

2,3-Difluoro-4-formylphenylboronic acid

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Received 29 December 2006

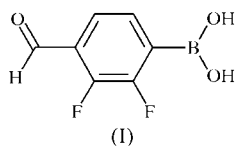
Accepted 12 January 2007

Online 10 February 2007

The molecule of the title compound, $2,3\text{-F}_2\text{-4-(CHO)C}_6\text{H}_2\text{-B(OH)}_2$ or $\text{C}_7\text{H}_5\text{BF}_2\text{O}_3$, contains a formyl group coplanar with the benzene ring. The boronic acid group is twisted with respect to the benzene ring plane. The molecules are organized into infinite chains *via* intermolecular $\text{O—H}\cdots\text{O}$ hydrogen bonds. These chains are additionally connected *via* strong $\text{O—H}\cdots\text{O}$ hydrogen bonds, producing a folded layer structure perpendicular to the *a* axis. These layers are paired due to $\text{B}\cdots\text{F}$ interactions.

Comment

Arylboronic acids containing a carbonyl group are valuable starting materials in organic synthesis. The high reactivity of this group enables modification of the structure of boronic acids to obtain a wide range of compounds possessing interesting properties. Recently, the synthesis of (*N*-alkylamino)-methylphenylboronic acids *via* reductive amination of formylphenylboronic acids has been published (Gravel *et al.*, 2002). The formation of arylboronic acids containing a chalcone moiety in an aldol-type reaction between 4-acetylphenylboronic acids and aldehydes is also known (DiCesare & Lakowicz, 2002). The products obtained have found applications as potential saccharide (Wang *et al.*, 2002) and hormone receptors (Secor & Glass, 2004) or as reagents in Suzuki coupling (Miyaura & Suzuki, 1995). The determination of the crystal structures of boronic acids can be helpful in the elucidation of the influence of hydrogen-bond formation on the activity of these compounds as potential pharmaceutical agents (Yang *et al.*, 2003). Against this background, we present here the crystal structure of the title compound, (I).



The molecular structure of (I) is presented in Fig. 1, with selected geometry details given in Table 1. The formyl group is essentially coplanar with the benzene ring [torsion angle C5—

$\text{C4—C7—O3} = -0.7(2)^\circ$] and the boronic acid group is twisted around the C—B bond [torsion angle $\text{C2—C1—B2—O2} = 18.2(2)^\circ$], thus producing a non-planar six-membered ring. The boronic acid group has an *exo-endo* conformation. The *endo*-oriented OH group is engaged in a relatively weak intramolecular $\text{O—H}\cdots\text{F}$ interaction with atom F1.

The supramolecular assembly in (I) (Fig. 2) is primarily achieved due to $\text{O—H}\cdots\text{O}$ intermolecular hydrogen-bonding interactions (Table 2), of which there are two types. The *exo*-oriented OH group is the H-atom donor engaged in the nearly linear hydrogen bond with the O atom from the formyl group of an adjacent molecule. As a result, the molecules are connected in a 'head-to-tail' fashion, forming an infinite chain aligned along the crystallographic *b* axis. The *exo* OH group acts simultaneously as the H-atom acceptor for the *endo* OH group of another molecule; this hydrogen bond is weaker, but it seems to be responsible for the twisting of the boronic acid group. Thus, the hydrogen-bonded network in (I) can be described as a folded layer. It should be noted that a similar

