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2,7-Dimethyl-2,7-diazoniapyrene bis(hexafluorophosphate)

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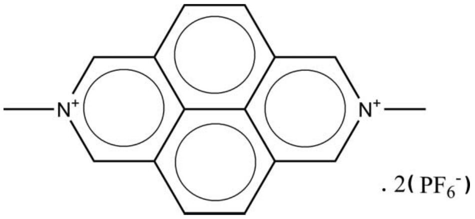
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.059; wR factor = 0.182; data-to-parameter ratio = 12.0.

In the title compound, $C_{16}H_{14}N_2^{2+}\cdot 2PF_6^-$, the 2,7-dimethyl-2,7-diazapyrenium (DM-diaz) cation lies on a crystallographic twofold rotation axes. The diaz groups are nearly coplanar, with a maximum deviation of 0.008 (3) Å. In the crystal, molecules are linked into a two-dimensional lamellar framework parallel to (104) through weak C—H···F interactions.

Related literature

For general background to 2,7-disubstituted diazapyrenium dications, see: Ashton *et al.* (1999); Yen *et al.* (2009); Steuerman *et al.* (2004); Lilienthal *et al.* (1996); Sindelar *et al.* (2005); Lin *et al.* (2006). For related structures, see: Blake *et al.* (1997); Dinolfo *et al.* (2004).



Experimental

Crystal data

$C_{16}H_{14}N_2^{2+}\cdot 2PF_6^-$
M_r = 524.23
Monoclinic, $P2_1/n$
a = 6.7654 (14) Å
b = 10.653 (2) Å
c = 13.422 (3) Å
β = 91.03 (3)°
V = 967.2 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 293 K
0.31 × 0.31 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995) T_{min} = 0.899, T_{max} = 0.937
7699 measured reflections
1756 independent reflections
1439 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.182
S = 1.06
1756 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···F2^{i}	0.93	2.48	3.367 (4)	160
C7—H7···F4^{ii}	0.93	2.51	3.418 (5)	167

Symmetry codes: (i) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, y-1, z$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2385).

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supplementary materials

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2,7-Dimethyl-2,7-diazoniapyrene bis(hexafluorophosphate)

L. Ang

Comment

2,7-Disubstituted diazapyrenium dications, which combine the features of pyrene, methylviologen, and nucletic acid intercalators, are charming pi-electron deficient building blocks in supramolecular chemistry (Ashton *et al.*, 1999; Yen *et al.*, 2009). They have been widely used as the electron-acceptors for electron-donating units such as hydroquinones and aromatic carboxylates (Steuerman *et al.*, 2004; Lilienthal *et al.*, 1996). Furthermore, due to their luminescence properties, they have also been as fluorescence probes for ion detection (Sindelar *et al.*, 2005) and neurotransmition (Lin *et al.*, 2006). Herein, we report the crystal structure of one of these disubstituted diazapyrenium dications, the *N*,*N*'-dimethyl-2,7-diazapyrenium, $C_{16}H_{14}N_2.2PF_6$, (*DM*-diaz).

The cation lies on a crystallographic twofold rotation axes; diaz groups are nearly coplanar with a maximum deviation of 0.008 (3) Å. Unlike many structures that contain diaz (Blake *et al.*, 1997; Dinolfo *et al.*, 2004), Dm-diaz exhibits no face-to-face pi-pi interactions between diaz molecules in the structure. C—H···F interactions are observed between the methyl groups of the *DM*-diaz molecules and hexafluorophoshate counterions (Table 1), forming a two-dimensional lamellar framework parallel to ($10\overline{1}$) (Figure 2).

Experimental

A solution of 2,7-diazapyrene (0.210 g, 1.03 mmol) and iodomethane (0.568 g, 4.02 mmol) in acetonitrile (15 ml) was stirred and refluxed for 3 h. After it was cooled to room temperature, a red solid was isolated on a filter and washed with ethyl ether (30 ml). The solid was dissolved with water (75 ml) and a saturated aqueous solution of NH_4PF_6 (2.44 g, 15.0 mmol) was added until no further precipitate was observed. The red solid was isolated on a filter, washed with water and dried under vacuum to afford the product (0.423 g, 78.4%). Red crystals were obtained by vapor diffusion of isopropyl ether into an acetonitrile solution over a period of 5 d. ^{1}H NMR (500 MHz, CD_3CN, 295 K) δ (p.p.m.) 9.88 (4*H*,s), 8.85 (4*H*, s), 5.14 (4*H*, t, J = 5.2 Hz), 3.45 (4*H*, m), 3.45 (2*H*, t, J = 5.5 Hz).

