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Anilinium Hydrogen Monofluorophosphate, $C_6H_8N^+.HPO_3F^-$

ABDALLAH KHAOULANI IDRISSI

Département de Chimie, Faculté des Sciences,
El Jadida, Morocco

MOHAMED RAFIQ

Laboratoire de Chimie Minérale Appliquée,
Faculté des Sciences, Dhar El Mahraz, Fès, Morocco

PATRICK GOUGEON AND ROLAND GUERIN

Laboratoire de Chimie du Solide et Inorganique
Moléculaire, URA CNRS 1495, Université de Rennes I,
Avenue du Général Leclerc, 35042 Rennes CEDEX,
France

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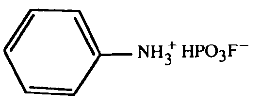
Abstract

The structure of the title compound shows a layer arrangement parallel to the *bc* plane. Two hydrogen monofluorophosphate anions are hydrogen-bonded and constitute $(H_2P_2O_6F_2)^{2-}$ anions, which are interconnected through strong N—H···O hydrogen bonds involving H atoms belonging to the $C_6H_5NH_3^+$ anilinium cations.

Comment

The monofluorophosphates of inorganic cations have been reported in several papers (Berndt, 1974; Durand, Cot & Galigné, 1974, 1978; Galigné, Durand & Cot, 1974; Durand, Granier, Cot & Galigné, 1975; Payen, Durand, Cot & Galigné, 1979; Durand, Larbot, Cot, Duprat & Dabosi, 1983; Durand, Cot, Berraho & Rafiq, 1987; Berraho, R'Kha, Vegas & Rafiq, 1992). Until now, no monofluorophosphate containing $C_6H_5NH_3^+$ organic cations has been reported.

In the present work, we describe the preparation and crystal structure of the first example of such a compound: the anilinium hydrogen monofluorophosphate, (I).



(I)

Figs. 1 and 2 give two different projections of this atomic arrangement, one along the *a* axis, the other along the *c* axis. The structure can be described as being built of atomic layers that are parallel to the *bc* plane and interact by van der Waals forces. In each layer, two HPO_3F^- anions are bonded together by means of two O(1)—H(1)···O(3) hydrogen bonds to form $(H_2P_2O_6F_2)^{2-}$ ring anions located around the inversion centres at the (0,0,0) and (1/2,1/2,0) positions.

The $C_6H_5NH_3^+$ cations are found alternately below and above the *bc* plane and are bonded to three $(H_2P_2O_6F_2)^{2-}$ dimers by means of the terminal H atoms of the NH_3 groups [N—H(7)···O(3), N—H(8)···O(2) and N—H(9)···O(2)]. The N—H distance varies according to the hydrogen-bond strength. The longest distance, N—H(9) (1.12 Å), induces a very strong hydrogen bond [N—H(9)···O(2) 1.62 Å].

The geometry of the HPO_3F^- tetrahedron is similar to that of its homologous hydrogen phosphite HPO_3H^- (Sghyar, Durand, Cot & Rafiq, 1990, 1991). It is characterized by two short and comparable P—O(2) and P—O(3) distances (1.48 Å) where the O atom is not directly linked to the H atom, and one longer P—O(1) distance (1.55 Å) to the O atom of the hydroxyl group. The lengthening of the latter distance can be correlated with the strength of the O(1)—H(1)···O(3) hydrogen bond (1.64 Å).

The averages of the P—O distances (1.508 Å) and of the F—P—O angles (105.6°) are comparable to those observed in the PO_3F^{2-} and $PO_2F_2^-$ groups. On the other hand, the average O—P—O angle (112.9°) is significantly smaller than all the values observed in the P^V oxyfluoride ions (Durand, Falius, Galigné & Cot, 1978).

The F atom of the HPO_3F^- ion, found in the *bc* plane, is only bonded to the P atom. This arrangement has been observed previously in the case of the monofluorophosphates of alkali and divalent transition metals (Durand, Granier, Cot & Galigné, 1975; Payen, Durand, Cot & Galigné, 1979; Durand, Larbot, Cot, Duprat & Dabosi, 1983; Durand, Cot, Berraho & Rafiq, 1987).

