those for hydrogen bonds) and that minor model alterations result in final similar energies. Both B—N-distance forced changes gave equivalent energies; refinement from the median values always gave non-equivalent B—N values in the final models, even though the energy gain for this configuration was less than 0.7 kcal mol⁻¹. Finally we generated and calculated the relative electronic energies for both are less stable, by approximately 7 and 5.5 kcal mol⁻¹, respectively, than the title bis-chelating BOC₃N structure. Thus, ignoring entropy effects, it appears that the most stable entities are those observed in the crystal structure. In summary, the observed differences in the B—N bond lengths in these three compounds are consistent with a small gain in electronic stability.

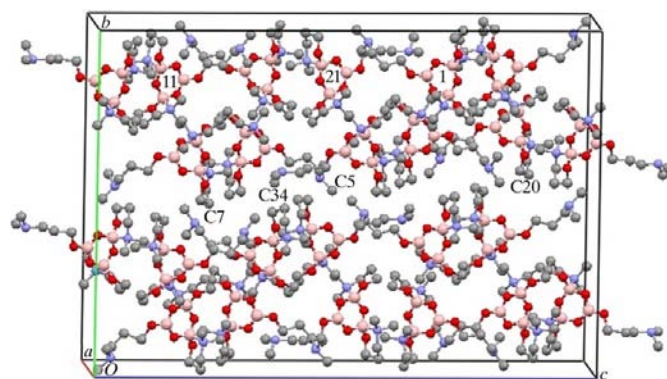


Figure 5
A MERCURY (Bruno *et al.*, 2002) view, down the *a* axis, of the unit-cell contents of (I). No H atoms are shown. The three independent molecules belonging to one set are indicated as 1, 11 and 21; a selection of the non-interacting terminal C atoms are labelled (see *Comment*).

Experimental

Boric acid (H_3BO_3 , 3.09 g, 0.05 mol) was dissolved in excess 3-(dimethylamino)propanol (25.8 g, 0.25 mol) in a rotary evaporator (353 K and 40 mm Hg vacuum), with strong bubbling due to the removal of water. When the bubbling subsided, the temperature was raised to 413 K to remove excess solvent, leaving a yellow liquid, which solidified when cooled to ambient temperature. The solid, which was very hygroscopic, was recrystallized from a benzene/pentane mixture (1:1, 30 ml) to afford white long-platelet crystals (yield 6 g, 93%). ^1H NMR analysis in CDCl_3 showed the absence of hydroxy H atoms.

Crystal data

$\text{C}_{15}\text{H}_{36}\text{B}_3\text{N}_3\text{O}_6$
 $M_r = 386.90$
 Orthorhombic, *Pbca*
 $a = 10.333$ (2) Å
 $b = 28.914$ (5) Å
 $c = 41.642$ (8) Å
 $V = 12441$ (4) Å³
 $Z = 24$
 $D_x = 1.239$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 2628 reflections
 $\theta = 2.6$ – 21.8°
 $\mu = 0.09$ mm⁻¹
 $T = 113$ (2) K
 Plate, colourless
 $0.67 \times 0.65 \times 0.09$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.855$, $T_{\max} = 1.000$
 105164 measured reflections

12733 independent reflections
 5839 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.277$
 $\theta_{\text{max}} = 26.4^\circ$
 $h = -12 \rightarrow 12$
 $k = -36 \rightarrow 36$
 $l = -51 \rightarrow 49$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.145$
 $S = 0.98$
 12733 reflections
 748 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0516P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–B1	1.359 (4)	O4–C1	1.435 (4)
O1–B3	1.442 (4)	O5–B2	1.446 (4)
O2–B2	1.467 (4)	N2–B2	1.721 (4)
O3–B2	1.394 (4)	N3–B3	1.685 (4)
B1–O1–B3	120.2 (3)	O3–B2–O2	116.2 (3)
O2–B1–O1	123.4 (3)	O5–B2–N2	103.7 (2)
O3–B2–O5	111.4 (3)	O3–B3–N3	105.6 (2)
B3–O1–B1–O4	–167.8 (3)	C19–N11–C18–C17	–60.2 (4)
C1–O4–B1–O1	168.7 (3)	C16–C17–C18–N11	–57.0 (4)
B1–O4–C1–C2	–140.1 (3)	B23–O21–B21–O24	–178.5 (3)
O4–C1–C2–C3	178.8 (3)	B21–O24–C31–C32	–162.8 (3)
C4–N1–C3–C2	60.5 (4)	O24–C31–C32–C33	68.6 (4)
C1–C2–C3–N1	60.9 (4)	C34–N21–C33–C32	–58.6 (4)
B11–O14–C16–C17	178.2 (3)	C31–C32–C33–N21	–172.4 (3)
O14–C16–C17–C18	172.9 (3)		

All H atoms were constrained to their expected geometries (C–H = 0.99 and 0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times $U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001) and *SADABS* (Sheldrick, 1996); structure solution: *SHELXS97* (Sheldrick, 1997); structure

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9–H9C \cdots O5 ⁱ	0.98	2.54	3.477 (4)	160
C13–H13A \cdots O11 ⁱⁱ	0.99	2.52	3.441 (4)	155
C14–H14A \cdots O11 ⁱⁱ	0.98	2.57	3.457 (4)	151
C28–H28A \cdots O1 ⁱⁱ	0.99	2.53	3.450 (4)	154
C29–H29A \cdots O1 ⁱⁱ	0.98	2.52	3.436 (4)	155
C30–H30C \cdots O6 ⁱⁱ	0.98	2.59	3.520 (4)	158
C38–H38B \cdots O15 ⁱⁱⁱ	0.99	2.43	3.345 (4)	153
C39–H39C \cdots O15 ⁱⁱⁱ	0.98	2.59	3.452 (4)	148
C40–H40A \cdots O13 ⁱⁱⁱ	0.98	2.52	3.464 (4)	161
C40–H40C \cdots O26	0.98	2.47	3.389 (4)	156
C43–H43A \cdots O21 ^{iv}	0.99	2.55	3.473 (4)	155
C44–H44A \cdots O21 ^{iv}	0.98	2.55	3.456 (4)	154

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1024). Services for accessing these data are described at the back of the journal.

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