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4-Bromoanilinium hexafluorophosphate monohydrate

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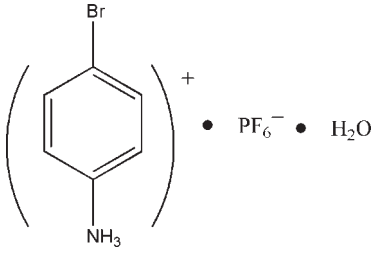
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; disorder in solvent or counterion; R factor = 0.051; wR factor = 0.143; data-to-parameter ratio = 13.7.

In the title compound, $C_6H_7BrN^+\cdot PF_6^-\cdot H_2O$, N—H···F, N—H···O and O—H···F hydrogen-bonding interactions stabilize the crystal structure and give rise to to chains running parallel to the c axis. In the anion, four of the F atoms are disordered over two sets of sites of equal occupancy.

Related literature

The title compound was synthesized as part of our group's search for ferroelectric compounds, which usually have a phase transition. For background to phase transition materials, see: Li *et al.* (2008); Zhang *et al.* (2009).



Experimental

Crystal data

$C_6H_7BrN^+\cdot PF_6^-\cdot H_2O$
M_r = 336.02
Monoclinic, $P2_1/c$
a = 14.646 (8) Å
b = 5.075 (3) Å
c = 15.314 (8) Å
β = 94.697 (11)°
V = 1134.5 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.82 mm^{-1}
T = 298 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.465, T_{max} = 0.484
11563 measured reflections
2584 independent reflections
1949 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.143
S = 1.05
2584 reflections
189 parameters
24 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···F6	0.89	2.59	3.13 (3)	120
N1—H1C···O1W	0.89	2.24	2.891 (5)	130
N1—H1A···F2^{i}	0.89	2.15	3.02 (2)	168
N1—H1B···O1W^{ii}	0.89	2.42	2.905 (5)	115
N1—H1B···F4^{iii}	0.89	2.45	3.252 (5)	149
N1—H1C···F5^{iv}	0.89	2.51	3.04 (2)	119
O1W—H1WB···F6^{v}	0.75 (7)	2.34 (8)	3.00 (3)	148 (6)
O1W—H1WB···F1^{v}	0.75 (7)	2.48 (7)	3.062 (5)	136 (6)
O1W—H1WA···F5^{vi}	0.62 (7)	2.36 (7)	2.92 (2)	151 (7)

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

The authors are grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2158).

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supporting information

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4-Bromoanilinium hexafluorophosphate monohydrate

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S1. Comment

As a continuation of our study of phase transition materials, including organic ligands (Li *et al.*, 2008), metal-organic coordination compounds (Zhang *et al.*, 2009), organic-inorganic hybrids, we studied the dielectric properties of the title compound, unfortunately, there was no distinct anomaly observed from 93 K to 350 K,suggesting that this compound should be not a real ferroelectrics or there may be no distinct phase transition occurred within the measured temperature range. In this article, the crystal structure of (I) has been presented.

The asymmetric unit of the title compound is made up of a almost coplanar 4-bromoanilimium cation with the mean deviation from the plan of 0.013 Å, a hexafluorophosphate anion disordered intwo orientations with site-occupancy factors of 0.7365 and 0.2635, and a water molecule. The chains of the molecular arrangement in the crystal structure is mainly determined by relatively strong and directional N—H···F, N—H···O and O—H···F hydrogen bonds (Table 1), and to a lesser degree by a π-π packing interaction between the adjacent aromatic rings, where the interplanar spacing is 5.855 (4) Å.

S2. Experimental

Single crystals of 4-bromoanilimium hexafluorophosphate monohydrate were prepared by slow evaporation at room temperature of an ethanol solution of equal molar 4-bromobenzenamine and hexafluorophosphoric acid.

S3. Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C and N atoms to which they are bonded, with U_{iso}(H) = 1.2U$_{eq}$(C),

U_{iso}(H) = 1.2U$_{eq}$(N).

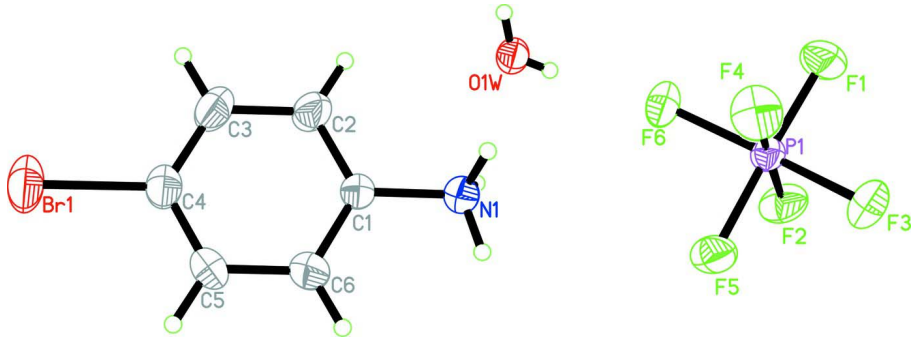

Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and all H atoms have been omitted for clarity.

