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2,4-Difluorophenylboronic acid

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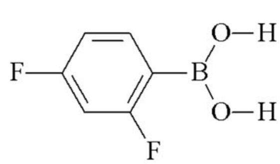
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.056; wR factor = 0.127; data-to-parameter ratio = 11.2.

The molecular structure of the title compound, $C_6H_5BF_2O_2$, is essentially planar (mean deviation = 0.019 Å), indicating electronic delocalization between the dihydroxyboryl group and the aromatic ring. In the crystal structure, inversion dimers linked by two O—H···O hydrogen bonds arise. An intramolecular O—H···F hydrogen bond reinforces the conformation and the same H atom is also involved in an intermolecular O—H···F link, leading to molecular sheets in the crystal.

Related literature

For general backround to boronic acids, see: Hall (2005); Höpfl (2002); Fujita *et al.* (2008); Soloway *et al.* (1998). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Desiraju (2002). For related structures, see: Wu *et al.* (2006); Bradley *et al.* (1996); Horton *et al.* (2004). For crystal engineering, see: Fournier *et al.* (2003); Rodríguez-Cuamatzi *et al.* (2004, 2005).



Experimental

Crystal data

$C_6H_5BF_2O_2$
M_r = 157.91
Monoclinic, $P2_1/n$
a = 3.7617 (11) Å
b = 12.347 (4) Å
c = 14.620 (4) Å
β = 95.450 (5)°
V = 676.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 293 (2) K
0.37 × 0.35 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.947, T_{max} = 0.968
3196 measured reflections
1190 independent reflections
1012 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.127
S = 1.15
1190 reflections
106 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···F1	0.841 (15)	2.16 (3)	2.799 (3)	133 (2)
O1—H1···F2^{i}	0.841 (15)	2.39 (2)	3.086 (3)	140 (3)
O2—H2···O1^{ii}	0.841 (19)	1.97 (2)	2.809 (3)	174 (3)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus-NT* (Bruker, 2001); data reduction: *SAINT-Plus-NT*; program(s) used to solve structure: *SHELXTL-NT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003) and *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2865).

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supporting information

Acta Cryst. (2009). E**65**, o44–o45 [doi:10.1107/S1600536808040646]

2,4-Difluorophenylboronic acid

Patricia Rodríguez-Cuamatzi, Hugo Tlahuext and Herbert Höpfl

S1. Comment

Boronic acids, $RB(OH)_2$ with R = alkyl and aryl, have applications in organic synthesis (Hall, 2005), host–guest chemistry (Höpfl, 2002), the molecular recognition of biochemically active molecules (Fujita *et al.*, 2008) and in medicine as antibiotics, inhibitors and for the treatment of tumors (Soloway *et al.*, 1998). Similar to carboxylic acids they are capable to form hydrogen-bonded dimeric units and, therefore, boronic acids have been used recently as new building blocks in crystal engineering (Fournier *et al.*, 2003; Rodríguez-Cuamatzi *et al.*, 2004; Rodríguez-Cuamatzi *et al.*, 2005). Previously, the structures of 3-fluorophenylboronic acid (Wu *et al.*, 2006), 2,6-difluoroboronic acid (Bradley *et al.*, 1996) and pentafluoroboronic acid (Horton *et al.*, 2004) had been reported. We now present the crystal structure of (**I**).

The molecular structure is essentially planar, O1—B1—C1—C2 = 4.4 (4)°, indicating that there is a $\pi\cdots\pi$ interaction between the dihydroxyboryl group and the aromatic ring, to which it is attached (Fig. 1). This interaction is also evidenced by the B—C bond length of 1.566 (3) Å, which is significantly shorter than that observed in boronates containing tetra-coordinate boron atoms (Höpfl, 2002). The crystal structure is stabilized by strong O2—H2···O1 hydrogen-bonding interactions, forming $R_2^2(8)$ motifs (Bernstein *et al.*, 1995), as well as, O1—H1···F1 and O1—H1···F2 bifurcated hydrogen bonds (Fig. 2; Table 1) (Desiraju, 2002). Due to these interactions each boronic acid homodimer is linked to two neighboring homodimeric units, thus creating a two-dimensional hydrogen-bonded network, in which fluorine is therefore an essential structural component.

