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3-Formyl-2-furanboronic acid: X-ray and DFT studies

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The molecule of the title compound, $C_5H_5BO_4$, is almost planar with the boronic acid group inclined to the furan ring by 3.7 (1)°. DFT (density functional theory) calculations at the B3LYP/6-311+G** level of theory (with no imaginary frequencies) were used to approximate the influence of hydrogen bonding on the molecular geometry and have confirmed the planarity of the molecule. No significant differences in geometrical parameters in the solid state and in the gas phase are associated with the presence of the O—H···O intermolecular hydrogen-bonding network. The crystal packing is characterized by O—H···O hydrogen-bonded dimers, which are additionally linked by O—H···O, as well as C—H···O interactions, resulting in the formation of a three-dimensional network.

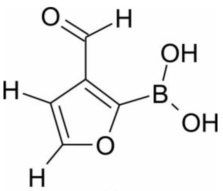
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.106
Data-to-parameter ratio = 12.8

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

Comment

Arylboronic acids, $ArB(OH)_2$, have been used for many years in organic syntheses, mainly as coupling agents in the Suzuki reaction (Miyaura & Suzuki, 1995). However, recently, great attention has been paid to a new application of these compounds, *viz*. construction of receptors for carbohydrates and other polyols (James & Shinkai, 2002). Hence, structural parameters and information concerning such interactions as inter- and intramolecular hydrogen bonds are important for the design of new systems. The presence of a substituent on the aromatic ring of an arylboronic acid can influence the structure of the boronic acid molecule. Recently, the structures of two boronic acids possessing a formyl group on the aromatic ring were determined: 5-formyl-2-furanboronic acid (Ejsmont *et al.*, 2003) and 3-formylphenylboronic acid (Zarychta *et al.*, 2004). In both cases, intra- and intermolecular hydrogen bonds influence the structure and crystal packing. The aim of the present work was to investigate the influence of the formyl group in the position *ortho* to the boronic group on the furan ring. Therefore, X-ray analysis as well as DFT (density functional theory) calculations, as a complementary method, were used to study the crystal and molecular structure of the title compound, (I).



(I)

The molecular structure of (I) is depicted in Fig. 1. The molecule is nearly planar. The group that deviates most from

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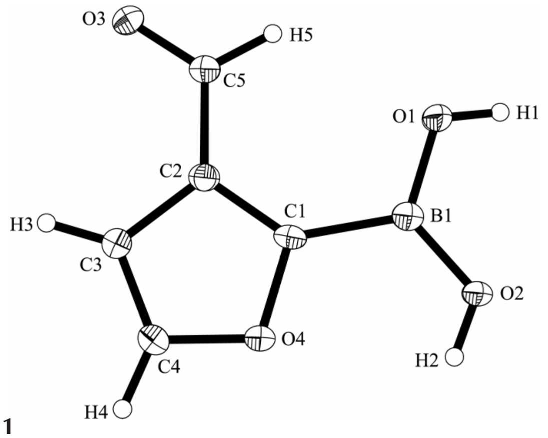

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

the plane of the molecule is the boronic acid group. It is twisted by 3.4 (2)° from the plane of the furan ring. Such a distortion has also been reported previously (Ejsmont *et al.*, 2003). In most cases, the boronic acid group is almost coplanar with the aromatic ring (Ejsmont *et al.*, 2003; Fronczek *et al.*, 2001; Shull *et al.*, 2000; Zarychta *et al.*, 2004). This suggests that the planar conformation, in contrast to the twisted one (Ganguly *et al.*, 2003; Soundararajan *et al.*, 1993), is the preferred arrangement and stabilizes the crystal packing of boronic acid derivatives. It should be emphasized that such a small twist about the B1—C1 bond (Fig. 1) is unusual among the *ortho* isomers of aromatic boronic acids (Ganguly *et al.*, 2003; Soundararajan *et al.*, 1993).

The furan ring is planar. The bond length which most deviates from the value found in the structure of unsubstituted furan (Fourme, 1972) is C1—C2 [1.372 (2) Å]. It was found to be longer by 0.05 Å, due to the presence of the substituents on atoms C1 and C2. The remaining bond lengths and angles of the furan ring are typical and are in good agreement with those reported earlier (Fourme, 1972). The comparison of the geometrical parameters of the two isomers, 5-formyl-2-furanboronic acid, (II) (Ejsmont *et al.*, 2003), and compound (I), suggests that the position of the formyl group has a weak influence on the distortion of the furan ring.

The formyl group is essentially coplanar with the furan ring. Its geometry differs slightly from that found in (II). The C2—C5—O3 angle [123.17 (15)°] is smaller by 2.4 (2)° and the C2—C5 bond length [1.452 (2) Å] is longer by 0.021 (2) Å than the corresponding values observed in (II). Simultaneously, the C5—O3 bond length [1.223 (2) Å] is in good agreement with the value observed in (II). The differences in geometry of the formyl group in various formyl derivatives of furan- or phenylboronic acids (Ejsmont *et al.*, 2003; Fronczek *et al.*, 2001; Scouten *et al.*, 1994; Zarychta *et al.*, 2004) are strongly connected with the dissimilarity of the hydrogen-bonding shell around the formyl O atom.

The crystal packing is stabilized by two types of hydrogen bonds, *viz*. stronger O—H···O and relatively weak C—H···O bonds. The O1—H1···O2^{i} bonds [symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*] are almost linear and form centrosymmetric dimers of (I) (Fig. 2 and Table 1). This is similar to the pattern found in (II) (Ejsmont *et al.*, 2003). The intermolecular C—H···O and remaining O—H···O hydrogen bonds link the dimers together to form a complicated three-dimensional network. Two intramolecular C5—H5···O1 and O2—H2···O4 interactions have also been found (Table 1).