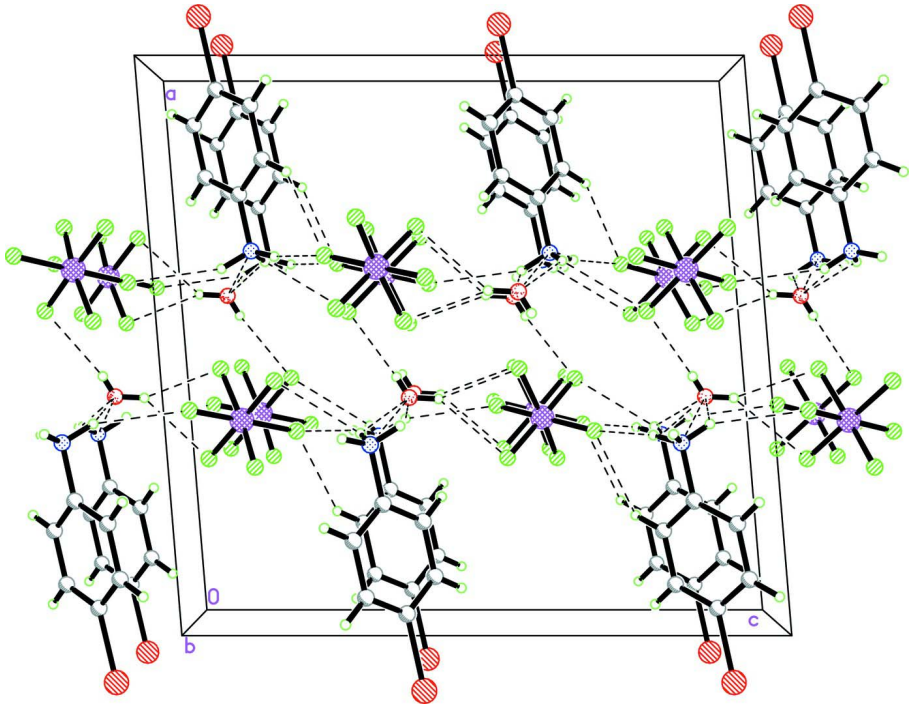

Figure 2

A view of the packing of the title compound, stacking along the *b* axis. Dashed lines indicate hydrogen bonds.

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$V = 1134.5\ (10)$ Å^3
$Z = 4$
$F(000) = 656$
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Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2551 reflections
$\theta = 3.7–27.5°$
$\mu = 3.82$ mm^{-1}
$T = 298$ K
Prism, colorless
0.20 × 0.20 × 0.20 mm

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Rigaku SCXmini diffractometer
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Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.465$, $T_{max} = 0.484$
11563 measured reflections
2584 independent reflections
1949 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.1°$
$h = -18\rightarrow18$
$k = -6\rightarrow6$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.143$
$S = 1.05$
2584 reflections
189 parameters
24 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 0.7365P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}	Occ. (<1)
Br1	−0.07352 (3)	0.12750 (14)	0.89407 (4)	0.0887 (3)	
C1	0.2358 (2)	0.1568 (7)	0.8526 (2)	0.0410 (8)	
C2	0.2022 (3)	0.3220 (9)	0.9125 (3)	0.0690 (13)	
H2A	0.2410	0.4372	0.9449	0.083*	
C3	0.1092 (4)	0.3161 (11)	0.9246 (4)	0.0780 (15)	
H3A	0.0850	0.4279	0.9650	0.094*	
C4	0.0536 (3)	0.1443 (9)	0.8766 (3)	0.0564 (10)	
C5	0.0873 (3)	−0.0174 (13)	0.8167 (4)	0.0836 (16)	
H5A	0.0485	−0.1317	0.7840	0.100*	
C6	0.1802 (3)	−0.0121 (11)	0.8043 (4)	0.0770 (15)	
H6A	0.2041	−0.1228	0.7634	0.092*	
N1	0.3347 (2)	0.1574 (6)	0.8399 (2)	0.0449 (7)	
H1A	0.3460	0.0403	0.7989	0.067*	
H1B	0.3664	0.1151	0.8900	0.067*	
H1C	0.3513	0.3171	0.8231	0.067*	
O1W	0.4090 (2)	0.6558 (6)	0.9035 (3)	0.0497 (7)	
H1WB	0.407 (5)	0.646 (12)	0.952 (5)	0.10 (3)*	
H1WA	0.445 (5)	0.652 (12)	0.885 (4)	0.09 (3)*	
P1	0.62950 (6)	0.0473 (2)	0.87429 (6)	0.0426 (3)	
F1	0.69905 (19)	0.2001 (6)	0.94031 (19)	0.0747 (8)	
F2	0.6508 (16)	0.215 (4)	0.7908 (13)	0.069 (3)	0.50
F3	0.706 (2)	−0.161 (5)	0.852 (2)	0.067 (4)	0.50
F4	0.6103 (2)	−0.1569 (5)	0.95004 (19)	0.0753 (8)	
F5	0.5602 (14)	−0.141 (7)	0.8100 (14)	0.066 (5)	0.50

