Space-group revision for 4-formylphenylboronic acid

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The space group of the title compound, $C_7H_7BO_3$, previously reported to be $P\bar{1}$, is properly Cc. There is no disorder of the formyl group or in the H atoms of the $B(OH)_2$ group. Molecules lie on approximate twofold axes and are related by approximate centers, which relate all but the formyl O atom and boronic acid H atoms. The B—O distances are 1.363 (2) and 1.370 (2) Å.

Comment

During the course of studying the structure and mechanism of formation of colored products in resorcinarene solutions (Davis *et al.*, 1999; Lewis *et al.*, 2000), the model compound (I) was investigated. Thermolysis of (I) led to the formation of the title compound, (II), and its structure was determined to ascertain its identity.
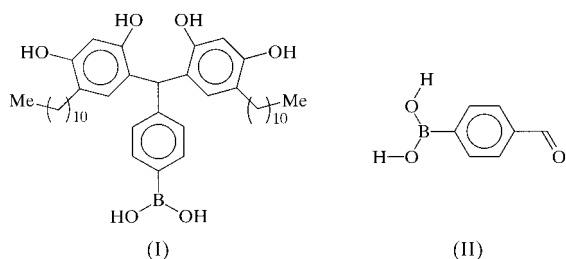
The published crystal structure of (II) (Feulner *et al.*, 1990) is in space group $P\bar{1}$ with $Z' = 1$ at 293 K, and has some unsettling features. In this model, the CHO group has a twofold disorder which superimposes its C—H and C=O bonds. The boronic acid H-atom positions are not sensible for the expected hydrogen bonding, and form impossibly short intermolecular H···H contacts. The model fits the data poorly ($R = 0.097$ and $wR = 0.181$), despite the fact that this compound forms high quality crystals. Furthermore, the triclinic cell can be transformed ($0\bar{1}\bar{1},01\bar{1},100$) to a C-centered cell with a monoclinic metric. Feulner *et al.* (1990) recognized this transformation, and attempted a structure solution in $C2/c$ with $Z' = \frac{1}{2}$. Their reported C-centered cell has dimensions $a = 11.177$ (5), $b = 9.891$ (4) and $c = 7.339$ (4) Å, and $\beta =$

118.37 (3)°. (Note: transformation of their triclinic cell yields $\beta = 119.11°$, which more closely matches our value.) Their model, deposited as the 'monoclinic form' (refcode VEXFUZ01) in the Cambridge Structural Database (Allen & Kennard, 1993) has the molecule on a twofold axis, which requires a similar disorder in the formyl group. This model produced worse R values ($R = 0.145$ and $wR = 0.151$). Despite intensity statistics suggesting a centrosymmetric structure, Feulner *et al.* (1990) also attempted structure solution in space group Cc, but were unsuccessful for reasons which are unclear.

Our structure of (II), with $Z' = 1$ in space group Cc (Fig. 1), exhibits none of these troubling features. The formyl group is ordered, and the H atoms of the $B(OH)_2$ group are ordered and in sensible positions for intermolecular hydrogen bonds (Table 2). The packing (Fig. 2) exhibits a pseudocenter near $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and a pseudo-twofold axis near $(\frac{1}{2},y,\frac{3}{4})$, running along the long axis of the molecule. The two molecules near the center of the cell are related by the c glide, and are approximately related by the pseudocenter. Treating the center as exact rather than the glide leads to the $P\bar{1}$ model, while treating both the center and the glide as exact leads to the $C2/c$ model. The cause of the disordered formyl group and boronic acid H atoms in the $P\bar{1}$ model can be seen in Fig. 2 by examination of the relative orientations of the two glide-related molecules about $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The formyl O and boronic acid H atoms do not conform to the inversion, while the remainder of the molecule nearly does. The pseudosymmetry does not lead to exceptionally high correlations, with the largest being 0.63, between displacement parameters of atoms related by the approximate twofold axis.

We have ruled out the possibility that a phase change on cooling causes the difference between the Cc structure which we observe at 120 K and that reported by Feulner *et al.* (1990) at room temperature. Using the same crystal, we collected intensity data at 296 K and obtained the same Cc structure, with cell dimensions $a = 11.1932$ (4), $b = 9.8820$ (5) and $c = 7.3373$ (3) Å, $\beta = 119.336$ (3)° and $R = 0.043$. Using this data set, we were also able to reproduce the results of Feulner *et al.* (1990), refining their $P\bar{1}$ model to $R = 0.099$.

