1,1′-(p-Phenylenedimethylene)-dipyridinium bis(hexafluoridophosphate)

Munirah Sufiyah Abdul Rahim, Yatimah Alias and Seik Weng Ng*

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: seikweng@um.edu.my

The title salt, $C_{18}H_{18}N_2^{2+}\cdot 2PF_6^-$, exists as non-interacting cations and anions. In the cation, the pyridine and phenylene rings are aligned at 62.9 (1)°; the pyridine ring lies on a special position of m site symmetry and the phenylene ring on a special position of $2/m$ site symmetry. The angle at the methylene C atom is 112.8 (1)°. The anion lies on a special position of m site symmetry; four F atoms lie on this mirror plane.

Related literature

For the tetraphenylborate salt, see: Wu et al. (2007) and for the tetracyanoquinodimethanide salt, see: Ashwell et al. (1975); Hudson & Robson (2009).
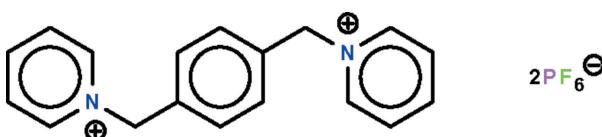
Experimental

Crystal data

$C_{18}H_{18}N_2^{2+}\cdot 2PF_6^-$
$M_r = 552.28$
Orthorhombic, $Pbam$
$a = 11.1013$ (11) Å
$b = 12.6742$ (12) Å
$c = 7.3483$ (7) Å

$V = 1033.91$ (17) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.33$ mm^{-1}
$T = 100$ K
$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.908$, $T_{max} = 0.968$

6200 measured reflections
1280 independent reflections
1121 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.088$
$S = 1.05$
1280 reflections

91 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

References

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supporting information

1,1′-(*p*-Phenylenedimethylene)dipyridinium bis(hexafluoridophosphate)

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S1. Comment

The structure of the 1,1′-(4-dimethylphenylene)dipyridinium cation has been reported in a number of examples (Ashwell *et al.*, 1975; Hudson & Robson, 2009; Wu *et al.*,2007). We ourselves have reported other examples. The title hexafluorophosphate (Scheme I, Fig. 1) exists as non-interacting cations and anions. In the cation, the pyridyl and phenylene rings are aligned at 62.9 (1) °. The angle at the methylene C atom is 112.8 (1) °. The anion lies on a mirror plane such that four F atoms lie within the mirror plane.

S2. Experimental

α,*α*′-Dibromo-*p*-xylene (5.28 g, 20 mmol) was dissolved in acetonitrile (30 ml) and to the solution was added pyridine (2.96 g, 40 mmol). The solution was heated for 2 h. The solid product was recrystallized from a methanol/ethanol mixture to afford 1,1′-(4-dimethylphenylene)dipyridinium bromide. The bromide ion was exchanged by the hexafluorophosphate ion by reaction of the salt (1 mmol) with ammonium hexafluorophosphate (2 mmol) in water. The reactants were mixed in water for 2 h to give a solid material. This was collected and recrystallized from acetonitrile.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U(C).
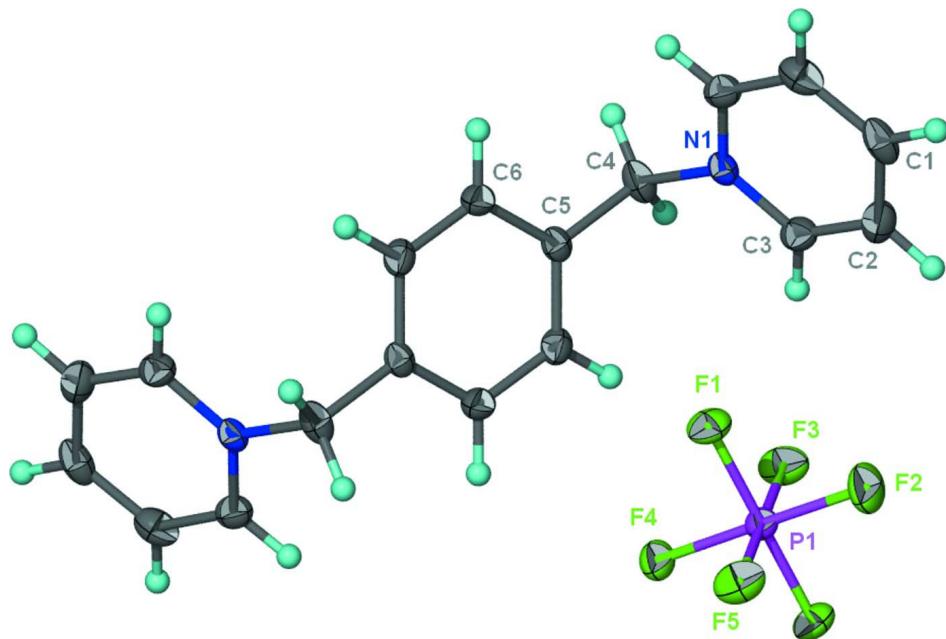
Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $C_{18}H_{18}N_2{}^{2+}$ $2PF_6{}^-$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

