

2-Acetylphenylboronic acid monohydrate

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Key indicators

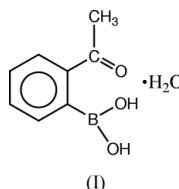
Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.034
 wR factor = 0.101
 Data-to-parameter ratio = 12.8

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

The title compound, $\text{C}_8\text{H}_9\text{BO}_3 \cdot \text{H}_2\text{O}$, displays extensive intermolecular hydrogen bonding of molecules of 2-acetylphenylboronic acid with each other and with molecules of water, producing infinite, two-dimensional molecular layers. There is no intramolecular hydrogen bonding between the *ortho* $\text{C}=\text{O}$ and $(\text{HO})_2\text{B}$ substituents.

Comment

We are investigating the hydrogen-bonding patterns and consequent stability of a series of *o*-substituted phenylboronic acids, which exhibit an intramolecular bonding pattern of the type $\text{B}-\text{O}-\text{H} \cdots \text{Y}$, where Y is any O, N or F atom of the *ortho*-substituent and is thereby capable of forming stable hydrogen-bonded intramolecular rings. In our search for phenylboronic acids with such substitution patterns, especially with *ortho* $\text{C}=\text{O}$ substitution, we found that, although the crystal structure and hydrogen-bonding pattern of 2-formylphenylboronic acid has been reported (Scouten *et al.*, 1994), no report of the crystal structure of the related 2-acetylphenylboronic acid has appeared. We now report the structure of 2-acetylphenylboronic acid monohydrate, (I), which we obtained on crystallization of 2-acetylphenylboronic acid from water. We shall subsequently report the structure of the anhydrous compound and compare it to that of the monohydrate, (I), as well as to that of anhydrous 2-formylphenylboronic acid reported by Scouten *et al.* (1994), to determine any differences in the pattern of hydrogen bonding.



The structure of (I) with its atom numbering is shown in Fig. 1. The plane formed by O1/B1/O2 is at an angle of $78.21 (16)^\circ$ to that of the phenyl-ring plane, while the C2/C7/O3/C8 plane is nearly coplanar with the phenyl ring, the dihedral angle being $7.75 (9)^\circ$. Other geometric values of interest are given in Table 1. As is readily apparent from Fig. 2, there is no intramolecular hydrogen bonding in (I), in contrast to the situation in the structure of anhydrous 2-formylphenylboronic acid (Scouten *et al.*, 1994), but there is an extensive system of intermolecular hydrogen bonding, producing infinite two-dimensional molecular sheets parallel to (100). Detailed hydrogen-bond geometry is given in Table 2. The carbonyl O atom of a molecule of (I) hydrogen bonds with one of the H

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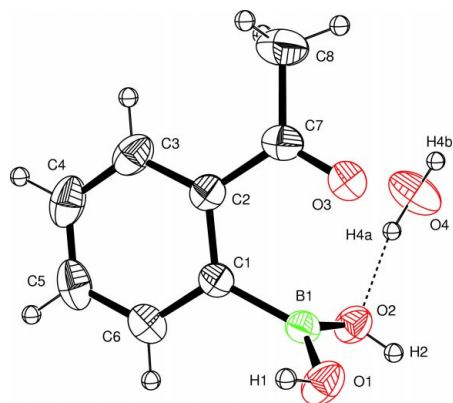


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probability level.

