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5-Fluoro-1,3-dihydro-2,1-benzoxaborol-1-ol

Izabela D. Madura,* Agnieszka Adamczyk-Woźniak,
Michał Jakubczyk and Andrzej SporzyńskiWarsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664
Warszawa, Poland

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

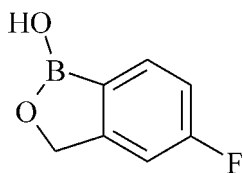
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
 R factor = 0.032; wR factor = 0.088; data-to-parameter ratio = 11.4.

In the crystal structure of the title compound, $\text{C}_7\text{H}_6\text{BFO}_2$, a broad-spectrum antifungal drug (AN2690), the planar [maximum deviation 0.035 (1) Å] molecules form centrosymmetric $R_2^2(8)$ dimers *via* strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The dimers are arranged into layers by weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds. The symmetry of this two-dimensional supramolecular assembly can be described by the layer group $p\bar{1}$ and topologically classified as a simple uninodal four-connected two-dimensional network of a (4.4.4.4.6.6) topology. Further weak $\text{C}-\text{H}\cdots\text{O}$ interactions build up the three-dimensional structure.

Related literature

For the review of the synthesis, properties and applications of benzoxaboroles, see: Adamczyk-Woźniak *et al.* (2009). For the biological activity of the title compound, see: Baker *et al.* (2005, 2006); Hui *et al.* (2007); Rock *et al.* (2007). For the synthesis see: Baker *et al.* (2006), Gunasekera *et al.* (2007). For related structures, see: Adamczyk-Woźniak *et al.* (2010); Tan *et al.* (2001); Yamamoto *et al.* (2005); Zhdankin *et al.* (1999). For hydrogen-bond graph-set descriptors and layer symmetry groups, see: Etter (1990) and International Tables for Crystallography (2006), respectively.



Experimental

Crystal data

 $\text{C}_7\text{H}_6\text{BFO}_2$
 $M_r = 151.93$
 Triclinic, $P\bar{1}$
 $a = 3.8799$ (3) Å
 $b = 6.3077$ (5) Å
 $c = 14.0735$ (12) Å

 $\alpha = 98.068$ (7)°
 $\beta = 91.564$ (7)°
 $\gamma = 100.473$ (7)°
 $V = 334.84$ (5) Å³
 $Z = 2$

 Cu $K\alpha$ radiation
 $\mu = 1.06$ mm⁻¹
 $T = 100$ K
 $0.60 \times 0.35 \times 0.20$ mm

Data collection

 Oxford Diffraction Gemini A Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2006)
 $T_{\min} = 0.731$, $T_{\max} = 1.000$

 3451 measured reflections
 1193 independent reflections
 1147 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.088$
 $S = 1.07$
 1193 reflections
 105 parameters

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2-\text{H}2\cdots\text{O}1^{\text{i}}$	0.83 (2)	1.93 (2)	2.7614 (13)	175 (2)
$\text{C}7-\text{H}7\text{B}\cdots\text{O}2^{\text{ii}}$	0.99	2.55	3.5325 (15)	172
$\text{C}5-\text{H}5\cdots\text{F}1^{\text{iii}}$	0.95	2.58	3.4779 (14)	157
$\text{C}7-\text{H}7\text{A}\cdots\text{O}2^{\text{iv}}$	0.99	2.66	3.2172 (14)	116
$\text{C}3-\text{H}3\cdots\text{O}2^{\text{iv}}$	0.95	2.70	3.4276 (14)	134

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2381).

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supporting information

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5-Fluoro-1,3-dihydro-2,1-benzoxaborol-1-ol

Izabela D. Madura, Agnieszka Adamczyk-Woźniak, Michał Jakubczyk and Andrzej Sporzyński

S1. Experimental

5-Fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole (I) was synthesized according to Fig. 3.

