Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Bromo-2-(2-fluorobenzyloxy)phenylboronic acid

Janusz Serwatowski,* Tomasz Klis and Kinga Kacprzak

Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

Correspondence e-mail: ktom@ch.pw.edu.pl

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.008 Å
R factor = 0.049
wR factor = 0.113
Data-to-parameter ratio = 13.0

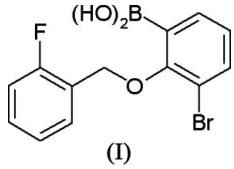
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 24 February 2006
Accepted 2 March 2006

The title compound, $C_{13}H_{11}BBrFO_3$, exists as an almost centrosymmetric dimer of two crystallographically independent molecules linked by hydrogen bonds. The $B(OH)_2$ groups are slightly twisted from the plane of the benzene ring. There are intra- and intermolecular hydrogen bonds.

Comment

Arylboronic acids $ArB(OH)_2$ are important starting materials in organic synthesis. They are valuable substrates in the formation of biaryls (Miyaura & Suzuki, 1995) or amino acids (Petasis *et al.*, 1997). The modern application of these compounds concerns the analysis of natural products such as carbohydrates (Samankumara Sandanayake & Shinkai, 1994) or hormones and saccharide transport through membrane cells (Bien *et al.*, 1995). Hence, the formation of the hydrogen bonds is important in order to understand the activity of these compound as receptors. The structure of boronic acids containing a benzyloxy group has not been published to date. The aim of this work was to investigate the influence of the F atom in the benzylic part of the molecule on the dihydroxyboryl group.



(I)

The title compound, (I), having two molecules per asymmetric unit, contains a $B(OH)_2$ group *ortho* to oxygen and an F atom *ortho* to the benzyl aliphatic C atom. Therefore, we

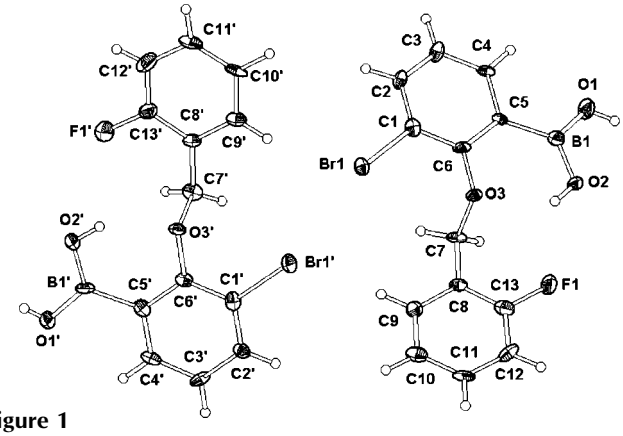


Figure 1
View of the two independent molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

expected the possible participation of the F atom in the hydrogen-bond formation. The $B(OH)_2$ group is twisted by 4.8 (8) and −5.2 (8)° from the plane of the benzene ring in the two independent molecules. The intermolecular hydrogen bonds (Table 2) are longer than the value of 2.745 Å reported for 4-toluyloboronic acid (Zheng *et al.*, 2001).

Experimental

The title compound was purchased from Aldrich and was recrystallized from toluene and dried in air.

Crystal data

$C_{13}H_{11}BBrFO_3$
M_r = 324.94
Triclinic, $P\overline{1}$
a = 4.0226 (5) Å
b = 15.278 (2) Å
c = 21.685 (3) Å
α = 105.084 (11)°
β = 90.026 (10)°
γ = 92.089 (11)°
V = 1285.9 (3) Å^3
Z = 4
D_x = 1.678 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10000 reflections
θ = 1.5–29.7°
μ = 3.21 mm^{-1}
T = 100 (2) K
Needle, colourless
0.53 × 0.07 × 0.05 mm