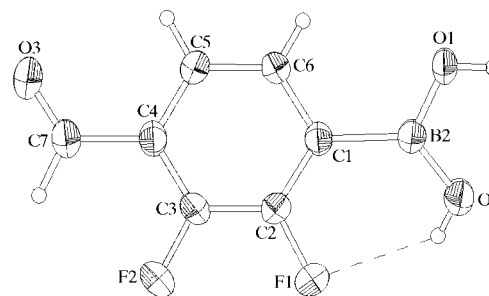


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

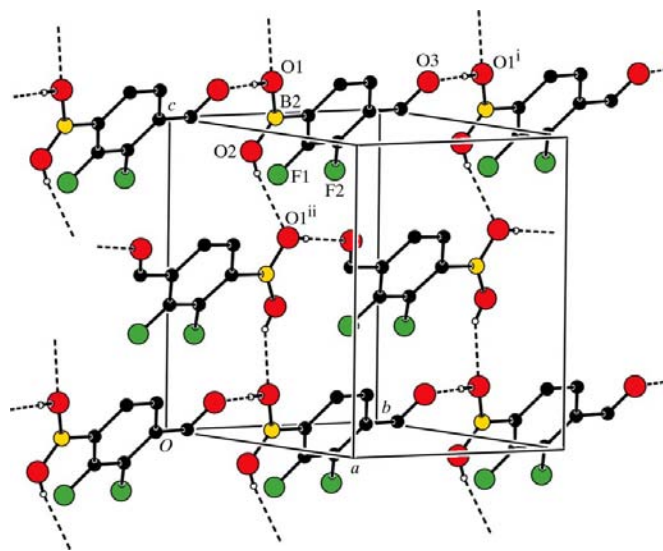
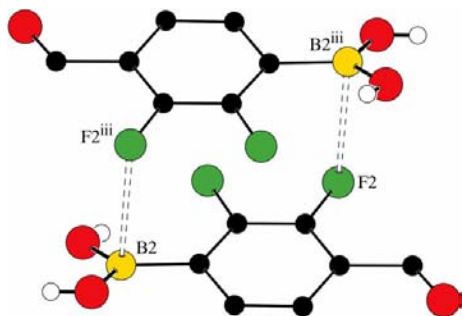


Figure 2

The hydrogen-bonding pattern for (I). Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x, y - 1, z$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$]


Figure 3

The crystal packing for (I), showing the B...F interactions as dashed lines. [Symmetry code: (iii) $-x, -y + 1, -z + 2$.]

structure was reported for the related 4-formylphenylboronic acid (Fronczek *et al.*, 2001), whereas molecules of the isomeric 3-formyl- (Zarychta *et al.*, 2004) and 2-formylphenylboronic acids (Scouten *et al.*, 1994) form centrosymmetric dimers *via* intermolecular hydrogen bonds between boronic acid groups.

Examination of the crystal packing in (I) reveals that layers are paired due to weak interactions of their 'fluorinated' sides. These interactions are represented by relatively short B2...F2ⁱⁱⁱ distances of 3.301 (2) Å [symmetry code: (iii) $-x, 1 - y, 2 - z$], presumably the result of electrostatic attractive forces between B and F atoms, producing centrosymmetric dimeric motifs. According to Batsanov (2000), the sum of the van der Waals radii for B and F is 3.51 Å.

In conclusion, the supramolecular structure of (I) is achieved *via* two types of intermolecular hydrogen bonds and displays a folded layer structure. In addition, the layers are paired due to B...F interactions.

Experimental

2,3-Difluoro-4-formylphenylboronic acid was obtained from Aldrich, crystallized from tetrahydrofuran and dried in air.

Crystal data

$C_7H_5BF_2O_3$	$Z = 4$
$M_r = 185.92$	$D_x = 1.618 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.9154$ (12) Å	$\mu = 0.15 \text{ mm}^{-1}$
$b = 9.8527$ (15) Å	$T = 293$ (2) K
$c = 9.8141$ (13) Å	Prismatic, colourless
$\beta = 94.198$ (12)°	$0.74 \times 0.21 \times 0.17 \text{ mm}$
$V = 763.33$ (19) Å ³	

Data collection

Kuma KM-4 CCD area-detector diffractometer	7011 measured reflections
ω scans	1827 independent reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2005)	1135 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.92, T_{\max} = 0.97$	$R_{\text{int}} = 0.014$
	$\theta_{\text{max}} = 28.6^\circ$

Refinement

Refinement on F^2	Only H-atom coordinates refined
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1827 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
133 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1—B2	1.3430 (18)	C1—B2	1.5851 (19)
O2—B2	1.3385 (18)		
O2—B2—O1	118.43 (13)	O2—B2—C1	125.51 (13)
O1—B2—C1	116.06 (12)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O3 ⁱ	0.826 (19)	1.929 (19)	2.7526 (14)	174.3 (16)
O2—H2...O1 ⁱⁱ	0.803 (18)	2.242 (17)	2.9744 (17)	152.0 (16)
O2—H2...F1	0.803 (18)	2.395 (17)	2.8917 (14)	121.1 (14)

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

All H atoms were located geometrically and their positions were refined, while their displacement parameters were not. The refined C—H distances are in the range 0.949–1.061 (16) Å. $U_{\text{iso}}(\text{H})$ values were fixed at 0.040 (aromatic C—H) and 0.057 Å² (hydroxy O—H).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1990).

This work was supported by the Aldrich Chemical Company through the donation of chemicals and equipment, and by the Warsaw University of Technology. The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Laboratory in the Chemistry Department of the University of Warsaw.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3045). Services for accessing these data are described at the back of the journal.

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