

Pentafluorophenylboronic acid

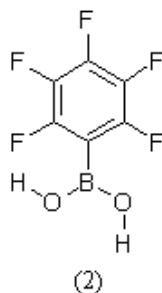
Peter N. Horton,^{a*}
Michael B. Hursthouse,^a
Michael A. Beckett^b and
Martin P. Rugen-Hankey^b^aSchool of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, England, and ^bChemistry Department, University of Wales, Bangor, LL57 2UW, Wales

Correspondence e-mail: pnh@soton.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.044
wR factor = 0.116
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Crystals of the title compound, $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$, were obtained from an attempted recrystallization of $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3 \cdot \text{Et}_3\text{PO}$ from THF/hexane solution. The central B atom of the boronic acid has a trigonal planar configuration with two hydroxyl groups and one pentafluorophenyl substituent.

Comment

There has been much recent interest in the chemistry of perfluoroarylboron compounds owing to their use as Lewis acid catalysts in organic transformations (Piers & Chivers, 1997; Ishihara & Yamamoto, 1999). We have recently explored the chemistry of phosphoryl donors towards $\text{B}(\text{C}_6\text{F}_5)_3$ (Beckett *et al.*, 2000, 2001) and are now examining the related boroxine, $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$. The adduct $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3 \cdot \text{Et}_3\text{PO}$, (1), is readily obtained from the stoichiometric reaction of Et_3PO with $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$ in THF solution. Compound (1), a colourless solid which gave satisfactory elemental analysis data, was characterized by IR and NMR spectroscopy. The strongly Lewis acidic nature of $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$ is reflected in the ^{31}P chemical shift of (1), which is considerably downfield of that of free Et_3PO (Mayer *et al.*, 1975). An attempted recrystallization of (1), by slow diffusion of hexane into a THF solution of the compound, afforded crystals of the title compound $(\text{C}_6\text{F}_5)\text{B}(\text{OH})_2$, (2). Presumably, (2) arose as a consequence of hydrolysis of (1), caused by H_2O in our recrystallization solvents. Compound (2) is well documented in the literature (Chambers & Chivers, 1965; Frohn *et al.*, 2002), but its crystal and molecular structure has not been previously reported.Crystallographic studies on compounds which contain a similar $(\text{C}_6\text{F}_5)\text{BO}_2$ motif are limited to the cyclic pentafluorophenylboronic acid ester of 2,3-dihydroxynaphthalene, $(\text{C}_6\text{F}_5)\text{BO}_2\text{C}_{10}\text{H}_6$ (Vagedes *et al.*, 1999) and the metallocycle $[\text{ZrCp}_2\{\mu\text{-O}_2\text{B}(\text{C}_6\text{F}_5)\}]_2$ (Balkwill *et al.*, 2002). The motif also appears in the borate anion of the salt $[\text{CpNi}(\text{C}_6\text{H}_6)\text{NiCp}][\text{B}_3\text{O}_3(\text{C}_6\text{F}_5)_3]$ (Priego *et al.*, 2000), in which there are B atoms with both trigonal and tetrahedral geometry. The cyclic trimeric borinic acid derivative $[\{(\text{C}_6\text{F}_5)_2\text{B}(\text{OH})\}_3]$ containsReceived 5 August 2004
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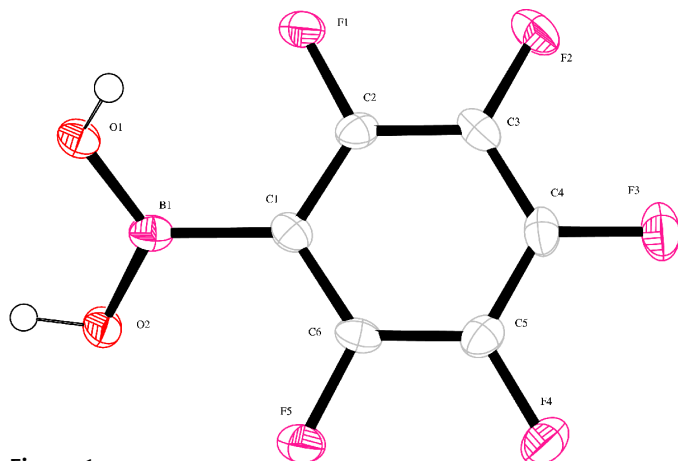


Figure 1
View of the structure of $(\text{C}_6\text{F}_5)\text{B}(\text{OH})_2$, showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

the $\text{C}_6\text{F}_5\text{BO}_2$ motif with tetrahedral boron (Beringhelli *et al.*, 2003).