The structure of the molecule itself is unremarkable. The formyl group is essentially coplanar with the phenyl ring, while the $B(OH)_2$ group is rotated by 20.6 (3)° out of the phenyl plane. One hydroxyl H atom is *syn* to the phenyl group, while the other is *anti*, as is typical for phenylboronic acids (Bradley *et al.*, 1996; Gainsford *et al.*, 1995; Pilkington *et al.*, 1995; Shull
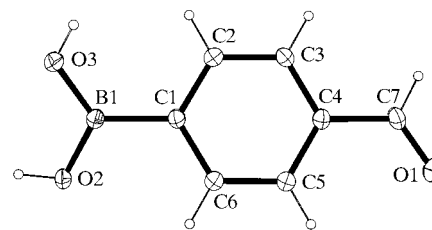

Figure 1
A view of the molecule of (II) with the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

organic compounds

et al., 2000; Soundararajan *et al.*, 1993), including unsubstituted phenylboronic acid (Rettig & Trotter, 1977) and the *ortho* isomer of the title compound (Scouten *et al.*, 1994).

Baur & Kassner (1992) and Marsh (1997) have warned of the perils of space group *Cc*. In the present structure, more
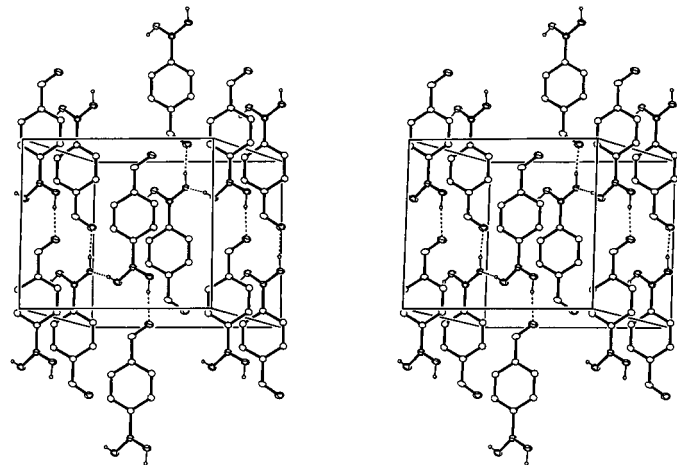

Figure 2
A stereoview of the unit cell of (II), illustrating the hydrogen bonding and pseudosymmetry. The *a* axis is horizontal and the *b* axis is vertical.

perilous is the imposition of centrosymmetry on the basis of centric intensity statistics. From our data, a chemically correct structure, albeit unnecessarily low symmetry, may be easily obtained in space group *P*1. However, no chemically correct model can be obtained in any centrosymmetric space group.

Experimental

The preparation of the title compound has been previously described by Feulner *et al.* (1990). In our preparation, compound (I) (300 mg, 0.448 mmol), dimethyl sulfoxide (DMSO, 27 ml), and water (3 ml) were mixed and heated for 5 d at 493 K in a sealed tube. The reaction mixture was cooled, filtered, and DMSO/H_2O was removed *in vacuo*. The yellowish substance obtained was washed with ethyl acetate (EtOAc) and upon drying afforded colorless crystals of the title compound (0.210 g) in 72% yield. Diffraction-quality crystals of (II) were grown by evaporation of an EtOAc solution.

Crystal data

$C_7H_7BO_3$	$D_x = 1.441$ Mg m^{-3}
$M_r = 149.94$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 1107
$a = 11.1238$ (3) Å	reflections
$b = 9.8718$ (3) Å	$\theta = 2.5$–$32.0°$
$c = 7.1988$ (2) Å	$\mu = 0.11$ mm^{-1}
$\beta = 119.071$ (2)°	$T = 120$ K
$V = 690.92$ (3) Å^3	Lath fragment, colorless
$Z = 4$	$0.37 \times 0.25 \times 0.22$ mm

Data collection

Nonius KappaCCD area-detector diffractometer (with an Oxford Cryosystems Cryostream cooler)	1110 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$
ω scans with κ offsets	$\theta_{max} = 32°$
4518 measured reflections	$h = -15 \rightarrow 16$
1192 independent reflections	$k = -14 \rightarrow 14$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 0.1001P]$
$wR(F^2) = 0.104$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1192 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
106 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.222 (2)	O3—B1	1.363 (2)
O2—B1	1.370 (2)	B1—C1	1.5724 (17)
O3—B1—O2	117.70 (11)	O2—B1—C1	118.21 (15)
O3—B1—C1	124.09 (16)	O1—C7—C4	123.21 (19)
O3—B1—C1—C2	−20.6 (3)	C5—C4—C7—O1	−1.8 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2O$\cdots$O1^i	0.87 (3)	1.86 (3)	2.7209 (16)	171 (3)
O3—H3O$\cdots$O2^{ii}	0.83 (3)	2.02 (3)	2.8321 (13)	165 (3)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

Systematic absences indicated space group *Cc* or *C*2/*c*. Although intensity statistics suggested *C*2/*c* ($|E^2 - 1| = 0.992$), the non-centrosymmetric space group *Cc* proved correct. The absolute structure could not be determined. The coordinates of the hydroxyl H atoms were refined. Other H atoms were treated as riding in idealized positions, with C—H distances of 0.95 Å. Displacement parameters for H atoms were assigned as $U_{iso} = 1.2U_{eq}$ of the attached atom (1.5 U_{eq} for hydroxy H atoms).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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