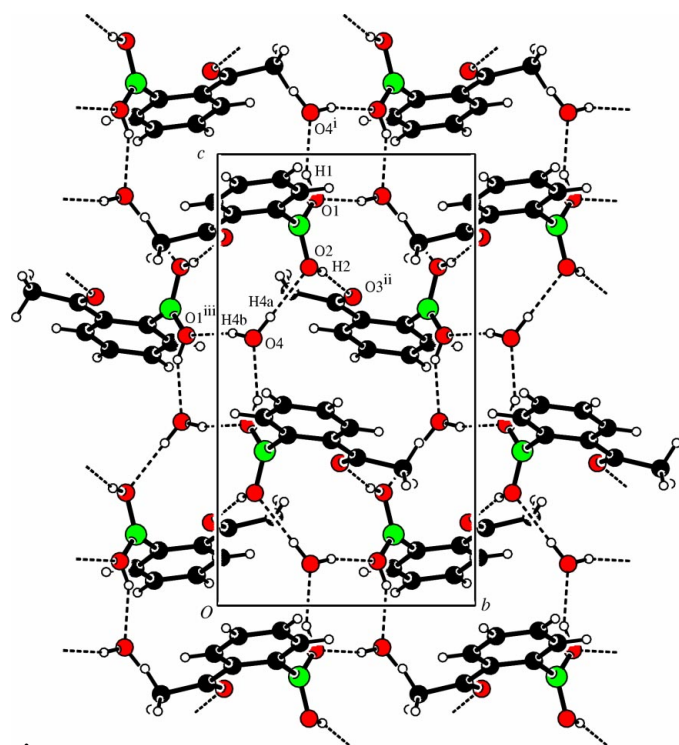


Figure 2
The molecular packing and hydrogen bonding in (I), viewed down the a^* axis. The structure is made up of infinite hydrogen-bonded sheets which are parallel to (100). [Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$.]

atoms of the $\text{B}(\text{OH})_2$ group of another molecule but not with water molecules, and there is no hydrogen bonding between the $\text{B}(\text{OH})_2$ groups themselves. The latter hydrogen bond extensively with water molecules and both are hydrogen-bond donors and acceptors. The absence of water in anhydrous crystalline 2-acetylphenylboronic acid will most likely produce an entirely different picture.

Experimental

Anhydrous 2-acetylphenylboronic acid, a powder melting at 441–443 K (decomposition), was purchased from COMBI-BLOCKS Inc. Very slow crystallization from an aqueous solution over a period of

several days afforded the title crystalline monohydrate, (I), used for this study. It melted slowly with decomposition between 361 and 366 K, becoming a viscous amber oil above 391 K, which partly became an amorphous solid at room temperature after several days. Scouten *et al.* (1994) reported that their 2-formylphenylboronic acid hydrate also melted over a similar range, 383–393 K, but resolidified at 398–403 K.

Crystal data

$\text{C}_8\text{H}_9\text{BO}_3 \cdot \text{H}_2\text{O}$
 $M_r = 181.98$
 Monoclinic, $P2_1/c$
 $a = 7.884$ (4) Å
 $b = 8.1279$ (17) Å
 $c = 14.500$ (3) Å
 $\beta = 100.47$ (2)°
 $V = 913.7$ (5) Å³
 $Z = 4$

$D_x = 1.323$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 25 reflections
 $\theta = 11.1$ – 11.3°
 $\mu = 0.10$ mm⁻¹
 $T = 296$ K
 Irregular fragment, colorless
 $0.46 \times 0.38 \times 0.38$ mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: none
 1745 measured reflections
 1621 independent reflections
 1229 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.007$

$\theta_{\text{max}} = 25.1^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 9$
 $l = -17 \rightarrow 16$
 3 standard reflections
 every 100 reflections
 intensity decay: 0.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.101$
 $S = 1.02$
 1621 reflections
 127 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.2641P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–B1	1.363 (2)	C1–B1	1.579 (2)
O2–B1	1.362 (2)	O3–C7	1.226 (2)
O2–B1–O1	118.28 (15)	O1–B1–C1	123.35 (14)
O2–B1–C1	117.48 (14)	O3–C7–C2	118.74 (14)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1–H1 \cdots O4 ⁱ	0.82	2.02	2.745 (2)	148
O2–H2 \cdots O3 ⁱⁱ	0.82	1.94	2.745 (2)	166
O4–H4a \cdots O2	0.86 (2)	2.00 (2)	2.854 (2)	170 (2)
O4–H4b \cdots O1 ⁱⁱⁱ	0.85 (2)	2.11 (2)	2.938 (2)	165 (2)

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

The atomic coordinates of the water H atoms were refined with fixed isotropic displacement values. The rotational orientations of the methyl and hydroxyl H atoms were refined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). All non-water H atoms were treated as riding, with C–H distances in the range 0.82–0.96 Å.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON*.

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