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A 2-Alkyl Substituted 2,3,1-Benzodiazaborine

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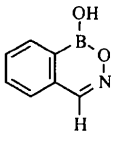
(*Received 29 August 1997; accepted 22 September 1997*)

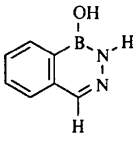
Abstract

The structure of the fourth member of a family of structurally related 2,3,1-benzodiheteroborines has been solved by crystallographic means, providing data for proper direct comparison with the others. The title compound, 1,2-dihydro-1-hydroxy-2-methyl-2,3,1-benzodiazaborine ($C_8H_9BN_2O$) is obtained *via* condensation of 2-formylbenzeneboronic acid and methylhydrazine, and is similar in most respects to its 2-unsubstituted parent, in internal geometry and intramolecular association topography, but has some subtle oxazaborine-like characteristics.

Comment

Although it has been known for quite some time that condensation of 2-formylbenzeneboronic acid with hydroxylamines or hydrazines affords 2,3,1-benzoxaza- or benzodiazaborines, respectively (Tschampel & Snyder, 1964; Dewar & Dougherty, 1964), these and related boron heterocycles have until recently received little attention. We are interested in them as they are quite robust and potentially useful as platforms for the construction of new biologically active compounds (see, for example, Groziak *et al.*, 1994). To develop the 2,3,1-benzodiheteroborines further, we are undertaking a systematic physicochemical study of heterocycles like compounds (1)–(5) by crystallographic and other means.


(1)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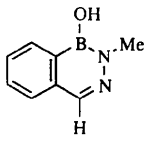
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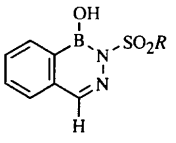
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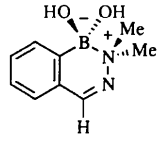
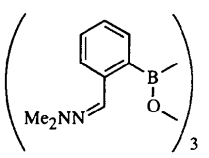

(5a)


(5b)

The parent oxaza- and diazaborines, (1) and (2), respectively, were the subjects of our most recent report (Groziak *et al.*, 1997), which among other determinations reported their crystal structures. The structure of the title compound (3), which is the 2-methyl-substituted version of (2), is presented here, while that of a representative 2-alkyl- or arylsulfonylated version, (4), is currently being sought. Although a crystal structure determination of a thiophene analog of (3), 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]-pyridine, has been reported (Aurivillius & Löefving, 1974), we solved the structure of (3) in order to compare it directly with (1) and (2) without the need to allow for differences in ring-fusion identity. Interestingly, the thiophene analog reportedly decomposed in air of normal humidity so rapidly that the crystal for analysis had to be kept over a saturated aqueous solution of the substance. No such unusual lability was noted for our crystalline (3).

The 2,3,1-benzodiazaborines in particular can exhibit a wide diversity of structures. Some of the known biocidal (Grassberger *et al.*, 1984) heterocycles, (4), have been found by crystallography to form a tetrahedral borate complex in the active site of enoyl reductase (Baldock *et al.*, 1996) and the 2-dimethyl-substituted 2,3,1-benzodiazaborine, (5*a*), exists as a zwitterion, but only in water. An unusual double intramolecular chelate form of triarylboroxine (5*b*) was found to be its structure in the solid state (Robinson *et al.*, 1996).

An *ORTEP* (Johnson, 1965) view of the molecule of crystalline (3), together with its atom numbering, is given in Fig. 1. This molecule is a true B—N for C=C replacement analog of the enol form of 3-methyl-3*H*-isoquinolin-4-one, but to our knowledge no simple 3-alkyl-4-hydroxyisoquinoline has yet been studied crystallographically. Instead, the closest nitrogen heterocycle reference compounds for (3) appear to be several 3,4-dihydro-4-oxo-3-(arylmethyl)-1-phthalazineacetic acids (Mylari *et al.*, 1991) and a 4-(*p*-chlorobenzyl)-2-(alkyl)-1(2*H*)-phthalazinone monohydrate (Scheffler *et al.*, 1988). Features associated with the benzene ring and methyl substituent of (3) are

