organic papers

Pentafluorophenylboronic acid

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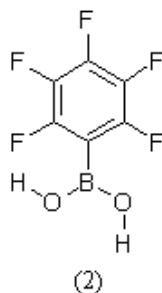
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Crystals of the title compound, $C_6F_5B(OH)_2$, were obtained from an attempted recrystallization of $(C_6F_5)_3B_3O_3 \cdot Et_3PO$ from THF/hexane solution. The central B atom of the boronic acid has a trigonal planar configuration with two hydroxyl groups and one pentafluorphenyl 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 $B(C_6F_5)_3$ (Beckett *et al.*, 2000, 2001) and are now examining the related boroxine, $(C_6F_5)_3B_3O_3$. The adduct $(C_6F_5)_3B_3O_3 \cdot Et_3PO$, (1), is readily obtained from the stoichiometric reaction of Et_3PO with $(C_6F_5)_3B_3O_3$ 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 $(C_6F_5)_3B_3O_3$ 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 $(C_6F_5)B(OH)_2$, (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.

(2)

Crystallographic studies on compounds which contain a similar $(C_6F_5)BO_2$ motif are limited to the cyclic pentafluorophenylboronic acid ester of 2,3-dihydroxynaphthalene, $(C_6F_5)BO_2C_{10}H_6$ (Vagedes *et al.*, 1999) and the metallocycle $[ZrCp_2\{\mu\text{-}O_2B(C_6F_5)\}]_2$ (Balkwill *et al.*, 2002). The motif also appears in the borate anion of the salt $[CpNi(C_6H_6)NiCp]$-$[B_3O_3(C_6F_5)_5]$ (Priego *et al.*, 2000), in which there are B atoms with both trigonal and tetrahedral geometry. The cyclic trimeric borinic acid derivative $[\{(C_6F_5)_2B(OH)\}_3]$ contains

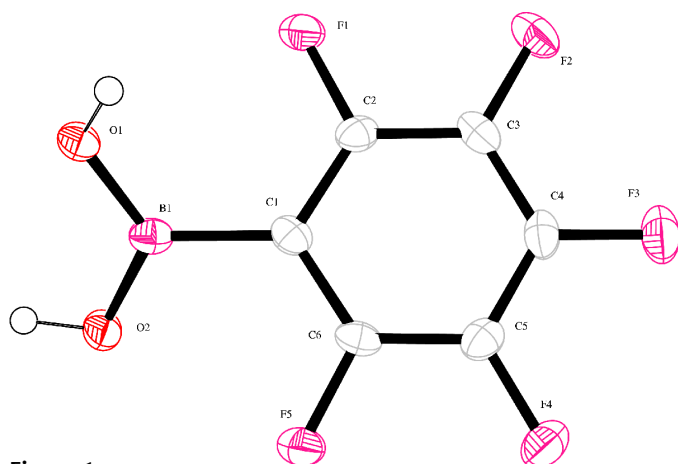**Figure 1**
View of the structure of $(C_6F_5)B(OH)_2$, showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2
View showing hydrogen bonding (dashed lines).

the $C_6F_5BO_2$ 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 $C_6F_5BO_2$ 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 $B(OH)_2$ substituent on C1. Thus the angles C6—C1—C2 [115.31 (16)°], F1—C2—C3 [116.81 (17)°] and F5—C6—C5 [117.20 (16)°] are significantly smaller than the other C—C—C and C—C—F angles respectively. The $B(OH)_2$ group is twisted by 38.14 (15)° relative to the C_6F_5 group. The B—O distances are equivalent and average 1.359 Å, consistent with relatively strong π-interactions and a bond order >1 (Beckett *et al.*, 1996). Conversely, the C1—B1 bond length [1.579 (3) Å] is slightly greater than that typically found in boroxines *e.g.* (4-$MeC_6H_4)_3B_3O_3$, 1.543 (4) Å (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 Å, 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 $(C_6F_5)_3B_3O_3$ (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 $(C_6F_5)_3B_3O_3\cdot Et_3PO$, (1), a colourless solid (0.58 g; 94%). NMR (δ/p.p.m.; C_6D_6/RT): ^{1}H (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, η_{max} 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 $C_{24}H_{15}B_3F_{15}PO_4$: C 40.3, H 2.1; Found: C, 40.2, H 2.0%. A few crystals of $C_6F_5B(OH)_2$, (2), suitable for X-ray diffrac-