2-Bromo-5-fluorobenzaldehyde was purchased from Sigma-Aldrich and used as received. 2-Bromo-5-fluorobenzaldehyde (5.00 g, 0.025 mol) and 2.69 g (0.025 mol) of trimethoxymethane was dissolved in 100 ml of methanol in a two-necked vessel. 0.4 ml of concentrated H₂SO₄ was added. The solution was refluxed for one hour and left to cool down. Then the solution was brought to pH=11 with a concentrated solution of NaOMe in methanol. The reaction mixture was distilled under vacuum to give 5.90 g of 1-Bromo-2-(dimethoxymethyl)-4-fluorobenzene as a colorless liquid (yield 96%; ¹H NMR (CDCl₃, 400 MHz): 7.49 (dd, 1H), 7.34 (dd, 1H), 6.91 (td, 1H), 5.49 (s, 1H), 3.37 (s, 6H) p.p.m.). The product was dissolved in 100 ml of dry Et₂O in a three-necked vessel under argon flow. The solution was cooled down to -78°C using dry ice/acetone bath. n-Butyllithium in hexane (2.5 M, 11 ml) was added dropwise to keep the temperature under -70°C. The solution was stirred for one hour, then 3.80 g (0.026 mol, 4.4 ml) of triethyl borate was added slowly, keeping the temperature under -70°C. The dry ice/acetone bath was removed and the solution was stirred for one hour. The solution was brought to pH≈3 with 3 M aq. HCl. The aqueous layer was separated and extracted with Et₂O (2 × 100 ml). The organic layers were combined and the solvent was partially removed under vacuum. The remaining thick solution was dissolved in hot water. Yellowish crystals of 4-fluoro-2-formylphenylboronic acid were filtered after a few hours. Recrystallization from water gave 1.79 g of the product (yield 49%; ¹H NMR (CDCl₃, 400 MHz): 9.89 (s, 1H), 8.31 (dd, 1H), 7.62 (dd, 1H), 7.40 (td, 1H) p.p.m.). The product (1.79 g, 0.011 mol) was dissolved in 100 ml of methanol in a one-necked vessel. 0.44 g (0.012 mol) of NaBH₄ was added in small portions. The solution was mixed for 12 h. Another portion of 0.22 g of NaBH₄ was added and the solution was mixed for 3 days. The solvent was removed under vacuum. The crude product was dissolved in water. Crystallization gave 0.82 g of 5-Fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole (I) as yellowish crystals (yield 51%; ¹H NMR (CDCl₃, 400 MHz): 7.72 (dd, 1H), 7.06 (m, 2H), 5.08 (s, 2H) p.p.m.; ¹⁹F NMR (CDCl₃, 376.3 MHz): -113.51 (q) p.p.m.; ¹¹B NMR ((CdD₃)₂CO, 64.1 MHz): 32.0 p.p.m.; m.p. 135–136°C).

S2. Refinement

H2 atom bonded to O2 atom was located in a difference map and freely refined. Other H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å and with $U_{iso}(H) = 1.2$ times $U_{eq}(C)$.

Figure 1

ORTEP plot of the hydrogen bonded dimer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2

Projection on (1 0 2) plane showing layers of molecules linked by O—H \cdots O (dashed lines), C—H \cdots O and C—H \cdots F (dotted lines) H-bonds.

Figure 3

Synthesis of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole (I).

5-Fluoro-1,3-dihydro-2,1-benzoxaborol-1-ol*Crystal data*

C₇H₆BFO₂

$M_r = 151.93$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 3.8799$ (3) Å

$b = 6.3077$ (5) Å

$c = 14.0735$ (12) Å

$\alpha = 98.068$ (7)°

$\beta = 91.564$ (7)°

$\gamma = 100.473$ (7)°

$V = 334.84$ (5) Å³

$Z = 2$

$F(000) = 156$

$D_x = 1.507$ Mg m⁻³

Melting point: 408 K

Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å

Cell parameters from 3116 reflections

$\theta = 3.2$ – 67.1 °

$\mu = 1.06$ mm⁻¹

$T = 100$ K

Prism, light yellow

$0.60 \times 0.35 \times 0.20$ mm

Data collection

Oxford Diffraction Gemini A Ultra diffractometer

Radiation source: Enhance Ultra (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.3347 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2006)

$T_{\min} = 0.731$, $T_{\max} = 1.000$

3451 measured reflections

1193 independent reflections

1147 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 67.1$ °, $\theta_{\min} = 3.2$ °

$h = -4 \rightarrow 4$

$k = -7 \rightarrow 7$

$l = -16 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.088$

$S = 1.07$

1193 reflections

105 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.1152P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.33$ e Å⁻³

$\Delta\rho_{\min} = -0.18$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.046 (5)

