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2,2,6,6-Tetramethyl-4-oxopiperidinium Hexafluorophosphate

By Stephen J. Simpson

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England

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Abstract. $C_9H_{18}NO^+.PF_6^-$, $M_r = 301.2$, monoclinic, Pc, $a = 7.752$ (4), $b = 7.539$ (3), $c = 12.096$ (7) Å, $\beta = 106.77$ (4)°, $V = 676.8$ (6) Å^3, $Z = 2$, $D_x = 1.478$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.54$ cm^{-1}, $F(000) = 312$, $T = 295$ (1) K, $R = 0.0737$ for 1667 unique reflections. The cation has a chair structure; two hydrogen-bonding networks link the cations and anions while a third hydrogen-bonding interaction links cation units into infinite chains.

Experimental. Obtained by anion exchange from 2,2,6,6-tetramethyl-4-piperidone hydrochloride and ammonium hexafluorophosphate and crystallized from dichloromethane–diethyl ether (1/3). Clear colourless block, 0.40 × 0.20 × 0.20 mm, mounted on a glass fibre. Nicolet *R3m/V* diffractometer, graphite monochromator, unit cell from 27 reflections (11.40 < 2θ < 39.17°). 1794 reflections measured, 1667 unique with 1261 having $F > 4.0\sigma(F)$, collected between $3.0 < 2\theta < 55.0°$, $0 \le h \le 10$, $0 \le k \le 9$, $-15 \le l \le 14$, using θ–2θ scans. Data were corrected for Lorentz and polarization effects. Neutral-atom scattering factors and complex anamolous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). During the collection of the intensity data, three check reflections were monitored every 100 reflections indicating no significant deterioration.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
P(1)	1118	4249 (2)	5748	66 (1)
F(1)	2236 (9)	5893 (7)	5542 (7)	164 (3)
F(2)	254 (7)	4055 (6)	4386 (4)	99 (2)
F(3)	−498 (10)	5477 (9)	5762 (8)	160 (4)
F(4)	1926 (14)	4365 (10)	7081 (5)	179 (4)
F(5)	2711 (9)	3006 (11)	5685 (7)	155 (3)
F(6)	−34 (8)	2574 (7)	5863 (4)	112 (2)
N(1)	7513 (6)	924 (5)	3733 (3)	44 (1)
C(1)	5858 (7)	1986 (7)	3054 (4)	48 (1)
C(2)	6316 (7)	2889 (7)	2050 (4)	54 (2)
C(3)	7158 (8)	1640 (7)	1396 (4)	48 (2)
C(4)	8861 (8)	791 (7)	2118 (4)	49 (2)
C(5)	8500 (8)	−285 (6)	3114 (4)	50 (2)
C(6)	7450 (11)	−1958 (8)	2684 (6)	72 (3)
C(7)	10288 (9)	−767 (8)	3995 (5)	67 (2)
C(8)	4211 (9)	773 (10)	2623 (6)	77 (3)
C(9)	5520 (10)	3355 (10)	3898 (5)	71 (2)
O(1)	6498 (7)	1307 (6)	371 (3)	70 (2)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

C(1)—C(2)	1.521 (8)	C(2)—C(3)	1.496 (8)
C(3)—C(4)	1.500 (7)	C(4)—C(5)	1.544 (8)
C(5)—C(6)	1.510 (8)	C(5)—C(7)	1.528 (8)
N(1)—C(1)	1.534 (6)	N(1)—C(5)	1.518 (8)
C(3)—O(1)	1.222 (6)	C(1)—C(8)	1.534 (8)
C(1)—C(9)	1.526 (9)		
C(1)—N(1)—C(5)	120.8 (4)	C(6)—C(5)—C(7)	109.4 (4)
C(8)—C(1)—C(9)	110.1 (5)	C(1)—C(2)—C(3)	112.3 (4)
C(3)—C(4)—C(5)	110.6 (5)	C(2)—C(3)—C(4)	113.9 (4)
C(2)—C(3)—O(1)	123.1 (5)	C(4)—C(3)—O(1)	122.9 (5)

Calculations were performed using *SHELXTL-Plus* (Sheldrick, 1987) on a MicroVAX II computer. All non-H atoms were located from a Patterson synthesis and the P atom was constrained to lie on

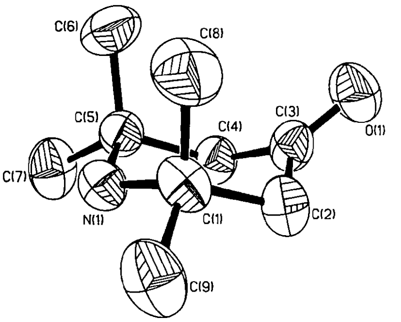

Fig. 1. Plot showing 30% thermal ellipsoids for the cation.