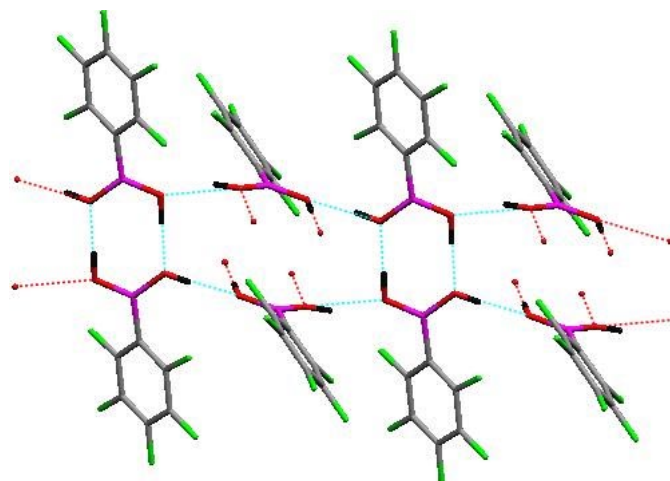tion, were grown by slow (14 days) diffusion of hexane into a THF solution of (1).

Crystal data

$C_6H_2BF_5O_2$	$D_x = 1.905$ Mg m^{-3}
$M_r = 211.89$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1621
$a = 12.6214$ (6) Å	reflections
$b = 6.2949$ (2) Å	$\theta = 2.9$–27.5°
$c = 9.3973$ (4) Å	$\mu = 0.22$ mm^{-1}
$\beta = 98.254$ (2)°	$T = 120$ (2) K
$V = 738.89$ (5) Å^3	Plate, colourless
$Z = 4$	$0.15 \times 0.08 \times 0.02$ mm

Data collection

Nonius Kappa CCD area-detector diffractometer	1692 independent reflections
φ and ω scans	1186 reflections with $>2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.070$
(*SORTAV*; Blessing, 1997)	$\theta_{max} = 27.5°$
$T_{min} = 0.968$, $T_{max} = 0.996$	$h = -16 \rightarrow 14$
5560 measured reflections	$k = -8 \rightarrow 6$
	$l = -10 \rightarrow 12$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
1692 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
135 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
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	0.92 (3)	1.81 (3)	2.7326 (18)	176 (2)
O1—H1O$\cdots$O2^{ii}	0.82 (3)	1.99 (3)	2.7653 (19)	160 (2)

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

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supporting information

Pentafluorophenylboronic acid

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Pentafluoroboronic acid

Crystal data

$C_6H_2BF_5O_2$	$F(000) = 416$
$M_r = 211.89$	$D_x = 1.905$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.6214$ (6) Å	Cell parameters from 1621 reflections
$b = 6.2949$ (2) Å	$\theta = 2.9$–27.5°
$c = 9.3973$ (4) Å	$\mu = 0.22$ mm^{-1}
$\beta = 98.254$ (2)°	$T = 120$ K
$V = 738.89$ (5) Å^3	Plate, colourless
$Z = 4$	$0.15 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD Area Detector diffractometer	5560 measured reflections
Radiation source: Nonius FR591 rotating anode	1692 independent reflections
Graphite monochromator	1186 reflections with $I > 2\sigma(I)$
Detector resolution: 9.091 pixels mm^{-1}	$R_{int} = 0.070$
φ and ω scans to fill Ewald Sphere	$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
Absorption correction: multi-scan (SORTAV; Blessing 1997)	$h = -16 \rightarrow 14$
	$k = -8 \rightarrow 6$
$T_{min} = 0.968$, $T_{max} = 0.996$	$l = -10 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.116$	All H-atom parameters refined
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
1692 reflections	where $P = (F_o^2 + 2F_c^2)/3$
135 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