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unremarkable, but the remainder of the molecular structure is important for direct comparison with (1) and (2). Most of the features of the heterocyclic periphery of (3) are similar to those of (2). Of particular interest to the development of these boron heterocycles is the long [1.433 (3) Å] B1—N2 distance relative to the adjacent heteroatoms [1.371 (2) Å] in (3). These relative lengths are reversed in (1) (Groziak *et al.*, 1997), but we note that unlike in (1), the N2—N3 electron-pair repulsion in (2) and (3) is minimal as the respective electron pair-containing N_p and N_{sp^2} orbitals in these molecules are orthogonal. Although tempting, it is too early to state that long B1—N2 and short N2—N3 distances will be a feature found common to all 2,3,1-benzodiazaborines because a planar form of a 2-sulfonylated analog (4) has yet to be examined crystallographically. Heterocycles like (4) may actually prove to be more like (1) than (2) in this regard.

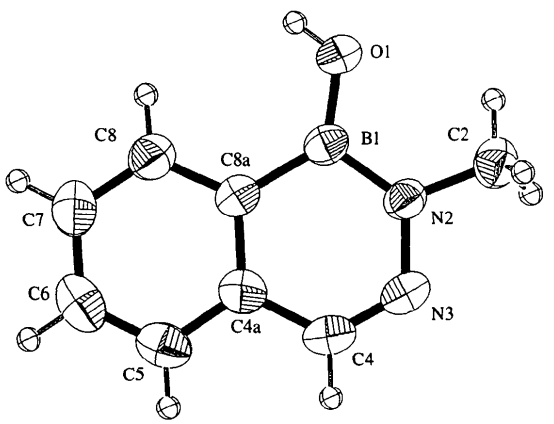

Fig. 1. The molecular structure and atom-numbering scheme for (3) with displacement ellipsoids at the 50% probabililty level.

Interestingly, the B1—O1 distance in (3) of 1.357 (3) Å is nearly the same as that [1.350 (6) Å] found in oxazaborine (1). That it is distinctly shorter than that [1.371 (3) Å] found in its parent diazaborine (2) has origins in the nature of the intermolecular hydrogen-bond associations. Like (1), the hydroxyl group moiety of (3) participates in only one intermolecular hydrogen-bond association (with N3), providing the basis for infinite hydrogen-bonded chains parallel to [101] (Table 2). In (2), however, the O1 atom also accepts a hydrogen bond from H2 of a neighboring molecule, thereby establishing a network of intermolecularly associated hydrogen-bonded pairs of molecules. The presence of the 2-methyl group in (3) prohibits such pairing and leaves it only with the ability to associate with a neighbor in the manner of compound (1) and adopt a similar B1—O1 distance. The sterically induced directionality of hydrogen bonding which places the O—H and B1—N2 bond vectors antiperiplanar in (3) [with torsion angle C8a—B1—O1—H1 1 (2)°] is noted in solution as well, since an evaluation by NOESY NMR showed a through-space spin-interactive proximity of the H1 and H8 atoms (Groziak *et al.*, 1997). It would be of interest to reverse this directionality by constructing a higher alkyl homolog of (3) which is equipped with an acceptor atom positioned to undergo intramolecular hydrogen-bond association with the hydroxyl group moiety. Finally, another subtlety which can be ascribed to the intermolecular associations in (3) is its O1—B1—N2—N3 torsion angle [177.24 (18)°] which is clearly closer to the corresponding torsion angle in (1) [177.4 (4)°] than that in (2) [174.46 (17)°].

A feature that appears to be independent of intermolecular hydrogen-bond associations is the relative size of the three bond angles centered about the B atom. The C8a—B1—O1, O1—B1—N2 and N2—B1—C8a angles of 128.2 (2), 116.3 (2) and 115.5 (2)°, respectively, contribute to a distinctive 'leaning' of the O1 atom away from the benzene ring. The magnitude of this angle deformation in (3) matches closely that observed in (2). In (1), the effect is not nearly as pronounced.

In conclusion, molecule (3) resembles both (2) and its earlier reported thiophene analog to a high degree and yet shows some subtle differences which are largely the result of intermolecular hydrogen-bonding association.