S2. Experimental

2,4-Difluorophenylboronic acid was purchased from Aldrich and crystallized from water to yield colourless blocks of (I).

S3. Refinement

The aromatic H atoms were positioned geometrically (C—H = 0.93Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The O—H hydrogen atoms were localized in a difference map and their coordinates were refined with O—H = 0.84+/0.01Å and $U_{iso}(H) = 1.5 U_{eq}(O)$.

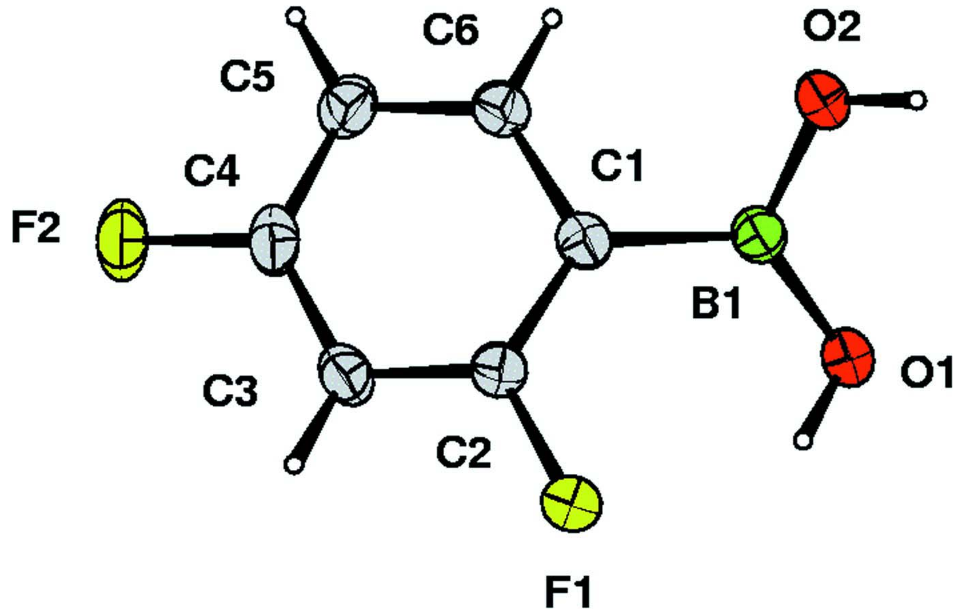

Figure 1

The molecular structure of **(I)** with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radius.