Data collection

Oxford Diffraction KM-4-CCD diffractometer
ω scans
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2001)
T_{min} = 0.522, T_{max} = 0.857
13268 measured reflections
4521 independent reflections
2963 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 25.0°
$h = -4 \rightarrow 4$
$k = -18 \rightarrow 18$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.113
S = 0.92
4521 reflections
347 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.014
$\Delta\rho_{max}$ = 1.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.906 (6)	O3′—C7′	1.471 (6)
Br1′—C1′	1.897 (5)	C5—C6	1.401 (7)
F1—C13	1.381 (6)	C5—B1	1.579 (8)
F1′—C13′	1.353 (6)	C7—C8	1.499 (7)
O1—B1	1.346 (7)	C8—C13	1.386 (7)
O2—B1	1.375 (7)	C5′—C6′	1.397 (7)
O3—C6	1.394 (6)	C5′—B1′	1.575 (8)
O3—C7	1.461 (6)	C7′—C8′	1.487 (7)
O2′—B1′	1.359 (7)	C8′—C13′	1.377 (7)
O3′—C6′	1.403 (6)		
C6—O3—C7	113.0 (4)	C6′—C5′—B1′	123.7 (5)
C6′—O3′—C7′	112.5 (4)	C5′—C6′—O3′	119.7 (4)
C6—C5—B1	124.9 (5)	O3′—C7′—C8′	108.0 (4)
O3—C6—C5	119.9 (4)	F1′—C13′—C8′	117.7 (5)
O3—C7—C8	108.1 (4)	O1—B1—O2	119.4 (5)
F1—C13—C8	117.1 (5)	O1′—B1′—O2′	120.1 (5)
B1—C5—C6—O3	4.7 (8)	C6′—O3′—C7′—C8′	−170.8 (4)
C6—O3—C7—C8	−164.3 (4)	C7′—C8′—C13′—F1′	2.7 (8)
C7—C8—C13—F1	2.1 (8)	C6—C5—B1—O2	−6.8 (9)
B1′—C5′—C6′—O3′	−5.4 (8)	C6′—C5′—B1′—O2′	−1.3 (9)

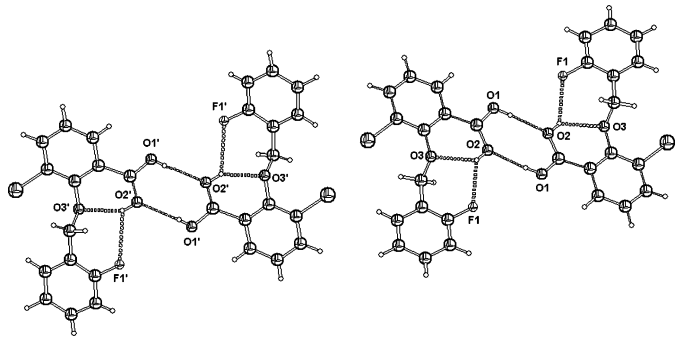


Figure 2
Intra- and intermolecular hydrogen bonds (dashed lines) in (I).

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2^{i}	0.84	1.97	2.803 (5)	172
O2—H2O···O3	0.84	2.11	2.830 (5)	143
O2—H2O···F1	0.84	2.33	2.895 (5)	125
O1′—H1O'···O2′^{ii}	0.84	1.97	2.800 (5)	172
O2′—H2O'···O3′	0.84	2.03	2.764 (5)	146
O2′—H2O'···F1′	0.84	2.59	3.057 (5)	116

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y+2, -z+1$.

Most of the H atoms were located in a difference map. They were refined with fixed individual displacement parameters [U_{iso}(H) = 1.2U_{eq}(C,O)] using a riding model, with C—H = 0.95 Å and O—H = 0.84 Å. In addition, the torsion angles of the hydroxyl groups were refined. The maximum electron-density peak in the final difference map is 1.18 Å from atom Br1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

The support of the Aldrich Chemical Co. Inc., Milwaukee, Wisconsin, USA, through the donation of chemicals and equipment, is gratefully acknowledged. The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

References

Bien, J. T., Shang, M. & Smith, B. D. (1995). *J. Org. Chem.* **60**, 2147–2152.
Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
Miyaura, N. & Suzuki, A. (1995). *Chem. Rev.* **95**, 2457–2483.
Oxford Diffraction (2001). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Poland, Wrocław, Poland.
Petasis, N., A., Goodman, A. & Zavialov, I. A. (1997). *Tetrahedron*, **53**, 16463–16470.
Samankumara Sandanayake, K. R. A. & Shinkai, S. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1083–1084.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Zheng, C., Spielvogel, B. F. & Hosmane, N. S. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 341–342.