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Coordinative N→B bond formation and hydrogen-bonded molecular ladders in 2,5-bis[(*N*→*B*)-(2-aminoethoxy)phenylboryl]thiophene

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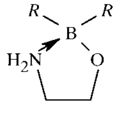
The molecular structure of the title compound, $C_{20}H_{24}B_2N_2O_2S$, is characterized by a twofold rotation axis passing through the S atom and the midpoint of the C—C single bond in the thiophene ring. A coordinative N→B bond is present in the boroxazolidine ring and a single N—H···O hydrogen bond [H···O 1.93 (3) Å, N···O 2.829 (3) Å and N—H···O 172 (2)°] links the molecules into a molecular ladder.

Comment

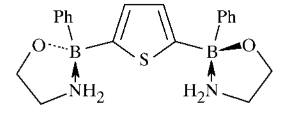
2-Aminoethoxyborinates, readily available from diorganoborinic acids and 2-aminoalcohols, have found various uses [see, for example, references cited in Höpfl, Farfán *et al.* (1998)]. The crystal structures of several of these important compounds have been reported, including those of $R_2BOCH_2CH_2NH_2$, (I), *e.g.* where *R* is 2-thienyl (Low *et al.*, 2000) or *R* is p-XC_6H_4 (*X* is H, F or Me; Rettig & Trotter, 1973, 1974, 1976). Similar to (I) is $R_2BOCH_2CHR'NHR''$, (II), where, for example, *R* is Ph, and *R′* and *R″* are $(CH_2)_4$ (Höpfl, Farfán *et al.*, 1998), and also $R_2BOCH_2CH_2NR'_2$, (III), where, for example, *R* is Ph and *R′* is $(CH_2)_5$ (Höpfl, Farfán *et al.*, 1998).

Invariably, the B centre in these compounds is four-coordinate as a result of intramolecular N→B interactions, which give rise to five-membered chelate rings (boroxazolidine rings). The N→B coordination greatly increases the hydrolytic stability of the B—O bond in such diorganoborinates (Zimmerman, 1963), to the extent that these compounds can be used as reagents and bioactive materials in aqueous media, unlike simple R_2BOR' compounds, which would hydrolyse back to diorganoborinic acids. Indications of the strengths of the N→B interactions have been provided by the N→B bond lengths determined in crystallographic studies, as well as from variable-temperature NMR spectroscopic studies in solution (*e.g.* Höpfl, Farfán *et al.*, 1998) and *ab initio* calculations at the HF/6-31G** level (Höpfl, Galván *et al.*, 1998).

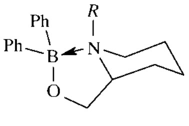
From such studies, it is clear that substitution both at B and especially at N can affect the strength of the N→B bond. When the amino group is primary, as in (I), the molecules are linked into chains *via* intermolecular N—H···O hydrogen bonds (Low *et al.*, 2000). Similar N—H···O hydrogen bonding should also arise in (II); however, no mention has been made of this in the literature. Such classical hydrogen bonding cannot occur in tertiary amino derivatives, and so (III), in condensed phases, would remain essentially molecular. Compounds containing two 2-aminoethoxyborinate groups have attracted less structural attention. We address this deficiency by reporting the structure of 2,5-bis[(*N*–*B*)-(2-aminoethoxy)phenylboryl]thiophene, (IV).



(I)



(IV)



(V)

Compound (IV), in addition to having two B centres, has two different organic substituents at each B centre, which results in chirality at B on N→B interaction, and also has primary amino groups, which results in the formation of hydrogen-bonded molecular aggregates. In (IV), there is a twofold axis passing through the S atom [in special position $(\frac{1}{2},y,\frac{1}{4})$] and the midpoint of the C^{β}—C^{β} bond [C1—C1^{i} in the crystallographic numbering scheme; symmetry code: (i) $1-x$, y, $\frac{1}{2}-z$] of the thiophene ring.

