The Crystal and Molecular Structure of 4-Methyl-2-phenyl-(3*H*)-1,3,5,2-oxadiazaboroline

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$C_8H_9BN_2O$ is orthorhombic, space group *Pbca* with $a = 8.818$ (1), $b = 10.174$ (2), $c = 19.021$ (2) Å, $Z = 8$. The structure was determined from diffractometer data by direct methods and was refined by full-matrix least-squares calculations to $R = 0.071$ for 674 observed reflections. Both rings in the molecule are planar; the dihedral angle between them is $4.5°$. Charge-density calculations revealed a sequence of alternating charges on the C atoms of the benzene ring. Bond lengths, as well as bond-order calculations, show that all bonds in the heterocyclic ring have significant π character, with the exception of N(3)–O(2); they also suggest that there is some π character in the B(1)–C(6) inter-ring bond. The molecules are linked by N–H···N hydrogen bonds [N···N = 2.95 (1) Å] along b, to form extended chains.

Introduction

The compound was synthesized by reacting phenyl-boronic acid with acetamide oxime. The principal items of structural interest are the relationship between the two constituent rings and the dimensions of the hetero-cyclic group. X-ray methods have been used to provide this information; in addition, charge-density and bond-order calculations have been performed in order to provide a more detailed understanding of the π-electron distribution in the heterocyclic ring.

Experimental

Crystal data

Colourless single crystals, elongated along [010], were obtained by evaporation from a 9:1 (v/v) mixture of benzene and toluene. Systematic absences on Weissenberg and precession photographs uniquely identified space group *Pbca*. Cell dimensions were determined on a Hilger & Watts four-circle diffractom-eter with Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation. Crystal data are summarized in Table 1.

Table 1. *Crystal data*

$C_8H_9BN_2O$	Systematic absences
FW 159.89	$0kl: k = 2n + 1$
Orthorhombic	$h0l: l = 2n + 1$
$a = 8.818$ (1) Å	$hk0: h = 2n + 1$
$b = 10.174$ (2)	Space group: *Pbca*
$c = 19.021$ (2)	$Z = 8$
$V = 1706.36$ Å³	μ(Mo $K\alpha$) = 0.88 cm^{-1}
$D_c = 1.24$ g cm^{-3}	$F(000) = 672$
$D_m = 1.22$ (flotation)	

Data collection and reduction

A crystal of dimensions $0.50 \times 0.30 \times 0.30$ mm was used to collect the data on a Hilger & Watts four-circle diffractometer with Mo $K\alpha$ radiation and a 3.5 mm collimator. A θ–2θ scan was used out to $2\theta = 45°$. Each scan consisted of 60 steps of $0.01°$ intervals; the counting time for each reflection was 180 s plus 30 s for each of two background counts performed before and after the scan. The $1\bar{2}3$, 306 and 060 reflections were used as standard at intervals of 25 reflections. Equiva-lent reflections were recorded from the *hkl* and *hkl̄* octants. Of the 1119 reflections measured 674 had $I > 3\sigma(I)$ and were considered observed. The data were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The structure was solved by direct methods using Ahmed & Hall's (1968) symbolic addition procedure for centrosymmetric crystals. The origin-determining reflections, chosen by the program, were 213; 1,7,11; and 121; in addition, tentative signs were allocated to the 619; 1,10,1; 204; and 278 reflections. These were used to generate a total of 80 signed reflections with $|E| \geq 1.8$; a further 49 signed reflections were then generated with $|E| \geq 1.5$. All signed reflections were used to calculate an E map from which the coordinates of all non-hydrogen atoms were obtained. Refinement was by anisotropic full-matrix least-squares methods. The weighting scheme used was: $\sqrt{w} = 1/[P_1 + |F_o| + P_2|F_o|^2 + P_3|F_o|^3]^{1/2}$, with $P_1 = 12.0$, $P_2 = 0.015$ and $P_3 = 1.5 \times 10^{-4}$.

A difference map was calculated at $R = 0.098$, which revealed the nine H atoms. These were included

in the calculations but were not refined. At $R = 0.071$, and with no parameter shift greater than one sixth of the corresponding e.s.d., refinement was stopped. A weighting analysis showed $\sum w\Delta^2/N$ to be independent of F_o and $\sin^2 \theta$. Final positional parameters are shown in Table 2.*

Scattering factors for C, N, O and B were obtained from *International Tables for X-ray Crystallography* (1962). The curve for H was that of Stewart, Davidson & Simpson (1965).