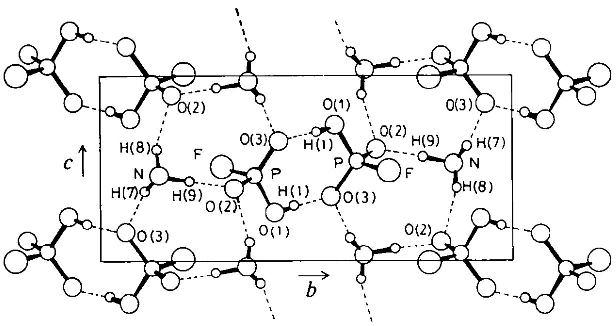


Fig. 1. Projection of the title structure along **a**.

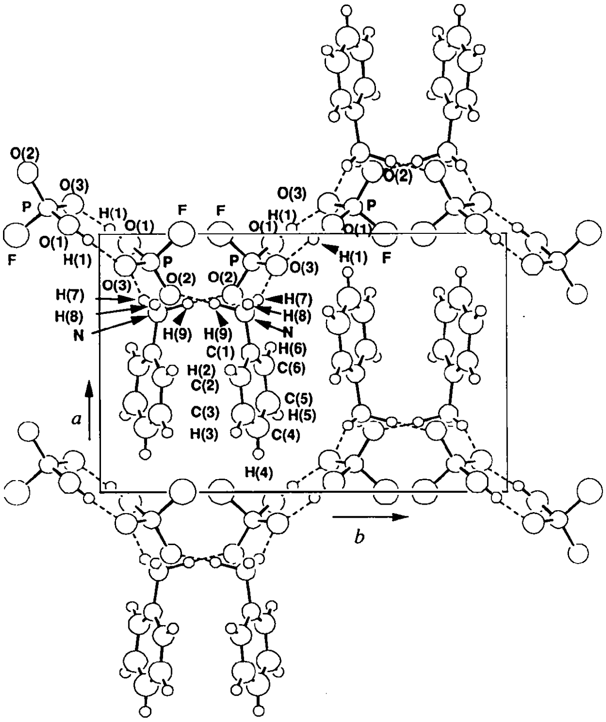


Fig. 2. Projection of the title structure along **c**.

The P—F distance [1.549 (3) Å] compares favourably with those observed in $ZnPO_3F.5/2H_2O$ (Durand, Larbot, Cot, Duprat & Dabosi, 1983), but is clearly shorter than those found in the other monofluorophosphates (Durand, Granier, Cot & Galigné, 1975; Payen, Durand, Cot & Galigné, 1979; Durand, Cot, Berraho & Rafiq, 1987; Berraho, R'Kha, Vegas & Rafiq, 1992).

The intramolecular bond distances and angles of the anilinium cation are in good agreement with the literature data (Fecher & Weiss, 1986; Tordjman, Masse & Guitel, 1988; Hartmann, Dou & Weiss, 1990; Masse & Levy, 1991). The C(1)—N distance (1.481 Å) and the C(6)—C(1)—C(2) angle (121.9°) are comparable with those [1.462 Å and 121.7°] given by Domenicano, Serantoni & Sanseverino (1977). The ring plane is inclined by 21.62° with respect to the *ac* plane. The N atom deviates by −0.078 Å from the phenyl plane and has a distorted tetrahedral environment.

Experimental

Single crystals were prepared by slow evaporation at 213 K of a mixture of an aqueous solution of $NH_4PO_3F.H_2O$ and C_6H_8ClN in the ratios 1:1. The IR spectrum revealed the presence of both $C_6H_5NH_3^+$ and HPO_3F^- ions.

Crystal data

$C_6H_8N^+.HPO_3F^-$
$M_r = 193.12$
Monoclinic
$P2_1/c$
$a = 9.418 (6)$ Å
$b = 14.31 (1)$ Å
$c = 6.303 (7)$ Å
$\beta = 92.45 (7)°$
$V = 848.7 (2)$ Å^3
$Z = 4$
$D_x = 1.51$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4–18°$
$\mu = 0.299$ mm^{-1}
$T = 295$ K
Needle
0.69 × 0.11 × 0.10 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2636 measured reflections
2505 independent reflections
779 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.042$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 20$
$l = -8 \rightarrow 8$
3 standard reflections
frequency: 90 min
intensity decay: 0.1%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.049$
$S = 1.165$
779 reflections
137 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.05F_o^2)^2]$
$(\Delta/\sigma)_{\rm max} = 0.04$