F6	0.541 (2)	0.203 (7)	0.908 (2)	0.065 (5)	0.50
F3′	0.7131 (19)	−0.097 (5)	0.8358 (18)	0.071 (5)	0.50
F6′	0.554 (2)	0.239 (7)	0.900 (2)	0.073 (6)	0.50
F2′	0.6400 (18)	0.284 (4)	0.8075 (12)	0.073 (3)	0.50
F5′	0.5575 (14)	−0.078 (7)	0.8065 (14)	0.071 (6)	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0451 (3)	0.1472 (7)	0.0747 (4)	0.0010 (3)	0.0107 (2)	0.0271 (3)
C1	0.0418 (18)	0.0409 (19)	0.0404 (18)	0.0011 (15)	0.0029 (14)	0.0040 (15)
C2	0.063 (3)	0.069 (3)	0.079 (3)	−0.017 (2)	0.025 (2)	−0.029 (2)
C3	0.064 (3)	0.087 (4)	0.087 (4)	−0.001 (3)	0.031 (3)	−0.026 (3)
C4	0.044 (2)	0.079 (3)	0.046 (2)	0.004 (2)	0.0037 (17)	0.017 (2)
C5	0.047 (2)	0.117 (4)	0.086 (3)	−0.016 (3)	0.000 (2)	−0.039 (3)
C6	0.054 (3)	0.094 (4)	0.082 (3)	−0.003 (3)	0.001 (2)	−0.041 (3)
N1	0.0452 (16)	0.0415 (16)	0.0483 (17)	−0.0010 (13)	0.0057 (13)	0.0024 (14)
O1W	0.0439 (16)	0.0496 (17)	0.056 (2)	−0.0011 (13)	0.0094 (14)	−0.0043 (14)
P1	0.0394 (5)	0.0469 (5)	0.0426 (5)	−0.0052 (4)	0.0087 (4)	−0.0044 (4)
F1	0.0653 (16)	0.0864 (18)	0.0714 (17)	−0.0209 (14)	−0.0014 (13)	−0.0273 (15)
F2	0.085 (6)	0.075 (10)	0.051 (6)	−0.017 (6)	0.028 (4)	−0.002 (5)
F3	0.062 (8)	0.063 (9)	0.079 (8)	0.011 (6)	0.026 (5)	−0.006 (5)
F4	0.0805 (19)	0.0728 (17)	0.0732 (18)	−0.0039 (14)	0.0106 (14)	0.0252 (14)
F5	0.065 (5)	0.073 (13)	0.064 (5)	−0.030 (5)	0.021 (5)	−0.023 (5)
F6	0.045 (5)	0.077 (10)	0.075 (7)	0.008 (5)	0.018 (5)	−0.005 (7)
F3′	0.045 (4)	0.086 (13)	0.085 (11)	−0.005 (7)	0.026 (6)	−0.027 (8)
F6′	0.066 (11)	0.064 (8)	0.093 (9)	0.026 (9)	0.024 (7)	0.007 (5)
F2′	0.109 (8)	0.059 (8)	0.054 (7)	−0.013 (6)	0.027 (5)	0.007 (5)
F5′	0.060 (5)	0.077 (14)	0.072 (5)	−0.024 (5)	−0.015 (5)	−0.017 (5)

Geometric parameters (Å, º)

Br1—C4	1.904 (4)	N1—H1C	0.8900
C1—C6	1.359 (6)	O1W—H1WB	0.75 (7)
C1—C2	1.364 (6)	O1W—H1WA	0.62 (7)
C1—N1	1.477 (5)	P1—F6′	1.55 (3)
C2—C3	1.390 (7)	P1—F5′	1.55 (2)
C2—H2A	0.9300	P1—F3′	1.58 (3)
C3—C4	1.366 (7)	P1—F1	1.579 (3)
C3—H3A	0.9300	P1—F2′	1.59 (2)
C4—C5	1.353 (7)	P1—F2	1.59 (2)
C5—C6	1.390 (7)	P1—F4	1.597 (3)
C5—H5A	0.9300	P1—F3	1.60 (3)
C6—H6A	0.9300	P1—F6	1.64 (3)
N1—H1A	0.8900	P1—F5	1.66 (2)
N1—H1B	0.8900		
C6—C1—C2	121.4 (4)	F6′—P1—F2	93.1 (15)