Description and discussion of the structure

Bond lengths and angles for the non-hydrogen atoms are listed in Table 3. Similar data involving H atoms have not been included because the H-atom coordinates were not refined. Fig. 1 contains a labelled diagram of the molecule; H atoms take the number of the atom to which they are attached, the methyl H atoms are 51, 52 and 53. Charge densities (Table 4) have been calculated

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33755 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
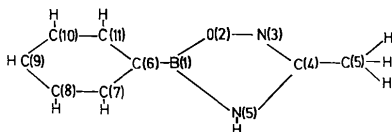

Fig. 1. Labelled diagram of the molecule.

Table 2. *Fractional positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
B(1)	6268 (8)	4589 (6)	4251 (4)
O(2)	6607 (5)	3259 (4)	4317 (2)
N(3)	7621 (6)	3099 (5)	4907 (3)
C(4)	7834 (7)	4271 (6)	5155 (3)
C(5)	8824 (8)	4553 (7)	5771 (4)
N(5)	7057 (5)	5223 (5)	4803 (3)
C(6)	5236 (7)	5137 (6)	3658 (4)
C(7)	4908 (8)	6481 (6)	3622 (4)
C(8)	3993 (8)	6984 (7)	3100 (4)
C(9)	3447 (9)	6185 (9)	2583 (4)
C(10)	3764 (9)	4853 (8)	2602 (4)
C(11)	4660 (8)	4328 (6)	3135 (4)
H(51)	8234	4669	6225
H(52)	9073	3833	6046
H(53)	9800	4423	5552
H(5)	7336	6143	4837
H(7)	5240	6880	4038
H(8)	4548	8000	3196
H(9)	3062	6388	2077
H(10)	3493	4177	2187
H(11)	4741	3322	3196

by the CNDO/2 method; bond-orders, with and without overlap, have been calculated by Cohen's (1972) method (Table 5), with and without Löwdin deorthogonalization. These calculations apply to an isolated molecule.

(a) Planarity in the molecule

Table 6 contains the planes of best fit with their atomic displacements. Both the phenyl and the hetero-

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(4)—C(5)	1·49 (1)	C(6)—C(7)	1·38 (1)
C(4)—N(5)	1·36 (1)	C(7)—C(8)	1·38 (1)
C(4)—N(3)	1·30 (1)	C(8)—C(9)	1·37 (2)
N(5)—B(1)	1·41 (1)	C(9)—C(10)	1·39 (2)
N(3)—O(2)	1·45 (1)	C(10)—C(11)	1·39 (1)
O(2)—B(1)	1·39 (1)	C(11)—C(6)	1·39 (1)
B(1)—C(6)	1·56 (1)		

C(4)—N(5)—B(1)	107·1 (7)	B(1)—C(6)—C(7)	120·5 (8)
N(5)—B(1)—O(2)	105·6 (7)	B(1)—C(6)—C(11)	121·1 (8)
B(1)—O(2)—N(3)	108·1 (6)	C(6)—C(7)—C(8)	121·7 (9)
O(2)—N(3)—C(4)	105·6 (7)	C(7)—C(8)—C(9)	119·5 (9)
N(3)—C(4)—N(5)	113·6 (8)	C(8)—C(9)—C(10)	120·0 (10)
C(5)—C(4)—N(3)	123·1 (8)	C(9)—C(10)—C(11)	120·1 (9)
C(5)—C(4)—N(5)	123·3 (8)	C(10)—C(11)—C(6)	120·4 (9)
N(5)—B(1)—C(6)	131·8 (8)	C(11)—C(6)—C(7)	118·3 (8)
O(2)—B(1)—C(6)	122·6 (8)		

Table 4. *Atomic net charges in the molecule* (*electrons*)

C(5)	−0·0604	C(6)	−0·0832
C(4)	+0·2360	C(7)	+0·0441
N(3)	−0·1504	C(8)	−0·0076
O(2)	−0·2100	C(9)	+0·0294
B(1)	+0·2264	C(10)	−0·0115
N(5)	−0·1864	C(11)	+0·0474

Table 5. *Bond orders in the heterocyclic moiety*

(a) With overlap

	σ	π
C(4)—C(5)	0·933	0·107
C(4)—N(3)	0·563	0·890
C(4)—N(5)	0·789	0·263
N(5)—B(1)	0·738	0·500
B(1)—O(2)	0·623	0·508
N(3)—O(2)	0·40	0·089
B(1)—C(6)	0·971	0·204