Experimental

The condensation of 2-formylbenzeneboronic acid and methylhydrazine was conducted according to a literature procedure (Dewar & Dougherty, 1964) that afforded (3) in a 79% yield. Recrystallization of (3) from aqueous ethanol gave X-ray quality crystals with m.p. 432–444 K (literature m.p. 427–429 K, also from aqueous ethanol, but resolidification and remelting noted at 441 K). Extensive characterization data for (3) including those of ^1H, ^{13}C, ^{11}B, COSY and NOE NMR spectral analysis have been reported (Groziak *et al.*, 1997).

Crystal data

$C_8H_9BN_2O$
M_r = 159.98
Monoclinic
$P2_1/n$
a = 4.7100 (10) Å
b = 14.5119 (15) Å
c = 12.2120 (8) Å
β = 100.151 (10)°
V = 821.6 (2) Å^3
Z = 4
D_x = 1.293 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12.28–17.42°
μ = 0.086 mm^{-1}
T = 296 K
Prism
0.35 × 0.34 × 0.18 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 4° min^{-1} in ω)
Absorption correction: none

R_{int} = 0.019
θ_{max} = 25.05°
h = 0 → 5
k = 0 → 17
l = −14 → 14

1648 measured reflections
1460 independent reflections
839 reflections with $I > 2\sigma(I)$
3 standard reflections every 100 reflections
intensity decay: −1.6%

Refinement

Refinement on F^2
$R(F) = 0.034$
$wR(F^2) = 0.082$
$S = 1.086$
1460 reflections
115 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.1415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.165$ e Å^{-3}
$\Delta\rho_{min} = -0.148$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.038 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—B1	1.357 (3)	N3—C4	1.291 (3)
N2—N3	1.371 (2)	C4—C4a	1.437 (3)
N2—B1	1.433 (3)	C4a—C8a	1.404 (3)
N2—C2	1.457 (3)	C8a—B1	1.539 (3)
B1—O1—H1	118.1 (18)	C8a—C4a—C4	118.4 (2)
N3—N2—B1	124.4 (2)	C8—C8a—B1	125.8 (2)
N3—N2—C2	112.0 (2)	C4a—C8a—B1	117.0 (2)
B1—N2—C2	123.6 (2)	O1—B1—N2	116.3 (2)
C4—N3—N2	118.1 (2)	O1—B1—C8a	128.2 (2)
N3—C4—C4a	126.6 (2)	N2—B1—C8a	115.5 (2)
B1—N2—N3—C4	−0.4 (3)	C2—N2—B1—O1	−1.8 (3)
C2—N2—N3—C4	178.8 (2)	N3—N2—B1—C8a	−1.3 (3)
N2—N3—C4—C4a	1.4 (3)	C2—N2—B1—C8a	179.7 (2)
N3—C4—C4a—C8a	−0.6 (3)	C4a—C8a—B1—O1	−176.4 (2)
C4—C4a—C8a—B1	−1.2 (3)	C4a—C8a—B1—N2	2.0 (3)
N3—N2—B1—O1	177.3 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N3^{i}	0.82 (3)	2.02 (3)	2.810 (2)	161 (3)

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

The H1 atom was refined isotropically. All other H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*93, and *PLATON* (Spek, 1990).

This work was supported by grant GM44819 from the National Institutes of Health. We thank Mr Lin Yi for conducting the first preparation of (3) in our laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1385). Services for accessing these data are described at the back of the journal.

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Exclusivity of the *sp* Rotamers of 9-(*o-tert*-Butylphenyl)fluorene and 9-(*o-tert*-Butylphenyl)-9-fluorenol in Solution and the Crystalline State

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(*Received 1 August 1997; accepted 26 September 1997*)

Abstract

Both 9-(*o-tert*-butylphenyl)fluorene ($C_{23}H_{22}$) and 9-(*o-tert*-butylphenyl)-9-fluorenol ($C_{23}H_{22}O$) maintained *sp* rotameric structures exclusively in crystalline form as well as in solution. This result is in contrast to that