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Structure of 10c-Azoniafluoranthene Hexafluorophosphate

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Abstract. $(C_{15}H_{10}N)PF_6$, $M_r = 349{\cdot}22$, monoclinic, $P2_1/m$, $a = 6{\cdot}276\ (2)$, $b = 11{\cdot}340\ (3)$, $c = 9{\cdot}730\ (2)$ Å, $\beta = 97{\cdot}17\ (2)°$, $V = 687{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}69$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}58$ cm^{-1}, $F(000) = 352$, $R = 0{\cdot}045$ for 950 observed reflections with $I \geq 3\sigma(I)$. The planar aromatic cation is located on a mirror plane containing the N atom.

Experimental. Clear colorless single crystals were obtained by recrystallization from acetonitrile. Crystal dimensions 0·36 × 0·18 × 0·12 mm. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters refined by least-squares fitting of 2θ values of 25 reflections in the range 10·6–34·8°; ω–2θ scan mode, $\omega = (1{\cdot}00 + 0{\cdot}35\text{tg}\theta)°$; 1421 reflections collected, $2\theta_{max} = 52°$, $\pm h,k,l$ (max. range 7,14,12); 1342 unique reflections ($R_{int} = 0{\cdot}012$) of which 950 with $I \geq 3\sigma(I)$; three standard reflections showed an intensity variation less than 0·1% over 24·5 hours of X-ray exposure time. Lp correction applied, no correction for absorption. Space group $P2_1/m$ from intensity statistics and successful refinement. The structure was solved by direct methods with *MULTAN*11/82 (Main *et al.*, 1982), refined by full-matrix least squares (on F's); all H atoms were found from a difference Fourier map. Non-H atoms refined with anisotropic thermal parameters, and H atoms ($B = 4{\cdot}0$ Å^2) simply included in structure factor calculations. $\sum w(F_o - F_c)^2$ minimized, $w = 1/[\sigma^2(F_o) + 0{\cdot}04F_o^2]$. Final $R = 0{\cdot}045$, $wR = 0{\cdot}042$, $S = 0{\cdot}671$ for 112 variables, $\Delta/\sigma = 0{\cdot}00$, largest peak in final ΔF map 0·50 e Å^{-3} near the F atoms; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were done on DEC MicroVAX/VMS using the Enraf–Nonius (1985) *SDP* programs. Table 1 gives atom parameters and Table 2 bond lengths and angles.* A drawing of the molecular cation is presented in Fig. 1 and the unit-cell content is depicted in Fig. 2.

Table 1. *Non*-H-*atom parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
P	0·6168 (2)	0·250	0·6731 (1)	3·24 (2)
F(1)	0·3660 (4)	0·250	0·6797 (4)	5·36 (8)
F(2)	0·8688 (4)	0·250	0·6668 (4)	5·14 (8)
F(3)	0·6496 (4)	0·1521 (2)	0·7884 (3)	7·71 (7)
F(4)	0·5878 (4)	0·1514 (3)	0·5588 (3)	9·24 (8)
N	0·7861 (6)	0·250	0·2597 (4)	2·71 (7)
C(1)	0·9853 (7)	0·250	0·3376 (5)	3·2 (1)
C(2)	1·0741 (5)	0·1837 (3)	0·3715 (3)	3·95 (8)
C(3)	0·9664 (6)	0·0385 (3)	0·3301 (4)	4·10 (8)
C(4)	0·7632 (6)	0·0417 (3)	0·2522 (3)	3·50 (7)
C(5)	0·6747 (5)	0·1484 (3)	0·2170 (3)	2·89 (6)
C(6)	0·4757 (5)	0·1882 (3)	0·1384 (3)	3·05 (6)
C(7)	0·3043 (6)	0·1247 (3)	0·0694 (3)	4·87 (9)
C(8)	0·1362 (6)	0·1884 (4)	0·0006 (4)	4·84 (9)

* Tables of H-atom coordinates, anisotropic thermal parameters, bond distances and angles involving H atoms, least-squares planes, thermal vibration amplitudes and a list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51870 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