(b) Without overlap

	σ	π
C(4)—C(5)	0·948	0·225
C(4)—N(3)	0·930	0·858
C(4)—N(5)	0·908	0·403
N(5)—B(1)	0·885	0·574
B(1)—O(2)	0·873	0·559
N(3)—O(2)	0·701	0·195
B(1)—C(6)	0·955	0·314

cyclic rings are planar with mean atomic displacements of 0·007 and 0·005 Å respectively. The mean atomic displacement for the entire molecule is larger, 0·037 Å, and suggests a slight loss in overall planarity for the molecule, with respect to the individual rings. This is supported by the fact that the dihedral angle between the constituent planes of the molecule is only 4·5 (2·0)°. This is an unusually small value for systems containing phenyl groups linked with heterocyclic molecules (Form, Raper & Downie, 1974), and suggests that the rings are effectively coplanar.

(b) Molecular dimensions

The mean C—C bond length and the mean angle for the phenyl group are 1·38 (1) and 120·0 (9)°; there are no significant differences between maximum and minimum values in either case. The interesting sequence of alternating charges (Table 4) on the C atoms of the phenyl group arises from the attachment, at C(6), of the relatively less electronegative B(1) atom. Mean total bond orders ($\sigma + \pi$) within the phenyl group are 1·56 (including overlap) and 1·63 (without overlap).

The B—N, B—O and C—N distances are all significantly shorter than those reported by Rettig & Trotter (1973, 1974, 1975, 1976) for saturated, five-membered, oxazaborolidine rings, thus confirming the essentially aromatic character of this oxadiazaboroline system.

Table 6. *Equations of mean planes with atomic displacements*

The equation of the plane is $lX + mY + nZ - P = 0$, where X, Y and Z are fractional coordinates and P is the origin to plane distance in Å.

(a) Complete molecule

$$0.8002X + 0.1293Y - 0.5856Z - 0.3214 = 0$$

Atomic displacements and e.s.d.'s (Å)

C(5)	+0·076 (10)	C(6)	−0·023 (9)
C(4)	+0·025 (9)	C(7)	−0·041 (9)
N(5)	−0·006 (7)	C(8)	−0·037 (11)
N(3)	−0·003 (8)	C(9)	+0·049 (11)
O(2)	−0·041 (6)	C(10)	+0·076 (10)
B(1)	−0·031 (9)	C(11)	+0·043 (10)

(b) Heterocyclic ring

$$0.7826X + 0.1230Y - 0.6193Z + 0.0458 = 0$$

Atomic displacements and e.s.d.'s (Å)

C(5)	+0·0065 (10)	N(3)	−0·0042 (8)
C(4)	+0·0020 (9)	O(2)	+0·0003 (6)
N(5)	−0·0068 (7)	B(1)	+0·0116 (9)

(c) Phenyl ring

$$0.1872X + 0.1583Y - 0.5542Z - 0.7502 = 0$$

Atomic displacements and e.s.d.'s (Å)

C(6)	−0·004 (9)	C(9)	+0·008 (11)
C(7)	+0·011 (9)	C(10)	+0·001 (10)
C(8)	−0·014 (11)	C(11)	−0·002 (10)

The B(1)—N(5) distance [1·41 (1) Å] is close to those found in aminoboranes (Bullen, 1973), in oxazaboroles (Anzenhofer, 1966) and in a cyclic tetraazenoborane (Chang, Porter & Bauer, 1969). The B(1)—O(2) distance closely resembles values found in trigonal borates (Kuribayashi, 1973; Krogh-Moe, 1974; Rettig & Trotter, 1977). As expected from their bond lengths, there is significant π character in both the B—O and the B—N bonds (Table 5). The situation with regard to the π content of the inter-ring B(1)—C(6) bond is less clear however. The average B—C bond length in triphenylborane is 1·577 (5) Å (Zettler, Hausen & Hess, 1974) and that in trivinylborane is 1·558 (3) Å (Foord, Beagley, Reade & Steer, 1975); the shortening in the latter is considered sufficient to indicate the existence of π bonding in the B—C bond.

In this molecule the B(1)—C(6) bond length [1·56 (1) Å] is not significantly different from either of the above values; nor is it significantly different from the average B—C bond length [1·560 (2) Å] in phenylboronic acid (Rettig & Trotter, 1977). However, some π contribution to the B(1)—C(6) bond is indicated in the bond-order calculations (Table 5). Furthermore, the rings are effectively coplanar in this molecule, whereas in B(Ph)₃, the phenyl rings make an angle of 30° with the planar BC₃ skeleton. The most likely explanation for the coplanarity in this molecule would seem to be the presence of some degree of π bonding in the inter-ring B(1)—C(6) bond.

