

3-Formylphenylboronic acid

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Received 24 February 2004

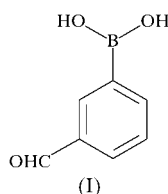
Accepted 19 March 2004

Online 21 April 2004

The molecule of the title compound, C₇H₇BO₃, is planar, and the bond lengths and angles are typical. The formyl group is essentially coplanar with the benzene ring but does not influence significantly the distortion of the ring, although the formyl group does have a strong influence on the crystal packing. The geometry of the boronic acid group is typical. In the crystal structure, the molecules are linked by O—H...O hydrogen bonds.

Comment

Arylboronic acids, which have been known for more than a hundred years, are again the object of interest because of their new applications. The most important synthetic application is Suzuki coupling, *i.e.* the palladium-catalysed reaction of aryl halides with arylboronic acids to form biphenyls (Miyaura & Suzuki, 1995). Another rapidly increasing field is the biological application of arylboronic acids. They are used in boron neutron capture therapy (BNCT; Soloway *et al.*, 1998), as enzyme inhibitors (Myung *et al.*, 2001) and as saccharide sensors (Wang *et al.*, 2002). Recent developments in the use of boronic acids as potential pharmaceutical agents were reviewed by Yang *et al.* (2003).



The crystal structures of several arylboronic acids have been reported. In the structure of phenylboronic acid (Rettig & Trotter, 1977), two independent molecules are linked by two intermolecular hydrogen bonds, forming a nearly planar dimeric molecule. This type of planar hydrogen-bonded dimeric structure is characteristic of many other substituted phenylboronic acids. However, the presence of substituents on the benzene ring can change the geometry of the molecule. For

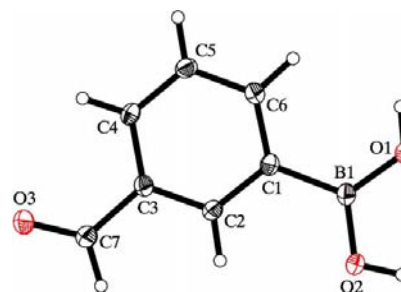


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

example, the formation of intramolecular hydrogen bonds is observed in 2-formylphenylboronic acid (Scouten *et al.*, 1994), but the presence of a nitro group in an *ortho* position forces the $-B(OH)_2$ group to lie perpendicular to the benzene ring (Soundararajan *et al.*, 1993). The aim of the present work is to investigate the influence of a formyl group in a *meta* position on the structure.

The molecular structure of the title compound, (I), is presented in Fig. 1. The molecule is planar. In most phenylboronic acids, the $-B(OH)_2$ group is twisted around the C—B bond (Gainsford *et al.*, 1995; Fronczek *et al.*, 2001; Ganguly *et al.*, 2003). The bond lengths and angles of the benzene ring in (I) (Table 1) are typical and in good agreement with the mean values found in other boron compounds (Rettig & Trotter, 1977; Shull *et al.*, 2000). It seems that the boronic acid group, as a result of its electron properties and characteristic hydrogen-bond shell, has a strong influence on the benzene-ring distortion (Fronczek *et al.*, 2001).

It is worth comparing the molecular structure of the title compound with those of its *ortho* and *para* isomers. Fronczek *et al.* (2001) reported a revised structure of 4-formylphenylboronic acid and Scouten *et al.* (1994) reported the structure of 2-formylphenylboronic acid. In these two compounds, the

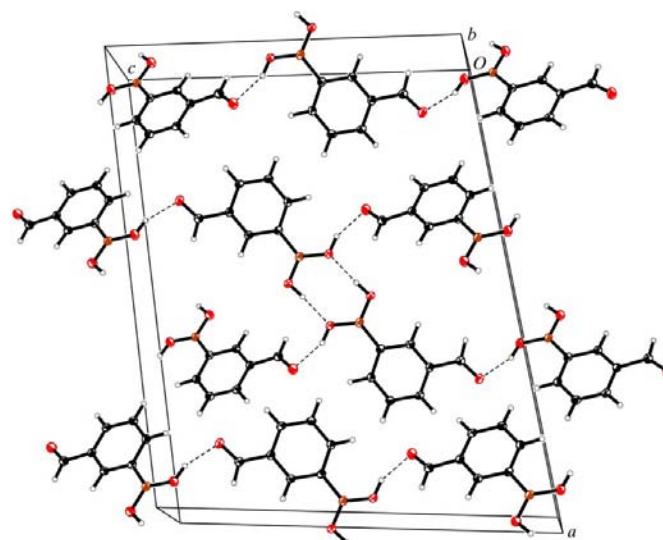


Figure 2

The crystal packing and hydrogen-bonding scheme of (I). Displacement ellipsoids are drawn at the 50% probability level.