Special details

Experimental. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. (Oxford Diffraction, 2006)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.9636 (2)	1.22613 (14)	0.60638 (7)	0.0189 (3)
F1	0.0385 (2)	0.70856 (13)	0.93059 (5)	0.0282 (3)
O1	0.7364 (2)	0.84381 (13)	0.56821 (6)	0.0171 (3)
C3	0.2566 (3)	0.6725 (2)	0.77652 (9)	0.0185 (3)
H3	0.1624	0.5207	0.7660	0.022*
C4	0.2168 (3)	0.8036 (2)	0.86129 (9)	0.0200 (3)
C2	0.4422 (3)	0.7757 (2)	0.70750 (9)	0.0162 (3)
C1	0.5825 (3)	0.9983 (2)	0.72234 (9)	0.0167 (3)
C5	0.3485 (3)	1.0251 (2)	0.87950 (9)	0.0207 (3)
H5	0.3121	1.1083	0.9388	0.025*
C6	0.5346 (3)	1.1237 (2)	0.80968 (9)	0.0186 (3)
H6	0.6291	1.2754	0.8210	0.022*
B1	0.7783 (3)	1.0404 (2)	0.63011 (10)	0.0164 (3)
C7	0.5248 (3)	0.6711 (2)	0.61026 (9)	0.0170 (3)
H7B	0.6562	0.5526	0.6164	0.020*
H7A	0.3064	0.6096	0.5701	0.020*
H2	1.061 (5)	1.212 (3)	0.5545 (15)	0.040 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0245 (5)	0.0147 (5)	0.0169 (5)	0.0025 (4)	0.0053 (4)	0.0011 (3)
F1	0.0329 (5)	0.0323 (5)	0.0196 (4)	0.0035 (4)	0.0106 (3)	0.0065 (3)
O1	0.0208 (5)	0.0145 (5)	0.0154 (5)	0.0019 (3)	0.0046 (3)	0.0017 (3)
C3	0.0178 (6)	0.0188 (6)	0.0193 (7)	0.0037 (5)	0.0009 (5)	0.0033 (5)
C4	0.0181 (6)	0.0273 (7)	0.0160 (6)	0.0052 (5)	0.0038 (5)	0.0061 (5)
C2	0.0149 (6)	0.0174 (6)	0.0168 (6)	0.0055 (5)	-0.0004 (4)	0.0014 (5)
C1	0.0154 (6)	0.0174 (6)	0.0178 (7)	0.0051 (5)	-0.0011 (5)	0.0021 (5)
C5	0.0212 (6)	0.0256 (7)	0.0155 (6)	0.0083 (5)	0.0008 (5)	-0.0016 (5)
C6	0.0187 (6)	0.0179 (6)	0.0188 (6)	0.0049 (5)	-0.0001 (5)	-0.0007 (5)
B1	0.0162 (6)	0.0162 (7)	0.0172 (7)	0.0055 (5)	-0.0011 (5)	0.0009 (5)
C7	0.0197 (6)	0.0135 (6)	0.0174 (6)	0.0017 (5)	0.0036 (5)	0.0021 (5)

Geometric parameters (Å, °)

O2—B1	1.3483 (18)	C2—C1	1.3948 (18)
O2—H2	0.83 (2)	C2—C7	1.5025 (17)
F1—C4	1.3562 (15)	C1—C6	1.4013 (17)
O1—B1	1.3922 (17)	C1—B1	1.5522 (18)
O1—C7	1.4471 (15)	C5—H5	0.9500
C3—H3	0.9500	C5—C6	1.3856 (18)
C3—C4	1.3822 (19)	C6—H6	0.9500
C3—C2	1.3897 (18)	C7—H7B	0.9900
C4—C5	1.3829 (19)	C7—H7A	0.9900
O2—B1—O1	121.51 (12)	C2—C3—H3	121.9
O2—B1—C1	130.25 (12)	C2—C1—C6	119.16 (12)
F1—C4—C3	117.85 (12)	C2—C1—B1	104.93 (11)
F1—C4—C5	118.27 (12)	C2—C7—H7B	110.7
O1—B1—C1	108.24 (11)	C2—C7—H7A	110.7
O1—C7—C2	105.45 (9)	C1—C2—C7	110.88 (11)
O1—C7—H7B	110.7	C1—C6—H6	120.2
O1—C7—H7A	110.7	C5—C6—C1	119.66 (12)
C3—C4—C5	123.88 (12)	C5—C6—H6	120.2
C3—C2—C1	122.36 (12)	C6—C1—B1	135.86 (12)
C3—C2—C7	126.75 (11)	C6—C5—H5	120.6
C4—C3—H3	121.9	B1—O2—H2	115.3 (13)
C4—C3—C2	116.12 (12)	B1—O1—C7	110.46 (10)
C4—C5—H5	120.6	H7B—C7—H7A	108.8
C4—C5—C6	118.82 (12)		
F1—C4—C5—C6	179.28 (10)	C2—C1—B1—O2	-179.25 (12)
C3—C4—C5—C6	-0.58 (19)	C2—C1—B1—O1	0.71 (13)
C3—C2—C1—C6	-0.23 (17)	C1—C2—C7—O1	2.08 (13)
C3—C2—C1—B1	177.60 (11)	C6—C1—B1—O2	-2.0 (2)
C3—C2—C7—O1	-177.19 (11)	C6—C1—B1—O1	178.00 (12)
C4—C3—C2—C1	0.24 (18)	B1—O1—C7—C2	-1.57 (13)
C4—C3—C2—C7	179.42 (11)	B1—C1—C6—C5	-177.18 (12)
C4—C5—C6—C1	0.57 (18)	C7—O1—B1—O2	-179.45 (10)
C2—C3—C4—F1	-179.69 (9)	C7—O1—B1—C1	0.59 (13)
C2—C3—C4—C5	0.17 (19)	C7—C2—C1—C6	-179.53 (10)
C2—C1—C6—C5	-0.19 (17)	C7—C2—C1—B1	-1.70 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots O1 ⁱ	0.83 (2)	1.93 (2)	2.7614 (13)	175 (2)
C7—H7B \cdots O2 ⁱⁱ	0.99	2.55	3.5325 (15)	172
C5—H5 \cdots F1 ⁱⁱⁱ	0.95	2.58	3.4779 (14)	157

C7—H7A···O2 ^{iv}	0.99	2.66	3.2172 (14)	116
C3—H3···O2 ^{iv}	0.95	2.70	3.4276 (14)	134

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