1,1′-(*p*-Phenylenedimethylene)dipyridinium bis(hexafluoridophosphate)

Crystal data
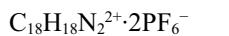
$C_{18}H_{18}N_2{}^{2+}\cdot 2PF_6{}^-$	$F(000) = 556$
$M_r = 552.28$	$D_x = 1.774$ Mg m^{-3}
Orthorhombic, *Pbam*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2 2ab	Cell parameters from 2836 reflections
$a = 11.1013$ (11) Å	$\theta = 2.8$–28.2°
$b = 12.6742$ (12) Å	$\mu = 0.33$ mm^{-1}
$c = 7.3483$ (7) Å	$T = 100$ K
$V = 1033.91$ (17) Å^3	Block, colorless
$Z = 2$	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX diffractometer	6200 measured reflections
Radiation source: fine-focus sealed tube	1280 independent reflections
Graphite monochromator	1121 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$
	$h = -14 \rightarrow 14$
$T_{min} = 0.908$, $T_{max} = 0.968$	$k = -12 \rightarrow 16$
	$l = -9 \rightarrow 8$

Refinement

Refinement on F^2	1280 reflections
Least-squares matrix: full	91 parameters
$R[F^2 > 2\sigma(F^2)] = 0.029$	0 restraints
$wR(F^2) = 0.088$	Primary atom site location: structure-invariant
$S = 1.05$	direct methods

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.3897P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.33$ e Å^{-3}
H-atom parameters constrained	$\Delta\rho_{min} = -0.44$ e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
P1	0.25173 (4)	0.14923 (4)	0.0000	0.01624 (16)	
F1	0.25218 (7)	0.14917 (6)	0.21872 (11)	0.0238 (2)	
F2	0.31281 (13)	0.26387 (9)	0.0000	0.0351 (3)	
F3	0.12080 (10)	0.20151 (10)	0.0000	0.0281 (3)	
F4	0.19348 (10)	0.03444 (8)	0.0000	0.0238 (3)	
F5	0.38395 (10)	0.09687 (10)	0.0000	0.0282 (3)	
N1	0.00180 (13)	0.29642 (11)	0.5000	0.0151 (3)	
C1	0.17001 (16)	0.45395 (14)	0.5000	0.0227 (4)	
H1	0.2269	0.5100	0.5000	0.027*	
C2	0.12837 (12)	0.41294 (11)	0.3374 (2)	0.0231 (3)	
H2	0.1579	0.4391	0.2247	0.028*	
C3	0.04351 (11)	0.33362 (10)	0.34067 (18)	0.0192 (3)	
H3	0.0143	0.3050	0.2296	0.023*	
C4	−0.09367 (16)	0.21325 (14)	0.5000	0.0203 (4)	
H4A	−0.1451	0.2225	0.3911	0.024*	0.50
H4B	−0.1451	0.2225	0.6089	0.024*	0.50
C5	−0.04278 (15)	0.10309 (13)	0.5000	0.0153 (4)	
C6	−0.02152 (11)	0.05152 (10)	0.66385 (17)	0.0181 (3)	
H6	−0.0364	0.0867	0.7758	0.022*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0184 (3)	0.0162 (3)	0.0141 (3)	−0.00093 (16)	0.000	0.000
F1	0.0274 (4)	0.0300 (5)	0.0140 (4)	−0.0014 (3)	−0.0013 (3)	−0.0022 (3)
F2	0.0502 (8)	0.0217 (6)	0.0333 (7)	−0.0156 (6)	0.000	0.000
F3	0.0272 (6)	0.0346 (7)	0.0224 (6)	0.0125 (5)	0.000	0.000
F4	0.0309 (6)	0.0196 (5)	0.0210 (6)	−0.0068 (5)	0.000	0.000
F5	0.0189 (6)	0.0400 (7)	0.0255 (6)	0.0042 (5)	0.000	0.000
N1	0.0150 (6)	0.0115 (6)	0.0187 (7)	0.0018 (5)	0.000	0.000
C1	0.0148 (8)	0.0134 (8)	0.0398 (11)	0.0014 (6)	0.000	0.000
C2	0.0222 (6)	0.0212 (6)	0.0260 (7)	0.0022 (5)	0.0048 (5)	0.0064 (5)
C3	0.0220 (6)	0.0197 (6)	0.0161 (6)	0.0030 (5)	−0.0002 (5)	0.0003 (5)
C4	0.0148 (8)	0.0136 (8)	0.0323 (10)	−0.0005 (6)	0.000	0.000
C5	0.0129 (7)	0.0130 (8)	0.0201 (9)	−0.0020 (6)	0.000	0.000
C6	0.0215 (6)	0.0167 (6)	0.0159 (6)	−0.0027 (5)	0.0021 (5)	−0.0021 (5)