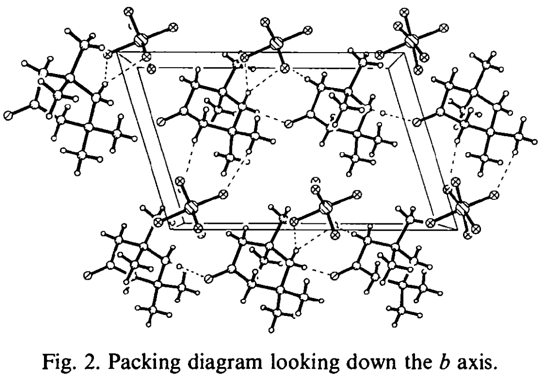

Fig. 2. Packing diagram looking down the *b* axis.

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the glide plane. All non-H atoms were refined with anisotropic thermal parameters and H atoms were placed in calculated positions and allowed to ride. An absorption correction was not applied. Full-matrix least-squares refinement on F using the weighting scheme $w = [\sigma^2(F) + 0.0014F^2]^{-1}$ converged to give $R = 0.0582$, $wR = 0.0722$ and $S = 1.49$, data/parameter ratio = 7.8. No shift in the final refinement (max. $\Delta/\sigma = 0.001$, mean $\Delta/\sigma = 0.000$). The highest unassigned electron density peaks (0.22–0.38 e Å^{-3}) were near the anion.

Fractional atomic coordinates are given in Table 1,* and selected bond distances and bond angles in Table 2. Fig. 1 shows the thermal ellipsoids drawn at the 30% probability level for the title compound and Fig. 2 illustrates the packing and hydrogen-bonding networks.

Related literature. The structure of 2,2,6,6-tetramethyl-4-piperidone hydrochloride (Rees & Weiss, 1971) contains N—H···Cl interactions and in 2,2,6,6-tetramethyl-4-piperidone monohydrate (De Camp, Micovic & Pelletier, 1974) there is evidence of hydrogen bonding from the water molecule. The title complex shows hydrogen bonding from N—H to the adjacent carbonyl O atom of another cation and two types of interactions to fluorines of the anion.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54824 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0037]

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Structure of an (*E*)-17-(Diethylphosphonoisocyanomethylene) Steroid

By A. Meetsma, J. Stoelwinder and A. M. van Leusen*

Department of Chemistry, Groningen University, Nijenborgh 16, 9747 *AG Groningen, The Netherlands*

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Abstract. (*E*)-17-(Diethylphosphonoisocyanomethylene)-3-methoxy-19-norandrosta-1,3,5(10)-triene, $C_{25}H_{34}NO_4P$, $M_r = 443.52$, monoclinic, $P2_1$, $a = 7.244$ (1), $b = 34.769$ (8), $c = 9.759$ (2) Å, $\beta = 105.70$ (1)°, $V = 2366.3$ (8) Å^3, $Z = 4$, $D_x = 1.245$ g cm^{-3}, λ(Mo $K\overline{\alpha}$) = 0.71073 Å, $\mu = 1.4$ cm^{-1}, $F(000) = 952$, $T = 130$ K, $R_F = 0.044$ for 3939 unique observed reflections with $I \geq 2.5\sigma(I)$ and 762 parameters. Two crystallographically independent molecules (*A* and *B*) of the title compound are present in the asymmetric unit. Their conformational flexibility, as measured by the different torsion angles about the P—O bonds, indicates that the crystal lattice plays a role in determining the molecular conformation. Both the exocyclic double bond of *A* as well as the exocyclic double bond of *B* exhibit *E* stereochemistry.

Experimental. The title steroid was prepared as one of a series from a 17-oxo steroid (Stoelwinder, van Zoest & van Leusen, 1992). A suitable colourless plate-like crystal of dimensions 0.10 × 0.25 × 0.43 mm, which was obtained by slow evaporation of a petroleum ether (b.p. 313–333 K) solution, was glued on top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit mounted on an Enraf–Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Unit-cell dimensions and their standard deviations and the orientation matrix were determined from the setting angles of 22 reflections in the range $14.49 < \theta < 21.36°$ in four alternative settings (de Boer & Duisenberg, 1984). Intensity data of 4690 reflections were collected [h: $-1\rightarrow 8$; k: $0\rightarrow 42$; l: $-12\rightarrow 11$; $1.17 \leq \theta \leq 26.00°$; $\omega/2\theta$-scan mode; $\Delta\omega = (0.75 + 0.34\mathrm{tg}\theta)°$; graphite-monochromated Mo $K\overline{\alpha}$ radiation]. The unit cell was identified as monoclinic, space group $P2_1$: the *E* statistics unambiguously showed a non-centrosymmetric space group (Snow & Tiekink, 1988). This assignment was confirmed by the solution and the successful refinement in this space group. Reduced-cell calculations did not indicate any

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* To whom correspondence should be addressed.