B and C atoms are essentially trigonal planar and most of the B—O, B—C, and C—F bond lengths are unremarkable, with structural data for the $\text{C}_6\text{F}_5\text{BO}_2$ motif similar to those previously reported. Bond angles at B and C are consistent with sp^2 hybridization but with significant deviations from the expected 120° angles occurring in close proximity to the $\text{B}(\text{OH})_2$ substituent on C1. Thus the angles C6—C1—C2 [$115.31(16)^\circ$], F1—C2—C3 [$116.81(17)^\circ$] and F5—C6—C5 [$117.20(16)^\circ$] are significantly smaller than the other C—C—C and C—C—F angles respectively. The $\text{B}(\text{OH})_2$ group is twisted by $38.14(15)^\circ$ relative to the C_6F_5 group. The B—O distances are equivalent and average 1.359 \AA , consistent with relatively strong π -interactions and a bond order >1 (Beckett *et al.*, 1996). Conversely, the C1—B1 bond length [$1.579(3) \text{ \AA}$] is slightly greater than that typically found in boroxines *e.g.* $(4\text{-MeC}_6\text{H}_4)_3\text{B}_3\text{O}_3$, $1.543(4) \text{ \AA}$ (Beckett *et al.*, 1996), indicating a weakening of this bond by the electron-withdrawing C_6F_5 group. The H atoms were located and H—O—B angles and H—O distances average 113.3° and 0.855 \AA , respectively. Both H atoms are involved in hydrogen bonds, H2O in a hydrogen-bond dimer (equivalent to the carboxylic acid dimer) and H1O in an extended tape (see Fig. 2), which combine, giving a two-dimensional extended structure.

Experimental

To a stirred solution of $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$ (0.50 g, 0.86 mmol) in THF (25 cm^3) was added Et_3PO (0.12 g; 0.89 mmol). The reaction mixture was stirred at room temperature for 1 h. Removal of volatiles *in vacuo* afforded the adduct $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3 \cdot \text{Et}_3\text{PO}$, (1), a colourless solid (0.58 g; 94%). NMR ($\delta/\text{p.p.m.}$; $\text{C}_6\text{D}_6/\text{RT}$): ^1H (500.1 MHz): 1.4 (*q*, 6H, 3J 6.6 Hz), 0.7 (*t*, 9H, 3J 6.6 Hz); ^{31}P (202.4 MHz): +80.0; [$\Delta\delta = 39.0$ p.p.m., AN (acceptor number) = 86 (Mayer *et al.*, 1975)]. IR (KBr disc, $\eta_{\text{max}} \text{ cm}^{-1}$): 3385 (*m*), 2984 (*m*), 1649 (*s*), 1486 (*s*), 1340 (*s*), 1244 (*s*), 1100 (*s*), 976 (*s*), 935 (*m*), 781 (*m*). Elemental analysis (%) required for $\text{C}_{24}\text{H}_{15}\text{B}_3\text{F}_{15}\text{PO}_4$: C 40.3, H 2.1; Found: C, 40.2, H 2.0%. A few crystals of $(\text{C}_6\text{F}_5)\text{B}(\text{OH})_2$, (2), suitable for X-ray diffrac-

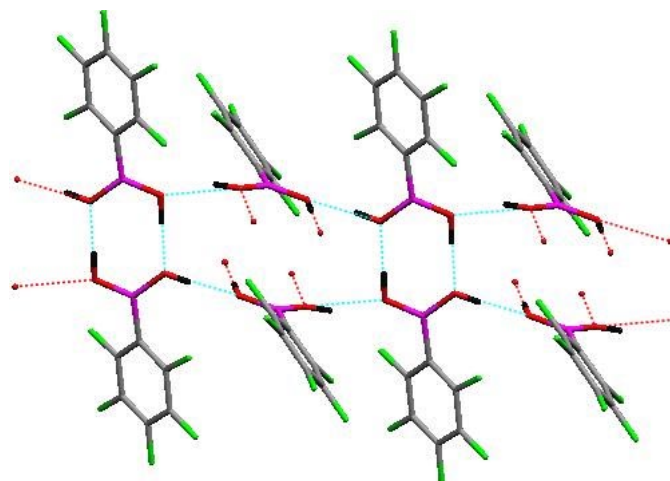


Figure 2
View showing hydrogen bonding (dashed lines).

tion, were grown by slow (14 days) diffusion of hexane into a THF solution of (1).

Crystal data

$\text{C}_6\text{H}_2\text{BF}_5\text{O}_2$
 $M_r = 211.89$
Monoclinic, $P2_1/c$
 $a = 12.6214(6) \text{ \AA}$
 $b = 6.2949(2) \text{ \AA}$
 $c = 9.3973(4) \text{ \AA}$
 $\beta = 98.254(2)^\circ$
 $V = 738.89(5) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.905 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1621 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 0.22 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
Plate, colourless
 $0.15 \times 0.08 \times 0.02 \text{ mm}$

Data collection

Nonius Kappa CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SORTAV; Blessing, 1997)
 $T_{\text{min}} = 0.968$, $T_{\text{max}} = 0.996$
5560 measured reflections

1692 independent reflections
1186 reflections with $>2\sigma(I)$
 $R_{\text{int}} = 0.070$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -16 \rightarrow 14$
 $k = -8 \rightarrow 6$
 $l = -10 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.116$
 $S = 1.03$
1692 reflections
135 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{O2---H2O}\cdots\text{O1}^{\text{i}}$	0.92 (3)	1.81 (3)	2.7326 (18)	176 (2)
$\text{O1---H1O}\cdots\text{O2}^{\text{ii}}$	0.82 (3)	1.99 (3)	2.7653 (19)	160 (2)

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

Data collection: COLLECT (Hoof, 1998) and DENZO (Otwinowski & Minor, 1997); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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