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4-Bromophenylboronic acid ethanol 0.04-solvate

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Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.049
wR factor = 0.149
Data-to-parameter ratio = 11.5

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

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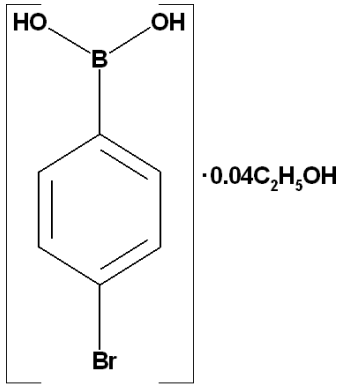
The title compound, $C_6H_6BBrO_2\cdot0.04C_2H_6O$, is known to show very high antibacterial activity in the family of aryl-substituted boronic acids. Individual molecules are interconnected by hydrogen bonding, resulting in an extended chain. These chains are held parallel by weak van der Waals forces.

Comment

Several boronic acids are known to inhibit bacterial growth through reversible transition state analog inhibitors that will form tetrahedral adducts with the active site serine of β-lactamases (Martin *et al.*, 1994).



(I)

Phenyl- and phenylethylboronic acids have been studied in order to understand their capacities to inhibit the RTEM-1 β-lactamase. In this regard, 3-bromophenylboronic acid (3-BPBA) and 4-bromophenylboronic acid (I) show superior inhibition properties. Owing to their interesting antibacterial properties, we previously investigated the crystal structures of the two compounds. Our results (Bhuvanesh *et al.*, 2005), obtained from micropowder X-ray diffraction studies using synchrotron X-rays indicated that the latter compound, as obtained from Aldrich, is the boroxine derivative of (I), *viz*. tris(4-bromophenyl)boroxine [or 2,4,6-tris(4′-bromophenyl)-1,3,4,2,4,6-trioxatriborane]. On the other hand, we found that 3-BPBA crystallizes in the monoclinic space group $P2_1/c$, and can be considered as a layered structure with individual 3-BPBA molecules linked through a hydrogen-bonded network to form two-dimensional sheets; the sheets are stacked along the a direction through weak van der Waals interactions. We expected that the crystal structure of (I) would consist of a hydrogen-bonded network similar to that of 3-BPBA, where all the individual molecules would be hydrogen bonded. However, in the structure reported by Zvonkova & Gluskova (1958) (hexagonal $P6/mcc$, with a = 28.730 Å, c = 9.740 Å and

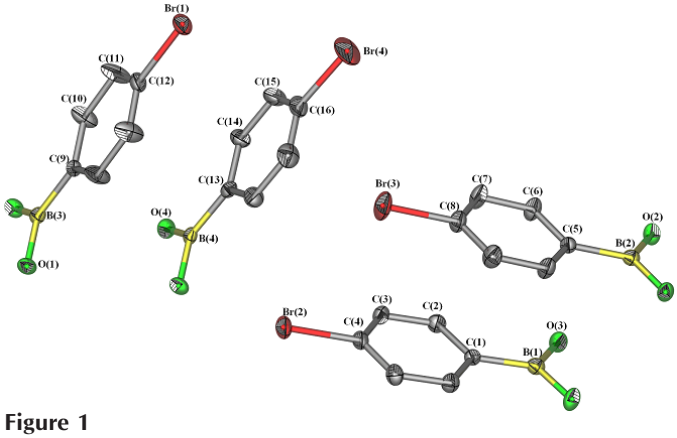


Figure 1
Displacement ellipsoid plot of (I), showing the four crystallographically independent molecules in the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. H atoms and ethanol molecules have been omitted for clarity.

$R = 0.24$) some of the molecules are discrete and not hydrogen bonded. This fact, along with the known pharmaceutical value of 4-BPBA, prompted us to redetermine the crystal structure.

