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4-(Piperidin-1-yl)pyridinium hexafluorophosphate at 150 K

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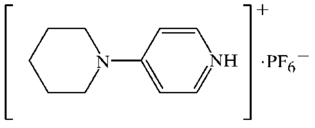
Structural characterization of the title compound, $C_{10}H_{15}N_2^+\cdot PF_6^-$, shows it to be ionic, with the pyridine rather than the piperidine N atom being protonated and forming hydrogen bonds to the counter-ions, resulting in two independent ion pairs. A number of unusual features are noted, in particular the remarkably close inter-ring hydrogen contacts [1.97 (3)–2.00 (3) Å] and the considerable differences in the pair of cations, in respect of the torsion angles within the piperidine ring involving the bonds to either side of the N atom.

Comment

A recent publication (James *et al.*, 2001) describes the room-temperature structural characterization of 4-piperidinylpyridinium tetrachloroferrate(III), which was undertaken in order to understand better the low-temperature magnetic ordering arising from the particular spatial distribution of the magnetic centres within the lattice. The results briefly drew attention to other features of interest peripheral to that objective, concerning the nature of the cation in which the inter-ring bond appeared to exhibit a high bond order not evident, for example, in the *N*-(4′-pyridyl)-4-ethoxypyridinium species coordinated to trichlorozincate(II) (Steffen & Palenik, 1978). As there appears to be no other structural characterization of the 4-piperidinylpyridinium species or close relatives in the literature, we considered it to be of interest to execute a further study under conditions conducive to providing a description of greater precision, *i.e.* at low temperature, using CCD rather than single-counter instrumentation. We thus record herein the structure determination of 4-(piperidin-1-yl)pyridinium as the hexafluorophosphate salt, (I).

4-(Piperidin-1-yl)piperidine, crystallized from aqueous solution, is, in principle, capable of protonation at either the piperidinyl or the pyridyl N atom. The isolated bases, piperidine and pyridine, have pK_a values of 11.1 and 5.2, respectively. However, the usefulness of these data as a guide as to which N atom would be most likely to protonate in the combined array will be affected by a variety of factors, leaving the likely outcome open to question. In the event, the results of the previous experiment suggested protonation at the pyridinium N atom, coupled with the assumption of a quinonoid bond distribution throughout the pyridinium ring and considerable double-bond character in the inter-ring bond, similar to that found in the numerous 4-(dimethylamino)-pyridinium species studied.



(I)

The results of the present study confirm the stoichiometry and connectivity of the present salt, (I), as consistent with that of the systematic name. Two independent formula units, devoid of crystallographic symmetry, comprise the asymmetric unit of the structure. The cations and anions are associated pairwise *via* hydrogen-bonding between the pyridinium protonating H atoms and the anions (Fig. 1), with generally close agreement in the corresponding parameters of the two cations (Table 1) (but see below). A notable feature of the structure of the tetrachloroferrate salt was the association of the protonating H atoms with Cl atoms arising from pairs of symmetry-related anions, linking them into a one-dimensional string. In (I), we find some ambivalence in the hydrogen associations, with N/H11···F24($1-x$, $2-y$, $1-z$) = 3.053 (3) and 2.23 (3) Å, compared with N/H11···F25($1-x$, $2-y$, $1-z$) = 2.952 (3) and 2.45 (3) Å, but N/H21···F11 = 3.012 (3) and 2.21 (3) Å is more clearcut (Fig. 1). These interactions have little, if any, apparent impact on the associated anion geometries.

The bonding within the cations of (I) exhibits prominent quinonoid characteristics in the pyridinium rings, the bond order between the rings (in C*n*4—N*n*1′, where *n* is 1 or 2) exhibiting consistent marked double-bond character [1.334 (3) and 1.336 (3) Å for $n = 1$ or 2, respectively]. The C_2NCC_2 arrays are closely planar ($\chi^2 = 818$ and 579 for $n = 1$ or 2, respectively), and the angle sums about N*n*1′ are 359.6 and 359.1° for $n = 1$ or 2, respectively. The torsion angles, pairwise in the bonds outward from N*n*1′ in the piperidine rings, are 61.9 (3) and −61.5 (3), −56.7 (3) and 56.3 (3), and 52.7 (3) and −52.4 (3)° for ring 1, and 55.4 (3) and −56.9 (3), −54.5 (3) and 57.7 (3), and 55.1 (3) and −56.4 (3)° for ring 2, the large difference between the first pairs of values being curious. In adopting this resonance form, a transfer of positive charge is implied from the protonated pyridine N atom to the N atom of the piperidine ring. This provides an interesting contrast with the *N*-(4′-pyridyl)-4-ethoxypyridinium species, in which not only is the central inter-ring bond much longer at 1.447 (11) Å, but the two ring planes have an interplanar dihedral angle of 40.5°, because of the steric interactions between the 3,5 H atoms on the ‘*A*’ ring and the 2,6 H atoms on the ‘*B*’ ring, the