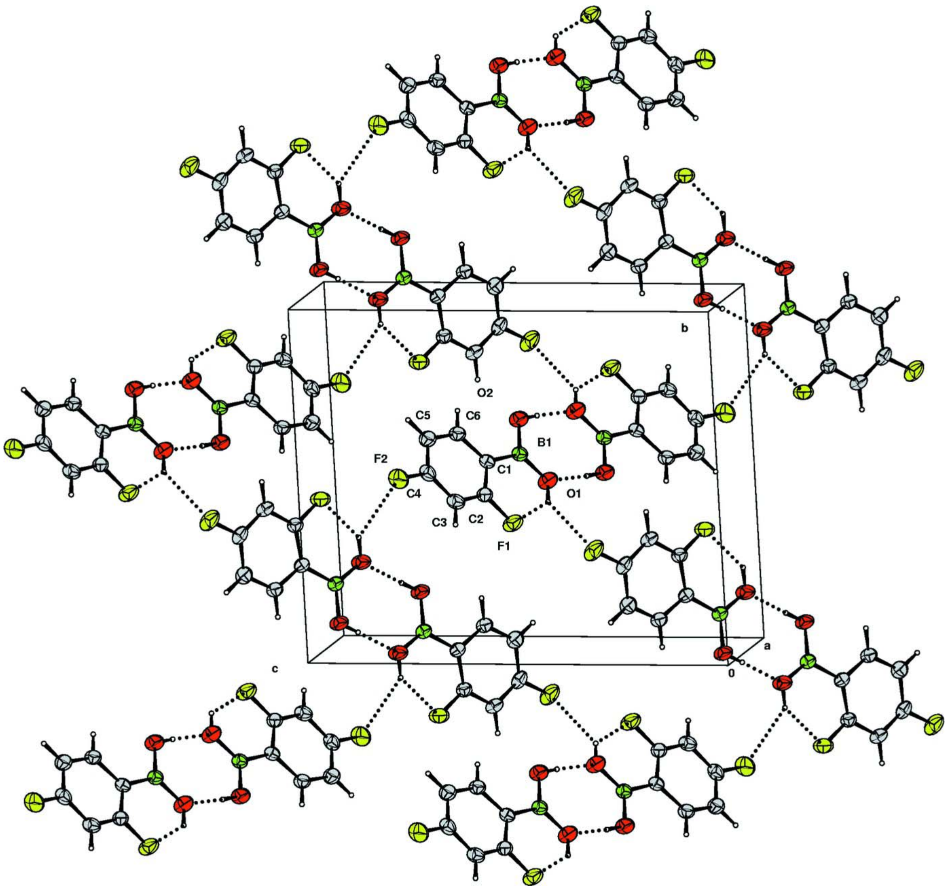

Figure 2

View of the packing arrangement of the two-dimensional network of **(I)(I)**.

2,4-Difluorophenylboronic acid

Crystal data

$C_6H_5BF_2O_2$
M_r = 157.91
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 3.7617 (11) Å
b = 12.347 (4) Å
c = 14.620 (4) Å
β = 95.450 (5)°
V = 676.0 (3) Å^3
Z = 4

F(000) = 320
D_x = 1.552 Mg m^{-3}
Melting point = 521–522 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1052 reflections
θ = 2.3–26.2°
μ = 0.15 mm^{-1}
T = 293 K
Block, colorless
0.37 × 0.35 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3 pixels mm^{-1}
φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.947, T_{max} = 0.968
3196 measured reflections
1190 independent reflections
1012 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

θ_{max} = 25.0°, θ_{min} = 2.2°
h = −3→4
k = −14→12
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.127
S = 1.15
1190 reflections
106 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.2673P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

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. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
B1	0.7704 (8)	0.4548 (2)	0.62567 (18)	0.0452 (7)
O1	0.6825 (6)	0.38623 (15)	0.55419 (13)	0.0695 (6)
H1	0.748 (9)	0.3215 (9)	0.562 (2)	0.104*
O2	0.6880 (6)	0.55977 (14)	0.61557 (12)	0.0630 (6)
H2	0.593 (8)	0.577 (3)	0.5632 (10)	0.094*
F1	1.0385 (5)	0.23728 (11)	0.67473 (11)	0.0768 (6)
F2	1.4329 (5)	0.33016 (14)	0.97634 (10)	0.0822 (6)
C1	0.9591 (6)	0.41789 (18)	0.72069 (15)	0.0424 (6)
C2	1.0796 (7)	0.31430 (18)	0.74175 (16)	0.0470 (6)
C3	1.2380 (7)	0.2819 (2)	0.82553 (17)	0.0539 (7)
H3	1.3138	0.2109	0.8363	0.065*
C4	1.2785 (7)	0.3593 (2)	0.89223 (17)	0.0547 (7)
C5	1.1696 (8)	0.4640 (2)	0.87828 (17)	0.0586 (7)
H5	1.2013	0.5150	0.9251	0.070*
C6	1.0119 (7)	0.49169 (19)	0.79282 (16)	0.0498 (6)
H6	0.9371	0.5628	0.7827	0.060*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.0451 (16)	0.0425 (15)	0.0471 (16)	−0.0009 (12)	−0.0005 (12)	0.0033 (12)
O1	0.1000 (17)	0.0484 (11)	0.0540 (11)	0.0158 (10)	−0.0241 (10)	−0.0009 (9)