The charge densities on and around the B(1) atom largely reflect the relative electronegativities of the elements concerned (Table 4). Thus, the polarities of the B—O and B—N bonds are very similar and significantly greater than that of the B—C bond. The two C—N distances are significantly different from one another: the much shorter C(4)—N(3) bond has the greater π character (Table 5); the magnitude of the π character between these atoms in fact is sufficient to suggest effective localization of the $p\pi$ electrons
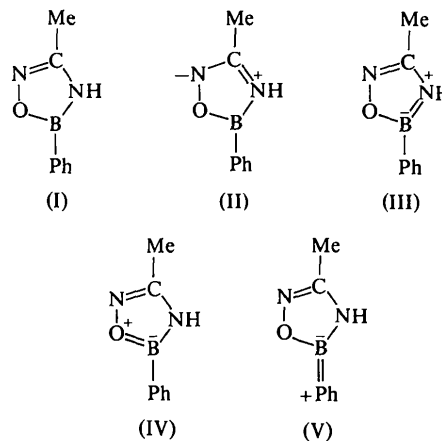

Fig. 2. Canonical forms of the molecule.

between them. However, the bond-order calculations also suggest some π character in the C(4)–N(5) bond. The N(3)–O(2) distance [1·45 (1) Å] is similar to values found in an isoxazoline derivative (Meunier-Piret, Piret, Germain, Putzeys & Van Meerssche, 1972) and in some furoxan derivatives (Cameron, 1974). The π character of this bond is negligible (Table 5), presumably because the two atoms involved have residual negative charges (Table 4). The exocyclic C(4)–C(5) contact [1·49 (1) Å] is within the range expected for $C(sp^2)$–$C(sp^3)$ bonds (Sutton, 1965).

The extensive delocalization of the $p\pi$ electrons in the oxadiazaboroline moiety may be rationalized in terms of the canonical forms shown in Fig. 2. The largest contributor is expected to be form (I).

(c) Molecular packing and hydrogen bonding

The unit-cell contents are shown in Fig. 3, together with the essential features of the hydrogen bonding. The molecules lie mainly in the *bc* plane and are inclined along *c*. Each molecule forms two hydrogen bonds to its nearest neighbours. The N(5)–H(5) group (donor) of one molecule is related to the N(3) atom (acceptor), in an adjacent molecule, by the *b* glide plane. Hence the molecules are effectively linked into extended chains parallel to *b*. The overall N(5)···N(3) distance [2·95 (1) Å] is normal for such contacts, and the angle [166·5 (5)°] at the H(5) atom suggests that the hydrogen bond is essentially linear.

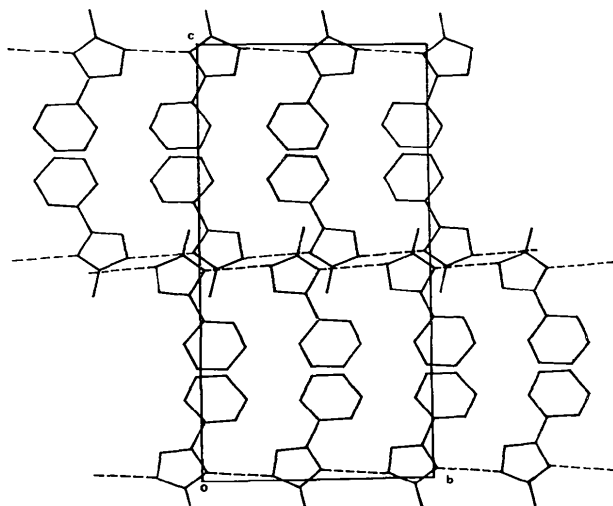The remaining intermolecular contacts are normal van der Waals values.

Fig. 3. Unit-cell contents and hydrogen-bonding contacts projected along *a*.

All the calculations were performed on the IBM 370/155 computer at the University of Cambridge *via* the NUMAC IBM 360/67 at the University of Newcastle upon Tyne. The programs, in addition to local programs, were from the integrated set derived by Dr F. R. Ahmed and his group at NRC, Ottawa, Canada. The *SFLS* block-diagonal refinement program was modified for full-matrix refinement by Dr H. M. M. Shearer of Durham University.

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