Experimental. PLEASE NOTE cell_measurement_ fields are not relevant to area detector data, the entire data set is used to refine the cell, which is indexed from all observed reflections in a 10 degree phi range.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.20469 (15)	−0.1065 (3)	−0.0334 (2)	0.0205 (4)
C2	0.28746 (15)	−0.1513 (3)	−0.1108 (2)	0.0215 (4)
C3	0.37112 (14)	−0.0124 (3)	−0.12031 (19)	0.0233 (4)
C4	0.37121 (15)	0.1827 (3)	−0.0553 (2)	0.0244 (5)
C5	0.28903 (15)	0.2369 (3)	0.0197 (2)	0.0232 (4)
C6	0.20904 (15)	0.0925 (3)	0.03115 (19)	0.0212 (4)
B1	0.11484 (17)	−0.2747 (3)	−0.0150 (2)	0.0208 (5)
O1	0.07353 (11)	−0.4073 (2)	−0.12348 (16)	0.0236 (3)
O2	0.07956 (11)	−0.2880 (2)	0.11424 (13)	0.0248 (3)
F1	0.29011 (9)	−0.33900 (16)	−0.17951 (12)	0.0257 (3)
F2	0.45090 (9)	−0.06577 (18)	−0.19359 (13)	0.0314 (3)
F3	0.45065 (10)	0.31949 (18)	−0.06461 (13)	0.0352 (3)
F4	0.28823 (10)	0.42794 (16)	0.08323 (12)	0.0308 (3)
F5	0.13194 (9)	0.15083 (17)	0.10926 (12)	0.0276 (3)
H1O	0.086 (2)	−0.374 (4)	−0.204 (3)	0.041 (7)*
H2O	0.029 (2)	−0.394 (4)	0.115 (3)	0.044 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0227 (10)	0.0246 (9)	0.0144 (9)	0.0001 (7)	0.0036 (8)	0.0033 (7)
C2	0.0292 (11)	0.0193 (9)	0.0160 (9)	0.0005 (7)	0.0036 (8)	0.0003 (7)
C3	0.0185 (10)	0.0335 (10)	0.0185 (10)	0.0014 (7)	0.0043 (8)	0.0041 (8)
C4	0.0245 (11)	0.0272 (10)	0.0208 (10)	−0.0083 (8)	0.0010 (8)	0.0045 (8)
C5	0.0307 (11)	0.0208 (9)	0.0175 (9)	−0.0017 (7)	0.0009 (8)	0.0000 (7)
C6	0.0248 (10)	0.0255 (9)	0.0141 (10)	0.0035 (7)	0.0059 (8)	0.0001 (7)
B1	0.0243 (12)	0.0214 (10)	0.0172 (11)	0.0021 (8)	0.0046 (9)	−0.0007 (8)
O1	0.0282 (8)	0.0288 (7)	0.0150 (8)	−0.0054 (5)	0.0071 (6)	−0.0002 (6)
O2	0.0281 (8)	0.0303 (8)	0.0170 (7)	−0.0084 (6)	0.0071 (6)	−0.0024 (5)
F1	0.0301 (7)	0.0247 (6)	0.0236 (6)	0.0011 (4)	0.0087 (5)	−0.0038 (4)
F2	0.0232 (6)	0.0430 (7)	0.0304 (7)	0.0010 (5)	0.0119 (5)	0.0006 (5)
F3	0.0327 (7)	0.0363 (7)	0.0370 (7)	−0.0142 (5)	0.0063 (5)	0.0037 (5)
F4	0.0447 (7)	0.0217 (6)	0.0257 (7)	−0.0057 (5)	0.0041 (6)	−0.0034 (4)
F5	0.0328 (7)	0.0261 (6)	0.0263 (7)	0.0005 (5)	0.0123 (5)	−0.0040 (4)

Geometric parameters (Å, º)

C1—C2	1.385 (3)	C4—C5	1.378 (3)
C1—C6	1.389 (3)	C5—F4	1.343 (2)
C1—B1	1.579 (3)	C5—C6	1.374 (3)
C2—F1	1.349 (2)	C6—F5	1.351 (2)
C2—C3	1.384 (3)	B1—O2	1.355 (3)
C3—F2	1.342 (2)	B1—O1	1.362 (2)
C3—C4	1.372 (3)	O1—H1O	0.82 (3)
C4—F3	1.334 (2)	O2—H2O	0.92 (3)
C2—C1—C6	115.31 (16)	F4—C5—C6	120.34 (17)
C2—C1—B1	121.92 (16)	F4—C5—C4	120.20 (16)
C6—C1—B1	122.73 (17)	C6—C5—C4	119.45 (17)
F1—C2—C3	116.81 (17)	F5—C6—C5	117.20 (16)
F1—C2—C1	120.14 (16)	F5—C6—C1	119.74 (16)
C3—C2—C1	123.04 (17)	C5—C6—C1	123.07 (17)
F2—C3—C4	120.00 (17)	O2—B1—O1	119.55 (18)
F2—C3—C2	120.72 (17)	O2—B1—C1	118.24 (17)
C4—C3—C2	119.28 (17)	O1—B1—C1	122.20 (18)
F3—C4—C3	120.10 (17)	B1—O1—H1O	115.6 (18)
F3—C4—C5	120.11 (16)	B1—O2—H2O	111.4 (16)
C3—C4—C5	119.79 (16)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1[i]	0.92 (3)	1.81 (3)	2.7326 (18)	176 (2)
O1—H1O···O2[ii]	0.82 (3)	1.99 (3)	2.7653 (19)	160 (2)

Symmetry codes: (i) −*x*, −*y*−1, −*z*; (ii) *x*, −*y*−1/2, *z*−1/2.