Refinement

H atoms bonded to C atoms were palced in geometrically calculated positionand were refined using a riding model, with C—$H_{aromatic}$ = 0.93 Å, *C*—H_{methyl} = 0.96 Å, and with $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$.

Figures

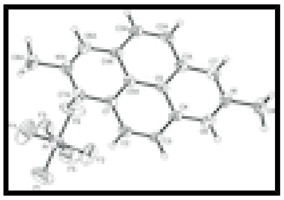

Fig. 1. *ORTEP* view of the title compound. The dispalcement ellipsoids are drawn at 30% probability level. Symmetry code: (A) 2-x, 1-y, 1-z

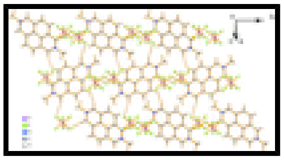

Fig. 2. The two-dimensional layer of the compound, parallel to (10$\overline{1}$).

2,7-Dimethyl-2,7-diazoniapyrene bis(hexafluorophosphate)

Crystal data

$C_{16}H_{14}N_2^{2+}\cdot 2PF_6^-$

M_r = 524.23

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

a = 6.7654 (14) Å

b = 10.653 (2) Å

c = 13.422 (3) Å

β = 91.03 (3)°

V = 967.2 (3) Å^3

Z = 2

F(000) = 524

D_x = 1.800 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 6424 reflections

θ = 3.0–27.5°

μ = 0.35 mm^{-1}

T = 293 K

Block, yellow

0.31 × 0.31 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 0 pixels mm^{-1}

ω scans

Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)

T_{min} = 0.899, T_{max} = 0.937

7699 measured reflections

1756 independent reflections

1439 reflections with $I > 2\sigma(I)$

R_{int} = 0.021

θ_{max} = 25.4°, θ_{min} = 3.0°

h = −8→7

k = −12→12

l = −16→16

Refinement

Refinement on F^2

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.059$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.182$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.106P)^2 + 0.7563P]$ where $P = (F_o^2 + 2F_c^2)/3$
1756 reflections	$(\Delta/\sigma)_{max} < 0.001$
146 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