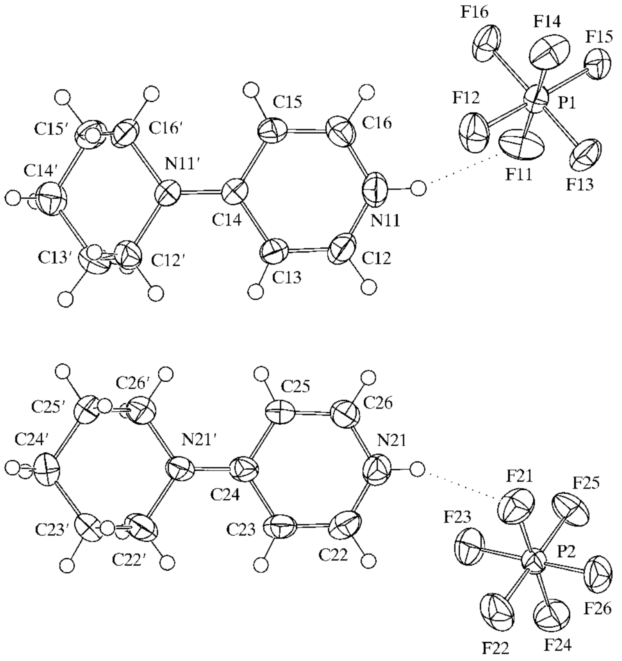


Figure 1
Projections of the two independent ion pairs of (I), viewed normal to their pyridine ring planes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

associated H···H distances being shown to lie at the van der Waals limit. Remarkably, in the structure of (I), the four H(ar)···H(eq) contacts between the rings (all H atoms refined) lie in the range 1.97 (3)–2.00 (3) Å.

Inspection of the angular geometries to either side of the H*n*3,5 attachments in the pyridinium ring of (I) suggests the H atoms bow away from the piperidine ring, all C4—C3,5—H angles being greater than 120° and all C2—C3—H3 and C6—C5—H5 angles less, at no great level of significance, but no such trend is discernable at the contacting piperidinium H atoms. Indeed, it may be surmised that such contacts might be avoided more effectively by adoption of a less rigorous chair conformation by the piperidine rings.

The extension of conjugation into the exocyclic bond in species of the present type is well known in derivatives of the type $R_2N{\cdot}C_6H_4NH^+$, there being an abundance of examples for *R* = H or Me. It is of interest to note that the inter-ring C—N distance in (I) is comparable with the latter and also with systems where the piperidine is supplanted by a pyrrolidine moiety, *e.g.* 1.324 (4) Å (Huang *et al.*, 1997) and 1.329 (5) Å (Wheeler & Foxman, 1992) [endocyclic C—N—C = 111.0 (3) and 111.6 (3)°, respectively], lengthening to 1.369 (2) Å [C—N—C = 112.43 (9)°] in a deprotonated analogue (Spivey *et al.*, 2000).

Experimental

Crystals of (I) were prepared by slow evaporation of an aqueous acidic (HCl) solution containing 4-(piperidin-1-yl)pyridine and a small excess of ammonium hexafluorophosphate (Aldrich Chemical Co.). Very pale yellow crystals of (I) were obtained (m.p. 409–410 K). Analysis found: C 39.05, H 4.95, N 8.94% (Campbell Microanalytical Laboratory, University of Otago, New Zealand); calculated for $C_{10}H_{15}F_6N_2P$: C 38.97, H 4.91, N 9.08%.

Crystal data

$C_{10}H_{15}N_2^+{\cdot}PF_6^-$
$M_r = 308.21$
Monoclinic, $P2_1/n$
$a = 12.8140\ (10)$ Å
$b = 10.4199\ (8)$ Å
$c = 20.072\ (2)$ Å
$\beta = 106.9370\ (10)^\circ$
$V = 2563.8\ (4)$ Å^3
$Z = 8$
$D_x = 1.597$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.5$–28.5°
$\mu = 0.28$ mm^{-1}
$T = 150\ (2)$ K
Prism, very pale yellow
0.45 × 0.35 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.820$, $T_{\max} = 0.949$
29 464 measured reflections
6423 independent reflections
4871 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 29^\circ$
$h = -17 \rightarrow 16$
$k = -14 \rightarrow 14$
$l = -27 \rightarrow 27$

Refinement

Refinement on F
$R = 0.042$
$wR = 0.048$
$S = 1.05$
4871 reflections
463 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.012$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C12	1.347 (3)	N21—C22	1.341 (3)
N11—C16	1.345 (3)	N21—C26	1.344 (3)
C12—C13	1.347 (4)	C22—C23	1.357 (3)
C13—C14	1.426 (3)	C23—C24	1.424 (3)
C14—C15	1.428 (3)	C24—C25	1.421 (3)
C14—N11′	1.333 (3)	C24—N21′	1.336 (3)
C15—C16	1.355 (4)	C25—C26	1.358 (3)
C12—N11—C16	120.1 (2)	N21—C22—C23	121.5 (2)
N11—C12—C13	121.6 (2)	N21—C22—H22	116.5 (14)
C12—C13—C14	121.0 (2)	C23—C24—N21′	122.7 (2)
C13—C14—C15	115.1 (2)	C25—C24—N21′	122.0 (2)
C12′—N11′—C16′	111.4 (2)	C22′—N21′—C26′	112.3 (2)
C22—N21—C26	120.0 (2)		

The H atoms were located from difference Fourier maps, placed at idealized positions (C—H = 0.95 Å and N—H = 0.92 Å) and refined in *x*, *y*, *z* and *U*.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *Xtal*3.4 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.4; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.4; molecular graphics: *Xtal*3.4; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.4.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1273). Services for accessing these data are described at the back of the journal.

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