The molecular and crystallographic symmetry of (IV) coincide such that the asymmetric unit contains one half molecule. Both B centres in the same molecule have the same chirality, *i.e.* molecules have either *R*,*R* or *S*,*S* configurations. As a consequence of the centrosymmetric space group, there are equal numbers of the *R*,*R* and *S*,*S* enantiomers. These are linked alternately into chains *via* N—H···O hydrogen bonds, involving the NH and O centres of each molecule. The overall

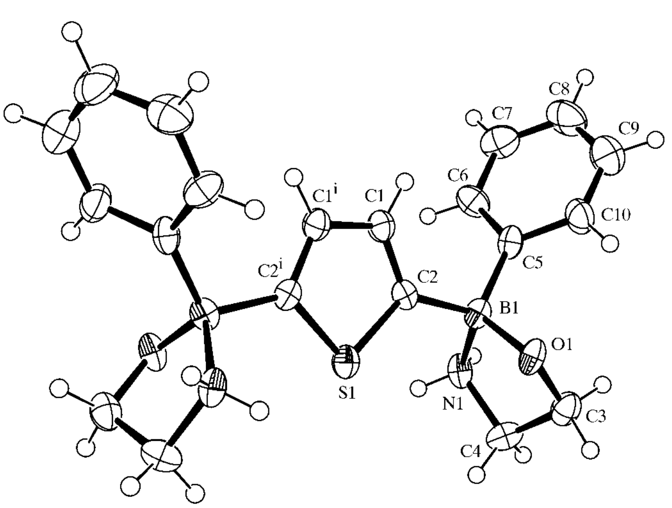


Figure 1
The atomic arrangement in the molecule of (IV). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $1-x$, y, $\frac{1}{2}-z$].

result is a molecular ladder running in the direction of the *c* axis. There are no interactions between the chains.

The B centres have slightly distorted tetrahedral geometries, with bond angles at B ranging around the ideal tetrahedral angle of 109.5°, between 100.3 (2) and 114.0 (3)°. The N→B bond length of 1.642 (4) Å in (IV) at 150 K is slightly shorter than those [both 1.654 (3) Å] in (I) with *R* = 2-thienyl (Low *et al.*, 2000) and *R* = Ph (Rettig & Trotter, 1973, 1976), both at 298 K. All these are only slightly longer than the sum of the covalent radii (1.51 Å), but considerably shorter than the sum of the van der Waals radii (3.18 Å; Spek, 2001).

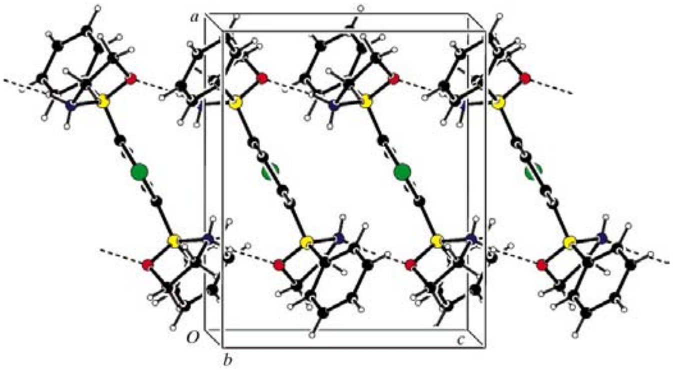


Figure 2
Part of the crystal structure of (IV), showing the formation of the molecular ladder in the direction of the *c* axis.

The B—O distance in (IV) at 150 K [1.477 (4) Å] is similar to those determined at 298 K for (I) with *R* = 2-thienyl [1.479 (3) Å; Low *et al.*, 2000] and *R* = Ph [1.480 (3) Å; Rettig & Trotter, 1973, 1976]. The differences in the N→B bond lengths are considered to be primarily consequences of the temperature difference, rather than any electronic effects of the substituents.