Geometric parameters (Å, º)

P1—F4	1.5921 (11)	C1—H1	0.9500
P1—F3	1.5975 (12)	C2—C3	1.3779 (18)
P1—F2	1.6034 (12)	C2—H2	0.9500
P1—F1[i]	1.6072 (8)	C3—H3	0.9500
P1—F1	1.6072 (8)	C4—C5	1.506 (2)
P1—F5	1.6107 (12)	C4—H4A	0.9900
N1—C3[ii]	1.3444 (15)	C4—H4B	0.9900
N1—C3	1.3444 (15)	C5—C6	1.3902 (15)
N1—C4	1.495 (2)	C5—C6[ii]	1.3902 (15)
C1—C2	1.3828 (18)	C6—C6[iii]	1.391 (2)
C1—C2[ii]	1.3828 (18)	C6—H6	0.9500
F4—P1—F3	90.54 (7)	C2[ii]—C1—H1	120.2
F4—P1—F2	178.95 (7)	C3—C2—C1	119.18 (14)
F3—P1—F2	90.51 (7)	C3—C2—H2	120.4
F4—P1—F1[i]	90.05 (3)	C1—C2—H2	120.4
F3—P1—F1[i]	90.17 (3)	N1—C3—C2	120.45 (13)
F2—P1—F1[i]	89.95 (3)	N1—C3—H3	119.8
F4—P1—F1	90.05 (3)	C2—C3—H3	119.8
F3—P1—F1	90.17 (3)	N1—C4—C5	112.81 (14)
F2—P1—F1	89.95 (3)	N1—C4—H4A	109.0
F1[i]—P1—F1	179.64 (7)	C5—C4—H4A	109.0
F4—P1—F5	89.64 (7)	N1—C4—H4B	109.0
F3—P1—F5	179.82 (7)	C5—C4—H4B	109.0
F2—P1—F5	89.31 (7)	H4A—C4—H4B	107.8
F1[i]—P1—F5	89.83 (3)	C6—C5—C6[ii]	120.02 (16)
F1—P1—F5	89.83 (3)	C6—C5—C4	119.97 (8)
C3[ii]—N1—C3	121.11 (16)	C6[ii]—C5—C4	119.97 (8)
C3[ii]—N1—C4	119.44 (8)	C5—C6—C6[iii]	119.99 (8)
C3—N1—C4	119.44 (8)	C5—C6—H6	120.0
C2—C1—C2[ii]	119.60 (17)	C6[iii]—C6—H6	120.0
C2—C1—H1	120.2		
C2[ii]—C1—C2—C3	1.7 (3)	C3—N1—C4—C5	90.39 (12)
C3[ii]—N1—C3—C2	−1.6 (2)	N1—C4—C5—C6	91.26 (13)
C4—N1—C3—C2	177.67 (13)	N1—C4—C5—C6[ii]	−91.26 (13)
C1—C2—C3—N1	−0.1 (2)	C6[ii]—C5—C6—C6[iii]	0.3 (3)
C3[ii]—N1—C4—C5	−90.39 (12)	C4—C5—C6—C6[iii]	177.77 (16)

Symmetry codes: (i) $x, y, -z$; (ii) $x, y, -z+1$; (iii) $-x, -y, z$.