formyl group is essentially coplanar with the phenyl ring, as it is in (I). The bond lengths of the formyl groups in the three molecules are in good agreement. The C7–C3–C4 angles for the *ortho*, *meta* and *para* isomers are 128.14, 121.4 (1) and 123.21 (19)°, respectively. The differences are caused by the dissimilarity of the hydrogen-bonding shell around the formyl O atom and the different steric environments (steric interactions between the formyl and boronic acid group in the *ortho* isomer). The position of the formyl group does not influence significantly the distortion of the benzene ring but does have a strong influence on the crystal packing.

The region of most interest is that of the boronic acid group. The geometry of this group is typical; in all of the aforementioned structures, the boronic acid group is effectively planar. The B–O bond lengths are slightly different [0.020 (2) Å]; this seems to be a characteristic property of this group of compounds. The geometry of the angles around the B atom is also typical. The angle that deviates most from 120° is that related to the O atom with a hydroxy H atom in a *syn* position relative to the benzene ring [123.1 (1)°]. Similar effects have been reported for 2-acetylphenylboronic acid monohydrate [123.35 (14)°; Ganguly *et al.*, 2003], *L-p*-boronophenylalanine (122.73°; Shull *et al.*, 2000) and phenylboronic acid (124.02°; Rettig & Trotter, 1977).

In the crystal structure of (I), the molecules are linked by O–H...O hydrogen bonds (Fig. 2 and Table 1), of which there are two types: one is formed between two boronic acid groups, causing dimerization, and the other is formed between formyl and boronic acid groups, linking the dimers to one another.

Experimental

3-Formylphenylboronic acid was purchased from Aldrich, crystallized from water and dried in air.

Crystal data

C ₇ H ₇ BO ₃	$D_x = 1.407 \text{ Mg m}^{-3}$
$M_r = 149.94$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 5047 reflections
$a = 22.635 (2) \text{ \AA}$	$\theta = 3.7\text{--}29.8^\circ$
$b = 3.7330 (3) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 17.126 (2) \text{ \AA}$	$T = 100.0 (1) \text{ K}$
$\beta = 102.054 (8)^\circ$	Irregular, colourless
$V = 1415.2 (2) \text{ \AA}^3$	$0.16 \times 0.15 \times 0.15 \text{ mm}$
$Z = 8$	

Data collection

Oxford Diffraction Xcalibur diffractometer	$R_{\text{int}} = 0.019$
ω scans	$\theta_{\text{max}} = 28.7^\circ$
4975 measured reflections	$h = -30 \rightarrow 19$
1795 independent reflections	$k = -5 \rightarrow 5$
1369 reflections with $I > 2\sigma(I)$	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1795 reflections	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
128 parameters	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

B1–O2	1.350 (2)	B1–O1	1.370 (1)
O2–B1–O1	118.2 (1)	C6–C1–B1	122.9 (1)
O2–B1–C1	118.7 (1)	C2–C3–C7	118.4 (1)
O1–B1–C1	123.1 (1)	C4–C3–C7	121.4 (1)
C6–C1–C2	117.1 (1)	O3–C7–C3	125.0 (1)
O2–B1–C1–C6	180.0 (1)	O1–B1–C1–C2	179.4 (1)
O1–B1–C1–C6	−0.3 (2)	C2–C3–C7–O3	178.2 (1)
O2–B1–C1–C2	−0.4 (2)	C4–C3–C7–O3	−0.4 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1–H11...O3 ⁱ	0.89 (2)	1.86 (2)	2.702 (1)	157 (2)
O2–H21...O1 ⁱⁱ	0.89 (2)	1.87 (2)	2.760 (1)	175 (2)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

The support of the Aldrich Chemical Co. Inc., Milwaukee, Wisconsin, through continuous donation of chemicals and equipment is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1046). Services for accessing these data are described at the back of the journal.

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