A comparison of N→B and B—O bond lengths in (I) determined at 298 K with those of (V) (Höpfl, Farfán *et al.*, 1998) clearly indicates the greater impact of substitution at N compared with that at other positions: N→B = 1.654 (3), 1.648 (3) and 1.73 (1) Å in (I), (V) with *R* = H and (V) with *R* = Me, respectively, and B—O = 1.479, 1.481 (3) and 1.45 (1) Å in (I), (V) with *R* = H and (V) with *R* = Me, respectively. As expected, a decrease in the N→B bond length occurs with an increase in the B—O bond length.

The planar thiophene and phenyl rings are inclined to each other by 72.54 (8)° in (IV), and the boroxazolidine rings adopt envelope conformations, with flaps at C3 and C3^{i}. There are also weak H···π interactions as atom H1*A* is 2.71 (3) Å from the centre (*Cg*) of the thiophene ring [where the *Cg* coordinates are transformed by $(1 - x, -y, -z)$ or $(x, -y, -\frac{1}{2} + z)$] (Table 2).

Experimental

The title compound was prepared according to the procedure of Coutts & Musgrave (1970) and was recrystallized from chloroform.

Crystal data

$C_{20}H_{24}B_2N_2O_2S$
$M_r = 378.10$
Orthorhombic, *Pbcn*
$a = 11.484$ (3) Å
$b = 18.385$ (6) Å
$c = 9.509$ (3) Å
$V = 2007.7$ (11) Å^3
$Z = 4$
$D_x = 1.251$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5000 reflections
$\theta = 2.1$–24.9°
$\mu = 0.18$ mm^{-1}
$T = 150$ (2) K
Lozenge, colourless
0.22 × 0.20 × 0.16 mm

Data collection

Delft Instruments FAST diffractometer with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
Area-detector scans
7298 measured reflections
1620 independent reflections
738 reflections with $I > 2\sigma(I)$
$R_{int} = 0.123$
$\theta_{max} = 24.9°$
$h = -10 \rightarrow 13$
$k = -19 \rightarrow 20$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.075$
$S = 0.63$
1620 reflections
141 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.744 (3)	B1—C2	1.612 (4)
O1—C3	1.420 (3)	C2—C1	1.348 (4)
O1—B1	1.477 (4)	C1—C1^{i}	1.415 (5)
N1—B1	1.642 (4)	C3—C4	1.505 (4)
B1—C5	1.600 (4)		
C2—S1—C2^{i}	95.0 (2)	C2—B1—N1	111.8 (3)
C4—N1—B1	106.1 (2)	C1—C2—B1	127.2 (3)
O1—B1—C5	114.0 (3)	C1—C2—S1	107.1 (2)
O1—B1—C2	110.1 (2)	B1—C2—S1	125.1 (2)
C5—B1—C2	111.2 (3)	C2—C1—C1^{i}	115.43 (18)
O1—B1—N1	100.3 (2)	O1—C3—C4	105.1 (2)
C5—B1—N1	108.9 (2)	N1—C4—C3	102.8 (3)
O1—B1—C2—C1	112.8 (3)	O1—B1—C2—S1	−57.1 (3)
C5—B1—C2—C1	−14.6 (4)	C5—B1—C2—S1	175.52 (18)
N1—B1—C2—C1	−136.6 (3)	N1—B1—C2—S1	53.5 (3)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

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

Cg is the centroid of the thiophene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O1^{ii}	0.93 (3)	1.91 (3)	2.829 (3)	172 (2)
N1—H1*A*···*Cg*^{iii,iv}	0.86 (3)	2.71 (3)	3.405 (4)	139 (2)

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

The low goodness-of-fit value and the simplistic weighting scheme appear to be consequences of an over-estimation of the uncertainties associated with the diffracted intensities. The amine H atoms were freely refined with isotropic displacement parameters. The remaining H atoms were initially placed in calculated positions and refined isotropically, and thereafter allowed to ride on their attached atoms, with C—H distances of 0.95 (Csp^2 atoms) and 0.99 Å (Csp^3 atoms).

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989); cell refinement: *MADNES*; data reduction: *ABSMAD* (Karaulov, 1992); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1498). Services for accessing these data are described at the back of the journal.

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