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}
P1	0.73691 (12)	0.87716 (8)	0.67479 (6)	0.0486 (4)
F1	0.7852 (5)	0.9813 (3)	0.7544 (3)	0.1277 (13)
F2	0.7768 (4)	0.7779 (3)	0.7596 (2)	0.1015 (10)
F3	0.5103 (3)	0.8793 (2)	0.7022 (2)	0.0842 (8)
F4	0.7012 (5)	0.9817 (4)	0.5943 (3)	0.1329 (14)
F5	0.9644 (3)	0.8750 (3)	0.6478 (2)	0.0953 (10)
F6	0.6946 (4)	0.7712 (3)	0.5961 (2)	0.1071 (11)
N1	1.1916 (4)	0.2419 (2)	0.61997 (19)	0.0458 (6)
C1	1.0682 (4)	0.6661 (3)	0.4751 (2)	0.0399 (7)
C2	1.2564 (4)	0.6724 (3)	0.5268 (2)	0.0459 (7)
H2	1.3272	0.7472	0.5275	0.055*
C3	1.3308 (4)	0.5710 (3)	0.5740 (2)	0.0463 (7)
H3	1.4527	0.5765	0.6068	0.056*
C4	1.2250 (4)	0.4551 (3)	0.5743 (2)	0.0390 (7)
C5	1.0387 (4)	0.4467 (2)	0.52485 (19)	0.0360 (6)
C6	1.2952 (4)	0.3482 (3)	0.6213 (2)	0.0459 (7)
H6	1.4170	0.3505	0.6545	0.055*
C7	1.0142 (4)	0.2319 (3)	0.5739 (2)	0.0448 (7)
H7	0.9465	0.1560	0.5750	0.054*
C8	1.2764 (7)	0.1282 (3)	0.6680 (3)	0.0680 (11)
H8A	1.1728	0.0810	0.6984	0.102*
H8C	1.3721	0.1526	0.7180	0.102*
H8B	1.3392	0.0774	0.6187	0.102*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0456 (6)	0.0520 (6)	0.0482 (6)	−0.0031 (3)	−0.0017 (4)	−0.0009 (4)
F1	0.142 (3)	0.105 (2)	0.136 (3)	−0.007 (2)	−0.003 (2)	−0.068 (2)
F2	0.097 (2)	0.105 (2)	0.103 (2)	0.0185 (16)	−0.0030 (16)	0.0420 (17)
F3	0.0548 (14)	0.105 (2)	0.0938 (18)	0.0116 (12)	0.0153 (12)	0.0123 (14)
F4	0.109 (2)	0.150 (3)	0.140 (3)	−0.012 (2)	−0.008 (2)	0.093 (2)
F5	0.0494 (13)	0.125 (2)	0.112 (2)	−0.0215 (13)	0.0103 (13)	−0.0286 (17)
F6	0.0775 (16)	0.143 (3)	0.101 (2)	−0.0446 (17)	0.0222 (15)	−0.0672 (19)
N1	0.0497 (14)	0.0464 (14)	0.0414 (13)	0.0030 (11)	0.0029 (11)	0.0041 (11)
C1	0.0359 (14)	0.0422 (15)	0.0418 (15)	−0.0054 (12)	0.0052 (12)	−0.0036 (12)
C2	0.0366 (15)	0.0449 (17)	0.0561 (19)	−0.0096 (12)	−0.0002 (14)	−0.0050 (14)
C3	0.0322 (14)	0.0558 (18)	0.0509 (17)	−0.0075 (13)	−0.0040 (13)	−0.0064 (14)
C4	0.0323 (14)	0.0464 (16)	0.0381 (14)	−0.0014 (11)	−0.0005 (11)	−0.0040 (12)
C5	0.0325 (14)	0.0415 (15)	0.0341 (14)	−0.0027 (11)	0.0043 (11)	−0.0053 (11)
C6	0.0409 (16)	0.0567 (18)	0.0399 (16)	0.0017 (13)	−0.0031 (13)	−0.0028 (13)
C7	0.0461 (17)	0.0434 (16)	0.0451 (16)	−0.0035 (13)	0.0076 (14)	−0.0001 (13)
C8	0.078 (3)	0.057 (2)	0.068 (2)	0.0077 (18)	−0.015 (2)	0.0186 (18)

Geometric parameters (Å, °)

P1—F4	1.567 (3)	C2—C3	1.346 (4)
P1—F6	1.568 (2)	C2—H2	0.9300
P1—F1	1.570 (3)	C3—C4	1.427 (4)
P1—F2	1.574 (3)	C3—H3	0.9300
P1—F3	1.583 (2)	C4—C6	1.382 (4)
P1—F5	1.587 (2)	C4—C5	1.417 (4)
N1—C6	1.332 (4)	C5—C5^{i}	1.413 (5)
N1—C7	1.344 (4)	C6—H6	0.9300
N1—C8	1.483 (4)	C7—H7	0.9300
C1—C7^{i}	1.382 (4)	C8—H8A	0.9600
C1—C5^{i}	1.402 (4)	C8—H8C	0.9600
C1—C2	1.440 (4)	C8—H8B	0.9600
F4—P1—F6	91.3 (2)	C1—C2—H2	119.7
F4—P1—F1	89.7 (2)	C2—C3—C4	120.8 (3)
F6—P1—F1	178.30 (18)	C2—C3—H3	119.6
F4—P1—F2	176.9 (2)	C4—C3—H3	119.6
F6—P1—F2	91.8 (2)	C6—C4—C5	117.2 (3)
F1—P1—F2	87.2 (2)	C6—C4—C3	123.1 (3)
F4—P1—F3	90.70 (16)	C5—C4—C3	119.7 (3)
F6—P1—F3	90.07 (15)	C1^{i}—C5—C5^{i}	120.2 (3)
F1—P1—F3	91.28 (17)	C1^{i}—C5—C4	120.6 (3)
F2—P1—F3	89.74 (15)	C5^{i}—C5—C4	119.3 (3)
F4—P1—F5	89.51 (18)	N1—C6—C4	121.2 (3)
F6—P1—F5	90.11 (14)	N1—C6—H6	119.4