C6—C1—N1	118.6 (4)	F5′—P1—F2	81.3 (13)
C2—C1—N1	120.0 (3)	F3′—P1—F2	75.0 (10)
C1—C2—C3	119.2 (4)	F1—P1—F2	95.3 (8)
C1—C2—H2A	120.4	F2′—P1—F2	16.8 (8)
C3—C2—H2A	120.4	F6′—P1—F4	93.1 (14)
C4—C3—C2	119.3 (4)	F5′—P1—F4	94.1 (11)
C4—C3—H3A	120.3	F3′—P1—F4	99.0 (8)
C2—C3—H3A	120.3	F1—P1—F4	89.78 (17)
C5—C4—C3	121.1 (4)	F2′—P1—F4	170.9 (5)
C5—C4—Br1	118.9 (4)	F2—P1—F4	172.1 (5)
C3—C4—Br1	119.9 (3)	F6′—P1—F3	177.2 (16)
C4—C5—C6	119.8 (4)	F5′—P1—F3	92.0 (16)
C4—C5—H5A	120.1	F3′—P1—F3	15.2 (13)
C6—C5—H5A	120.1	F1—P1—F3	92.0 (12)
C1—C6—C5	119.1 (4)	F2′—P1—F3	104.6 (9)
C1—C6—H6A	120.4	F2—P1—F3	89.6 (10)
C5—C6—H6A	120.4	F4—P1—F3	84.1 (7)
C1—N1—H1A	109.5	F6′—P1—F6	10 (3)
C1—N1—H1B	109.5	F5′—P1—F6	84.2 (15)
H1A—N1—H1B	109.5	F3′—P1—F6	176.7 (16)
C1—N1—H1C	109.5	F1—P1—F6	92.5 (11)
H1A—N1—H1C	109.5	F2′—P1—F6	87.8 (15)
H1B—N1—H1C	109.5	F2—P1—F6	102.1 (15)
H1WB—O1W—H1WA	124 (8)	F4—P1—F6	83.7 (13)
F6′—P1—F5′	87.9 (17)	F3—P1—F6	167.0 (15)
F6′—P1—F3′	167.6 (15)	F6′—P1—F5	95.4 (16)
F5′—P1—F3′	93.7 (15)	F5′—P1—F5	11 (2)
F6′—P1—F1	88.2 (14)	F3′—P1—F5	88.1 (14)
F5′—P1—F1	174.7 (13)	F1—P1—F5	174.3 (12)
F3′—P1—F1	89.3 (11)	F2′—P1—F5	97.9 (13)
F6′—P1—F2′	78.2 (15)	F2—P1—F5	89.0 (12)
F5′—P1—F2′	88.5 (15)	F4—P1—F5	85.6 (10)
F3′—P1—F2′	89.5 (10)	F3—P1—F5	84.2 (15)
F1—P1—F2′	87.2 (9)	F6—P1—F5	90.3 (14)
C6—C1—C2—C3	0.3 (8)	C3—C4—C5—C6	0.8 (9)
N1—C1—C2—C3	−179.0 (4)	Br1—C4—C5—C6	−178.7 (5)
C1—C2—C3—C4	0.3 (8)	C2—C1—C6—C5	−0.4 (8)
C2—C3—C4—C5	−0.9 (8)	N1—C1—C6—C5	179.0 (5)
C2—C3—C4—Br1	178.6 (4)	C4—C5—C6—C1	−0.1 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···F6	0.89	2.59	3.13 (3)	120
N1—H1*C*···O1*W*	0.89	2.24	2.891 (5)	130
N1—H1*A*···F2^{i}	0.89	2.15	3.02 (2)	168
N1—H1*B*···O1*W*^{ii}	0.89	2.42	2.905 (5)	115

N1—H1*B*···F4^{iii}	0.89	2.45	3.252 (5)	149
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O1*W*—H1*WB*···F6^{v}	0.75 (7)	2.34 (8)	3.00 (3)	148 (6)
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O1*W*—H1*WA*···F5^{vi}	0.62 (7)	2.36 (7)	2.92 (2)	151 (7)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) *x*, *y*−1, *z*; (iii) −*x*+1, −*y*, −*z*+2; (iv) −*x*+1, *y*+1/2, −*z*+3/2; (v) −*x*+1, −*y*+1, −*z*+2; (vi) *x*, *y*+1, *z*.