O2	0.0850 (15)	0.0441 (10)	0.0552 (11)	0.0087 (9)	−0.0172 (10)	0.0048 (8)
F1	0.1192 (15)	0.0456 (9)	0.0602 (10)	0.0151 (9)	−0.0187 (9)	−0.0046 (7)
F2	0.1070 (14)	0.0804 (12)	0.0527 (10)	−0.0120 (10)	−0.0262 (9)	0.0181 (8)
C1	0.0383 (13)	0.0412 (13)	0.0473 (13)	−0.0039 (10)	0.0019 (10)	0.0048 (10)
C2	0.0523 (16)	0.0410 (13)	0.0467 (13)	−0.0017 (11)	0.0001 (11)	0.0008 (10)
C3	0.0584 (17)	0.0449 (14)	0.0564 (15)	0.0002 (12)	−0.0053 (13)	0.0124 (12)
C4	0.0579 (17)	0.0613 (17)	0.0426 (13)	−0.0099 (13)	−0.0075 (12)	0.0135 (12)
C5	0.0696 (19)	0.0552 (16)	0.0489 (14)	−0.0109 (13)	−0.0058 (13)	−0.0020 (12)
C6	0.0559 (16)	0.0399 (13)	0.0522 (14)	−0.0011 (11)	−0.0011 (12)	0.0029 (11)

Geometric parameters (Å, º)

B1—O2	1.338 (3)	C1—C6	1.394 (3)
B1—O1	1.361 (3)	C2—C3	1.370 (3)
B1—C1	1.566 (3)	C3—C4	1.363 (4)
O1—H1	0.841 (15)	C3—H3	0.93
O2—H2	0.841 (15)	C4—C5	1.366 (4)
F1—C2	1.364 (3)	C5—C6	1.374 (3)
F2—C4	1.358 (3)	C5—H5	0.93
C1—C2	1.382 (3)	C6—H6	0.93
O2—B1—O1	118.7 (2)	C4—C3—H3	121.8
O2—B1—C1	117.4 (2)	C2—C3—H3	121.8
O1—B1—C1	123.8 (2)	F2—C4—C3	118.1 (2)
B1—O1—H1	116 (2)	F2—C4—C5	118.8 (2)
B1—O2—H2	115 (2)	C3—C4—C5	123.0 (2)
C2—C1—C6	114.6 (2)	C4—C5—C6	117.9 (2)
C2—C1—B1	125.3 (2)	C4—C5—H5	121.0
C6—C1—B1	120.1 (2)	C6—C5—H5	121.0
F1—C2—C3	116.7 (2)	C5—C6—C1	122.9 (2)
F1—C2—C1	118.2 (2)	C5—C6—H6	118.5
C3—C2—C1	125.1 (2)	C1—C6—H6	118.5
C4—C3—C2	116.4 (2)		
O2—B1—C1—C2	−176.5 (2)	C1—C2—C3—C4	−0.3 (4)
O1—B1—C1—C2	4.5 (4)	C2—C3—C4—F2	179.7 (2)
O2—B1—C1—C6	4.6 (4)	C2—C3—C4—C5	0.0 (4)
O1—B1—C1—C6	−174.5 (2)	F2—C4—C5—C6	−179.6 (2)
C6—C1—C2—F1	−179.9 (2)	C3—C4—C5—C6	0.1 (4)
B1—C1—C2—F1	1.1 (4)	C4—C5—C6—C1	0.0 (4)
C6—C1—C2—C3	0.4 (4)	C2—C1—C6—C5	−0.3 (4)
B1—C1—C2—C3	−178.6 (2)	B1—C1—C6—C5	178.8 (2)
F1—C2—C3—C4	180.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···F1	0.84 (2)	2.16 (3)	2.799 (3)	133 (2)

O1—H1···F2[i]	0.84 (2)	2.39 (2)	3.086 (3)	140 (3)
O2—H2···O1[ii]	0.84 (2)	1.97 (2)	2.809 (3)	174 (3)

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