F1—P1—F5	88.54 (17)	C4—C6—H6	119.4
F2—P1—F5	90.04 (17)	N1—C7—C1^{i}	120.4 (3)
F3—P1—F5	179.73 (16)	N1—C7—H7	119.8
C6—N1—C7	122.6 (3)	C1^{i}—C7—H7	119.8
C6—N1—C8	119.3 (3)	N1—C8—H8A	109.5
C7—N1—C8	118.1 (3)	N1—C8—H8C	109.5
C7^{i}—C1—C5^{i}	118.0 (3)	H8A—C8—H8C	109.5
C7^{i}—C1—C2	122.6 (3)	N1—C8—H8B	109.5
C5^{i}—C1—C2	119.4 (3)	H8A—C8—H8B	109.5
C3—C2—C1	120.6 (3)	H8C—C8—H8B	109.5
C3—C2—H2	119.7		

Symmetry codes: (i) −x+2, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···F2^{ii}	0.93	2.48	3.367 (4)	160
C7—H7···F4^{iii}	0.93	2.51	3.418 (5)	167

Symmetry codes: (ii) −x+5/2, y−1/2, −z+3/2; (iii) x, y−1, z.

Fig. 1

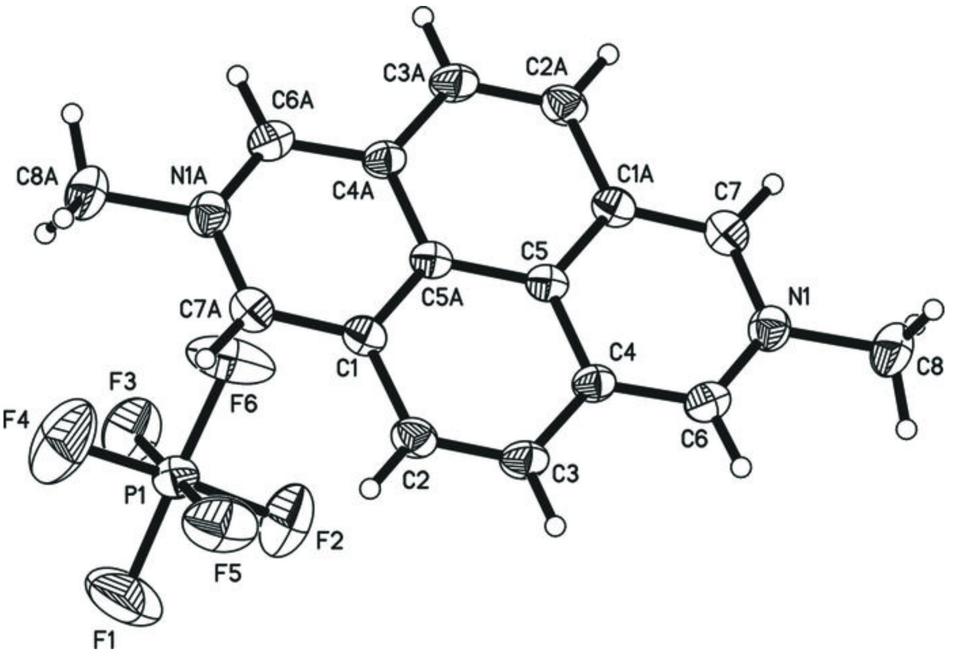
C3A
C2A
C6A
C8A
N1A
C4A
C1A
C7
C5
C5A
N1
C7A
C1
C4
C8
F3
F6
F4
C6
P1
C2
C3
F2
F5
F1

Fig. 2