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1,3-Bis(dimethylamino)-1-methyltrimethinium hexafluorophosphate

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Key indicators

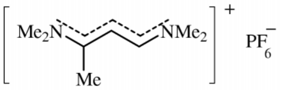
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.056
wR factor = 0.185
Data-to-parameter ratio = 9.9

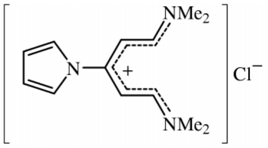
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

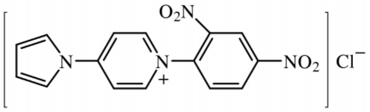
The synthesis and structure of the title compound, *N*-[3-(dimethylamino)-1-methyl-2-propenylidene]–*N*-methylmethanaminium hexafluorophosphate, $[Me_2N\{C(Me)(CH)_2\}NMe_2]^+\cdot PF_6^-$ or $C_8H_{17}N_2^+\cdot PF_6^-$, are reported. The cation is close to planar and adopts an all-*trans*-configuration.

Comment

Salts of the title cation have been prepared and characterized (Arnold & Zemlinka, 1959; Arnold, 1973), but a search of the Cambridge Structural Database (Allen & Kennard, 1993) shows that there have apparently been no crystal structure reports. The title salt, (1), was obtained as a by-product in the course of attempts to prepare the pyrrole-substituted pentamethinecyanine derivative (2).


(1)


(2)


(3)

The X-ray structural investigation of (1) shows the presence of discrete fully delocalized cations and hexafluorophosphate anions with unexceptional dimensions. The delocalized moiety (N1/C2/C3/C4/N5) of the cation is close to planar [maximum deviation 0.016 (4) Å for C3], and it adopts an all-*trans*-configuration as has been suggested by others on the basis of NMR studies (Filleux-Blanchard *et al.*, 1974) and found for the related cation $[Me_2N(CH)_3NMe_2]^+$ in 1,3-bis(dimethylamino)trimethinium perchlorate (Matthews *et al.*, 1973; Sieber *et al.*, 1974). The C atoms of all five methyl substituents also lie close to the N1/C2/C3/C4/N5 plane of the cation [maximum deviation 0.156 (14) Å for C12].

Experimental

A warm solution of pyridinium salt (3) (Ferguson & McAlees, 1990) (3.47 g, 10.0 mmol) in water (20 ml) was treated with an aqueous solution (25 ml) containing $Me_2NH_2^+\cdot Cl^-$ (9.00 g, 110 mmol) and sodium hydroxide (3.0 g, 75 mmol). A dark purple–brown precipitate formed immediately. Ethanol (20 ml) was added and the mixture was stirred and heated at the reflux for 2.5 h, then solvent was distilled to remove most of the ethanol. The resulting dark mixture was allowed

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to cool overnight and was then filtered to give an olive–brown solid (1.58 g after washing and drying; mainly 2,4-dinitroaniline) which was washed with warm water (3 × 10 ml). The combined filtrate and washings were washed with chloroform (3 × 30 ml) and treated with an aqueous solution (10 ml) of $NH_4^+ \cdot PF_6^-$ (1.63 g, 10.0 mmol), whereupon a light yellow precipitate appeared. The aqueous mixture was then extracted with CH_2Cl_2 (3 × 30 ml), and the combined extracts were dried (Na_2SO_4) and evaporated to leave an orange-yellow solid (1.89 g). Crystallization of this material from methanol gave (1) (0.70 g) as well formed straw-yellow prisms (m.p. 396.5–397.0 K). Concentration of the mother liquors and prolonged standing gave a further 0.51 g. of this material [total yield 42% based on (1)]. ^{1}H NMR (CD_3CN, 400 MHz) δ = 2.22 (*s*, C—Me), 3.01, 3.16, 3.23, 3.24 (each *s*, N—Me), 5.10 (*d*, *J* = 12.1 Hz, C2—H) and 7.74 (*d*, *J* = 12.1 Hz, C3—H).

Crystal data

$C_8H_{17}N_2^+ \cdot PF_6^-$
$M_r = 286.21$
Orthorhombic, $P2_12_12_1$
$a = 7.470$ (4) Å
$b = 11.110$ (3) Å
$c = 16.242$ (3) Å
$V = 1348.0$ (8) Å^3
$Z = 4$
$D_x = 1.410$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–$14.5°$
$\mu = 0.26$ mm^{-1}
$T = 293$ (1) K
Plate, yellow
0.50 × 0.50 × 0.35 mm

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
1540 measured reflections
1540 independent reflections
1042 reflections with $I > 2\sigma(1)$
$\theta_{max} = 26.0°$

$h = -9 \rightarrow 0$
$k = -13 \rightarrow 0$
$l = -20 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.185$
$S = 1.03$
1540 reflections
156 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1171P)^2 + 0.3108P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

N1—C2	1.301 (6)	N5—C52	1.452 (7)
N1—C11	1.478 (7)	C2—C3	1.401 (7)
N1—C12	1.458 (7)	C2—C21	1.513 (7)
N5—C4	1.325 (7)	C3—C4	1.374 (7)
N5—C51	1.431 (7)		

Molecule (1) crystallized in the orthorhombic system; space group $P2_12_12_1$ from the systematic absences. No Friedel reflections were collected and the resulting Flack (1983) parameter [0.5 (3)] is indeterminate. H atoms were treated as riding atoms with C—H distances of 0.93 and 0.96 Å. The methyl groups at C11, C12 and C21 were each modelled using six H sites, each with occupancy 0.50, mutually offset by 60°.

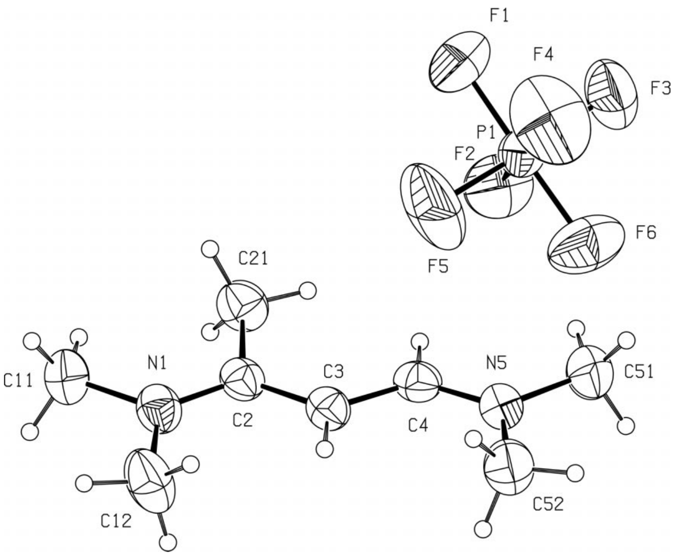

Figure 1
A view of (1) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one orientation is shown for the disordered methyl H atoms at C11, C12 and C21.

Data collection: *CAD*-4-*PC Software* (Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Nonius, 1992); data reduction: *HELENA* in *PLATON* (Spek, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 2001).

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