P—F(1)	1·584 (4)	C(3)—C(4)	1·400 (6)
P—F(2)	1·590 (4)	C(4)—C(5)	1·358 (6)
P—F(3)	1·574 (3)	C(5)—C(6)	1·452 (5)
P—F(4)	1·571 (3)	C(6)—C(6^i)	1·402 (8)
N—C(1)	1·378 (7)	C(6)—C(7)	1·395 (5)
N—C(5)	1·384 (4)	C(7)—C(8)	1·381 (6)
C(1)—C(2)	1·402 (5)	C(8)—C(8^i)	1·40 (1)
C(2)—C(3)	1·358 (7)		
F(1)—P—F(2)	180. (0)	C(2)—C(1)—C(2^i)	128·3 (6)
F(1)—P—F(3)	90·7 (2)	C(1)—C(2)—C(3)	121·0 (4)
F(1)—P—F(4)	90·0 (2)	C(2)—C(3)—C(4)	121·7 (4)
F(2)—P—F(3)	89·2 (2)	C(3)—C(4)—C(5)	118·4 (4)
F(2)—P—F(4)	90·0 (2)	N—C(5)—C(4)	119·4 (3)
F(3)—P—F(3^i)	89·7 (3)	N—C(5)—C(6)	105·6 (3)
F(3)—P—F(4)	89·8 (2)	C(4)—C(5)—C(6)	135·0 (4)
F(3)—P—F(4^i)	179·1 (2)	C(5)—C(6)—C(6^i)	108·1 (2)
F(4)—P—F(4^i)	90·7 (4)	C(5)—C(6)—C(7)	130·8 (4)
C(1)—N—C(5)	123·7 (2)	C(6^i)—C(6)—C(7)	121·1 (3)
C(5)—N—C(5^i)	112·6 (4)	C(6)—C(7)—C(8)	117·4 (4)
N—C(1)—C(2)	115·8 (3)	C(7)—C(8)—C(8^i)	121·5 (3)

(i) Denotes an atom generated by the mirror plane (x, $-y$, z).

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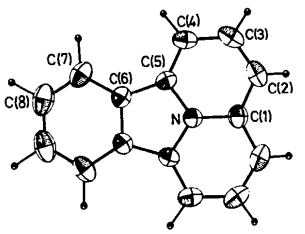

Fig. 1. Molecular drawing (*ORTEP*: Johnson, 1976) of the aromatic cation $C_{15}H_{10}N^+$ with the atomic numbering scheme.

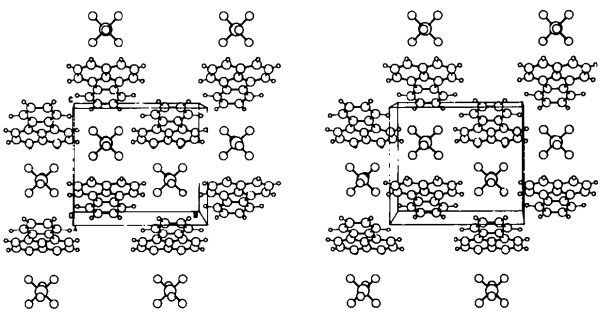

Fig. 2. Stereodrawing (*PLUTO*: Motherwell & Clegg, 1978) of the crystal structure viewed down **a**.

Related literature. A short and efficient synthesis of the title compound is reported separately (Fourmigué, Bechgaard, Auban, Jérome, Boubekeur & Batail, 1989; Fourmigué, Boubekeur, Batail & Bechgaard, 1989). The salient structural difference between this aromatic cation and its neutral analog, the fluoranthene (Hazell, Jones & Sowden, 1977) is a significant contraction [−0·025 (5) Å] of the N—C bond lengths and a similar shortening [−0·024 (5) Å] of the C(5)—C(6) bonds.

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Structure of 7,16-Dimethyl-7H^+,16H^+-1,4,10,13-tetrathia-7,16-diazoniacyclooctadecane Dipicrate

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Abstract. $C_{14}H_{32}N_2S_4^{2+}.2C_6H_2N_3O_7^-$, $M_r = 812{\cdot}79$, monoclinic, $P2_1/a$, $a = 16{\cdot}542\ (5)$, $b = 23{\cdot}750\ (9)$, $c = 9{\cdot}402\ (3)$ Å, $\beta = 105{\cdot}067\ (14)°$, $V = 3567$ Å^3, $Z = 4$, $D_x = 1{\cdot}513$ Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}328$ mm^{-1}, $F(000) = 1696$, $T = 293$ K, $R = 0{\cdot}0703$ for 1998 unique observed reflections. The asymmetric unit comprises two independent half-macrocycles and two independent picrates. The ring conformation is such that all six heteroatoms are exodentate. Each N-bound hydrogen of the macrocyclic dication is linked by a strong hydrogen bond to the phenolic oxygen of one picrate anion, yielding a neutral, centrosymmetric species.

Experimental. Compound prepared by reaction of 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane and picric acid (1:2 molar ratio) in nitromethane. Lath-shaped yellow crystal, 0·132 × 0·304 × 0·832 mm, mounted about **b** on a Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$. X-radiation, cell parameters from three 0k0 and 15 $h0l$ reflections. For data collection, ω scans

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