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Crystal structure of 3,3'-(1,2-phenylenebis(methylene))bis(1-methyl-1*H*-imidazol-3-ium) bis(hexafluoridophosphate), C₁₆H₂₀F₁₂N₄P₂

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$V = 2337.6(8) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0742$, $wR_{\text{ref}}(F^2) = 0.2262$, $T = 296(2) \text{ K}$.

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Abstract

C₁₆H₂₀F₁₂N₄P₂, monoclinic, $P2_1/c$ (no. 14), $a = 7.3086(15) \text{ \AA}$, $b = 12.174(3) \text{ \AA}$, $c = 26.355(6) \text{ \AA}$, $\beta = 94.500(2)^\circ$,

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.17 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.29 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	17696, 4351, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3316
$N(\text{param})_{\text{refined}}$:	309
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.1649(5)	0.3971(3)	0.66220(14)	0.0431(8)
C2	0.1323(5)	0.3453(3)	0.70776(15)	0.0512(10)
H2	0.2091	0.2889	0.7202	0.061*
C3	−0.0137(6)	0.3775(4)	0.73465(15)	0.0541(10)
H3	−0.0365	0.3420	0.7647	0.065*
C4	−0.1249(6)	0.4623(4)	0.71665(16)	0.0550(10)
H4	−0.2215	0.4852	0.7351	0.066*
C5	−0.0940(5)	0.5136(3)	0.67144(15)	0.0506(9)
H5	−0.1704	0.5706	0.6595	0.061*
C6	0.0497(5)	0.4811(3)	0.64378(14)	0.0413(8)
C7	0.3283(6)	0.3650(4)	0.63315(18)	0.0583(11)
H7A	0.2925	0.3679	0.5969	0.070*
H7B	0.4258	0.4181	0.6404	0.070*
C8	0.0856(5)	0.5355(3)	0.59381(15)	0.0502(9)
H8A	0.2012	0.5749	0.5982	0.060*
H8B	0.0982	0.4789	0.5684	0.060*
C9	0.5603(5)	0.2327(3)	0.66977(15)	0.0496(9)
H9	0.6471	0.2840	0.6821	0.060*
C10	0.4231(7)	0.0776(4)	0.6510(2)	0.0699(13)
H10	0.3998	0.0026	0.6485	0.084*
C11	0.3106(7)	0.1585(4)	0.6337(2)	0.0695(13)
H11	0.1951	0.1504	0.6166	0.083*
C12	0.7366(7)	0.0673(5)	0.6973(2)	0.0797(16)
H12A	0.7875	0.0199	0.6730	0.120*
H12B	0.6989	0.0242	0.7252	0.120*
H12C	0.8275	0.1196	0.7098	0.120*
C13	−0.0521(6)	0.7197(4)	0.57865(16)	0.0545(10)
H13	0.0442	0.7602	0.5944	0.065*
C14	−0.2220(6)	0.5833(4)	0.54924(17)	0.0602(11)
H14	−0.2623	0.5125	0.5412	0.072*
C15	−0.3128(6)	0.6771(4)	0.53787(19)	0.0672(13)
H15	−0.4283	0.6832	0.5206	0.081*
C16	−0.2498(9)	0.8783(4)	0.5513(2)	0.0917(19)
H16A	−0.1424	0.9210	0.5612	0.138*
H16B	−0.3452	0.8962	0.5730	0.138*
H16C	−0.2908	0.8945	0.5166	0.138*
N1	0.3987(4)	0.2555(3)	0.64592(13)	0.0506(8)
N2	0.5776(5)	0.1254(3)	0.67302(13)	0.0554(9)
N3	−0.0582(4)	0.6119(3)	0.57502(12)	0.0477(8)
N4	−0.2057(5)	0.7611(3)	0.55623(14)	0.0600(10)
P1	0.53757(15)	0.23823(9)	0.82279(4)	0.0523(3)
P2	0.19576(15)	0.77518(10)	0.45696(4)	0.0531(3)
F1	0.6281(5)	0.3101(3)	0.86834(13)	0.1000(11)
F2	0.4456(5)	0.1675(3)	0.77745(12)	0.0878(9)
F3	0.5182(4)	0.1379(3)	0.86050(12)	0.0839(9)
F4	0.5557(4)	0.3382(2)	0.78450(11)	0.0794(8)
F5	0.7355(4)	0.1961(3)	0.81161(14)	0.0931(10)
F6	0.3417(4)	0.2803(3)	0.83457(12)	0.0913(10)
F7	0.2538(5)	0.7065(6)	0.50536(17)	0.169(3)
F8	0.1368(6)	0.8391(6)	0.40864(18)	0.180(3)
F9	0.1263(10)	0.8624(4)	0.4912(3)	0.205(3)
F10	0.2708(10)	0.6852(3)	0.4248(2)	0.198(3)
F11	0.3860(5)	0.8305(5)	0.45589(17)	0.1450(19)
F12	0.0058(5)	0.7173(4)	0.45793(15)	0.1268(16)

Source of material

1-Methylimidazole (2.62 g, 0.032 mol) and 1,2-bis(bromomethyl)benzene (4.22 g, 0.016 mol) was added into a flask containing toluene (25 mL). Then the mixture was stirred vigorously at 105 °C for 16 h. After the reaction has been completed (monitored by TLC), the toluene top phase was decanted and the product was washed with ethyl acetate and anhydrous diethyl ether 3 times respectively. The intermediate product was dried in vacuo at 60 °C for 1 h to give a white powder in 98.9% yield. During the anion exchange reaction, the intermediate (1.07 g, 0.0025 mol) and KPF₆ (0.92 g, 0.005 mol) were dissolved in water (25 mL), and the reaction proceeded at 95 °C for 10 h before the reaction mixture was allowed to cool slowly to room temperature. After deionized water washing and air drying, the final product was obtained in 90.5% yield.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C—H = 0.90–0.97 Å with *U*_{iso}(H) = 1.5 *U*_{eq}(C) for methyl H atoms and 1.2 *U*_{eq}(C) for all other H atoms.

Comment

Ionic liquid (ILs) refers to a salt composed solely of ions which generally has a melting point of 100 °C or below [5]. Because of the advantages of low volatility, non-flammability, high polarity, wide window of electrochemical performance, and large structural adjustability, it has been widely studied and applied [6–9]. When the anion is hexafluorophosphate, this imidazole-based ionic liquids may show good hydrophobicity, and even temperature sensitivity of solubility. They can realize the function of “low temperature heterogeneous, high temperature homogeneous” in water or some organic solvents, which has application prospect in synthesis and natural product extraction [10, 11]. On the basis of our earlier work on aliphatic chain hydrocarbons [12–14], we now used halogenated arenes as starting material to react with methylimidazole, and the corresponding compound was obtained.

In the molecule of the title compound bond lengths and angles are very similar to those given in the literature [14]. The atoms of imidazole ring are coplanar, and the dihedral angle of the two imidazole rings and the phenyl group are 3.8(2)°, 82.8(2)° and 79.5(2)°, respectively. The torsion angles of C1—C7—N1—C9, and C6—C8—N3—C13 are 101.0(5)° and −112.9(4)°, respectively.

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