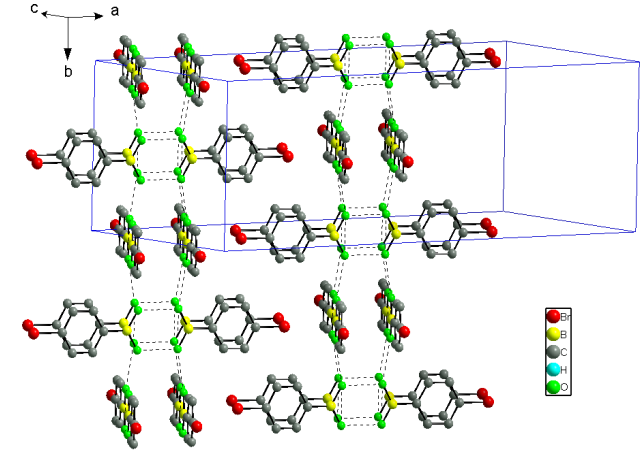
The title compound, (I) (Fig. 1), crystallizes, as expected, with an extended intermolecular hydrogen-bonding network similar to that of 3-BPBA; however, unlike the latter, the hydrogen bonding in (I) results in extended chains of interconnected molecules. The hydroxy groups (O1 and O2) of the BO_2 groups form pairs of individual molecules lying face-to-face, enabling hydrogen bonding (Fig. 2). These pairs of hydrogen-bonded molecules, in turn, form lateral hydrogen bonds with adjacent pairs lying perpendicular to each other, forming infinitely extended chains running along the *b* direction. In each chain, the $B(OH)_2$ groups point inwards, forming hydrogen bonds and terminated on the outside by the Br atoms; the chains are held parallel by weak van der Waals interactions (Fig. 2). The shortest Br···Br distance in the structure is 3.552 (4) Å. We found, after locating all the molecules of (I), a small amount of ethanol in the unit cell. The displacement parameters of the C and O atoms of the ethanol molecule were constrained to be the same to avoid divergence in their atom positions and displacement parameters.

Experimental

Hydrolysis of tris(4-bromophenyl)boroxine (0.5 g) (obtained as 4-bromophenylboronic acid from Aldrich) was carried out in dilute HBr (1 ml) in a 1:1 ethanol/water mixture (50 ml). The solution was heated to 333 K for 6 h and then cooled. Slow evaporation of the solution resulted in colorless single crystals of (I).

Crystal data

$C_6H_6BBrO_2·0.04C_2H_6O$
$M_r = 202.67$
Monoclinic, *C*2/*m*
$a = 29.1857$ (11) Å
$b = 9.8249$ (4) Å
$c = 12.0285$ (5) Å
$\beta = 101.902$ (2)°
$V = 3375.0$ (2) Å^3
$Z = 16$
$D_x = 1.595$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 5323 reflections
$\theta = 3.1$–58.5°
$\mu = 6.17$ mm^{-1}
$T = 110$ (2) K
Block, colorless
0.08 × 0.06 × 0.04 mm



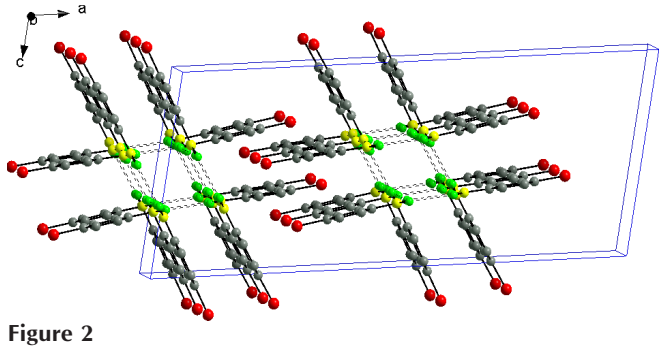


Figure 2
Packing of (I) along two different directions, showing intermolecular hydrogen bonding (dashed lines). H atoms and ethanol molecules are not shown.

Data collection

Bruker GADDS D8 Discover diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.638$, $T_{max} = 0.791$
15 334 measured reflections
2529 independent reflections
1953 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 58.9°$
$h = -32 \rightarrow 32$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.149$
$S = 1.05$
2529 reflections
219 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 7.7358P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

H atoms were constrained in the riding-model approximation, with C—H distances set at 0.95 Å. The hydroxy H atoms were constrained with the OH group *trans* to the longest bond to the adjacent atom, with O—H distances set at 0.85. U_{iso} values for the H atoms were set at $1.2U_{eq}$ of the parent atom. For the partially occupied ethanol molecule, H atoms were constrained in the riding-model approximation, with C—H distances set at 0.96 Å. The hydroxy H atoms were constrained with OH group *trans* to the longest bond to the adjacent atom, with O—H distances set at 0.85 Å. U_{iso} values for the H atoms were set at $1.2U_{eq}$ or $1.5U_{eq}$ of the parent atom. Since the diffraction quality of the larger crystals was not good, a small crystal was used for data collection. The highest electron-density peak is located at (0.2294, 0.0802, 0.1246).

Data collection: *FRAMBO* (Bruker–Nonius, 2003); cell refinement: *CELL-NOW* (Sheldrick, 2003) and *SAINT* (Bruker–Nonius, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2001); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2001); molecular graphics: *X-SEED* (Barbour, 1999) and *DIAMOND* (Brandenbourg, 2001); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2001) and *PLATON* (Spek, 2003) as incorporated in *WinGX* (Farrugia, 1999).

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