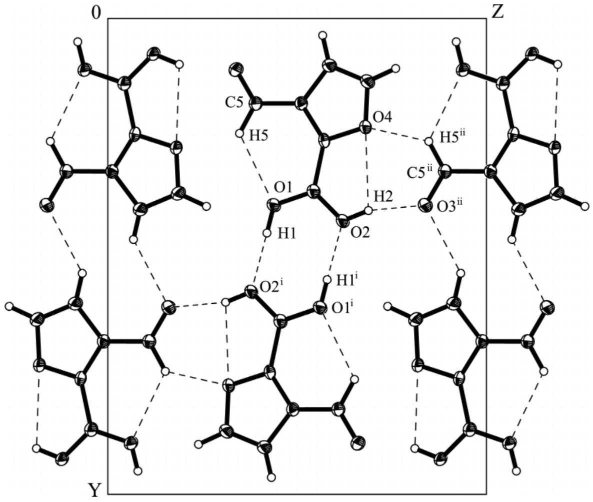

Figure 2
Crystal packing of (I) viewed down the *a* axis. The O—H···O and selected C—H···O hydrogen bonds are denoted by dashed lines. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) 1 + *x*, $\frac{1}{2}$ − *y*, $\frac{1}{2}$ + *z*.]

The DFT calculations (Frisch *et al.*, 1998) have confirmed that the planar conformation of (I) is the favourable one in the gas phase. The calculated and experimental values of the bond lengths and angles of (I) are in good agreement (Table 2). The differences do not exceed 0.02 Å for the bond lengths (*e.g.* C2—C5) and 3° for the valence angles (*e.g.* O1—B1—C1), and are undeniably associated with the characteristic pattern of the O—H···O hydrogen bonds. This could be considered as a proof that the intermolecular interactions do not significantly influence the molecular geometry of (I).

Experimental

3-Formyl-2-furanboronic acid was purchased from Aldrich and was crystallized from water and dried in air.

Crystal data

$C_5H_5BO_4$
M_r = 139.90
Monoclinic, $P2_1/c$
a = 3.660 (1) Å
b = 14.252 (2) Å
c = 11.447 (1) Å
β = 98.09 (1)°
V = 591.16 (19) Å^3
Z = 4

D_x = 1.572 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4208 reflections
θ = 3.4–28.0°
μ = 0.13 mm^{-1}
T = 100.0 (1) K
Irregular block, colourless
0.20 × 0.15 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
4208 measured reflections
1419 independent reflections
1143 reflections with *I* > 2*σ*(*I*)

R_{int} = 0.031
θ_{max} = 28.0°
h = −4 → 4
k = −18 → 18
l = −15 → 12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.08$
1419 reflections
111 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.3322P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O4	0.88 (3)	2.54 (3)	2.899 (2)	105 (2)
C5—H5···O1	1.02 (2)	2.45 (2)	3.133 (2)	123 (1)
O1—H1···O2$^{\rm i}$	0.89 (3)	1.86 (3)	2.749 (2)	177 (3)
O2—H2···O3$^{\rm ii}$	0.88 (3)	1.84 (3)	2.693 (2)	164 (2)
C3—H3···O3$^{\rm iii}$	0.95 (2)	2.56 (2)	3.351 (2)	140 (2)
C5—H5···O4$^{\rm iv}$	1.02 (2)	2.40 (2)	3.106 (2)	125 (1)

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

Table 2
Selected geometric data (Å,°) for (I).

	X-ray	DFT
B1—O1	1.352 (2)	1.36
B1—O2	1.359 (2)	1.37
B1—C1	1.562 (3)	1.56
O3—C5	1.223 (2)	1.21
O4—C1	1.373 (2)	1.38
O4—C4	1.374 (2)	1.37
C1—C2	1.372 (2)	1.38
C2—C3	1.429 (2)	1.44
C2—C5	1.452 (2)	1.47
C3—C4	1.342 (2)	1.36
O1—B1—O2	121.3 (2)	119.9
O1—B1—C1	117.0 (2)	119.0
O2—B1—C1	121.8 (2)	121.1
C1—O4—C4	107.5 (1)	108.0
C2—C1—O4	108.2 (1)	108.3
C2—C1—B1	135.0 (1)	136.1
O4—C1—B1	116.9 (1)	115.7
C1—C2—C3	107.6 (1)	107.2
C1—C2—C5	125.0 (2)	126.6
C3—C2—C5	127.3 (2)	126.2
C4—C3—C2	106.0 (2)	106.0
C3—C4—O4	110.7 (1)	110.6
O3—C5—C2	123.2 (2)	123.0
O1—B1—C1—C2	4.4 (3)	0.0
O2—B1—C1—C2	−175.3 (2)	−180.0
O1—B1—C1—O4	−176.9 (2)	−180.0
O2—B1—C1—O4	3.4 (2)	0.0

H atoms were located in Fourier difference maps and refined isotropically; C—H = 0.95 (2)–1.02 (2) Å and O—H = 0.88 (3)–0.89 (3) Å. The molecular geometry of (I) was optimized at the DFT B3LYP/6-311+G** level of theory (Becke, 1993; Frisch *et al.*, 1998). All species corresponded to minima at the B3LYP/6-311+G** level with no imaginary frequencies.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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