$\Delta\rho_{\rm max} = 0.52$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.05$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 2.9 (1) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$
P	0.8922 (1)	0.3748 (1)	0.5420 (2)	3.00 (2)
F	0.0010 (3)	0.2975 (2)	0.4924 (5)	5.77 (8)
O(1)	0.9628 (4)	0.4258 (3)	0.7369 (5)	4.06 (8)
O(2)	0.7621 (3)	0.3265 (2)	0.6080 (5)	3.55 (8)
O(3)	0.8787 (4)	0.4359 (3)	0.3512 (5)	4.00 (8)
N	0.3053 (4)	0.8568 (3)	0.4651 (6)	3.08 (9)
C(1)	0.4599 (5)	0.8706 (4)	0.4438 (7)	2.9 (1)
C(2)	0.5076 (5)	0.9042 (4)	0.2563 (8)	3.7 (1)
C(3)	0.6525 (6)	0.9130 (5)	0.2343 (8)	4.8 (1)

C(4)	0.7467 (5)	0.8867 (4)	0.3994 (9)	4.8 (1)
C(5)	0.6969 (6)	0.8521 (4)	0.5851 (9)	4.6 (1)
C(6)	0.5519 (5)	0.8448 (4)	0.6094 (8)	3.8 (1)

Table 2. *Selected geometric parameters* (Å, °)

P—F	1.549 (3)	C(3)—C(4)	1.390 (7)
P—O(2)	1.482 (3)	C(4)—C(5)	1.372 (8)
P—O(1)	1.554 (4)	C(5)—C(6)	1.385 (7)
P—O(3)	1.488 (4)	C(6)—C(1)	1.378 (7)
C(1)—N	1.481 (6)	N—H(7)	0.86 (5)
C(1)—C(2)	1.369 (7)	N—H(8)	0.91 (5)
C(2)—C(3)	1.383 (7)	N—H(9)	1.12 (6)
F—P—O(2)	106.6 (2)	N—C(1)—C(6)	119.0 (8)
F—P—O(1)	103.3 (4)	C(6)—C(1)—C(2)	121.9 (9)
F—P—O(3)	106.9 (4)	C(1)—C(2)—C(3)	118.7 (7)
O(2)—P—O(1)	109.1 (4)	C(2)—C(3)—C(4)	120.1 (9)
O(1)—P—O(3)	112.5 (4)	C(3)—C(4)—C(5)	120.4 (10)
O(2)—P—O(3)	117.2 (5)	C(4)—C(5)—C(6)	119.8 (10)
N—C(1)—C(2)	119.0 (8)	C(5)—C(6)—C(1)	119.2 (9)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*
N—H(7)···O(3^{i})	0.86 (5)	1.98 (5)	2.822 (5)
N—H(8)···O(2^{ii})	0.91 (5)	1.97 (5)	2.824 (5)
N—H(9)···O(2^{iii})	1.12 (6)	1.62 (6)	2.733 (5)
O(1)—H(1)···O(3^{iv})	0.92 (6)	1.64 (6)	2.554 (6)

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

Data were corrected for Lorentz–polarization effects. The structure was solved with the aid of *MULTAN*11/82 (Main *et al.*, 1982) and subsequent difference Fourier syntheses. All calculations were performed with the *MolEN* (Fair, 1990) programs on a Digital MicroVAX 3100 computer.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: DU1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloroxylenol, C_8H_9ClO

PHILIP J. COX

School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB9 1FR, Scotland

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Abstract

The crystal structure of 4-chloro-3,5-dimethylphenol has been determined. There are two independent molecules in the asymmetric unit and the molecules are held together by hydrogen bonding. Each O atom acts as both an acceptor and a donor in the intermolecular hydrogen-bonding scheme.

Comment

The crystal structures of numerous simple aromatic compounds were studied many years ago (Wyckoff, 1969) but today's instrumentation now results in molecular geometries with e.s.d.'s that can often be lower by a factor of ten.

4-Chlorophenol is used as an intermediate in the synthesis of some biocides, fungicides and drugs (Kroschwitz & Howe-Grant, 1992), whereas 4-chloro-3,5-dimethylphenol is a chlorinated phenolic antiseptic which is a bactericide against most Gram-positive bacteria (Reynolds, 1993). The crystal structures of two polymorphic forms of 4-chlorophenol have been reported (Perrin & Michel, 1973) and the molecule is known to form complexes (Shipley & Wallwork, 1967) and clathrates (Ung, Bishop, Craig, Dance & Scudder, 1993) with other molecules. Accurate studies of intermolecular forces exhibited by such molecules are of increasing importance because of the possibilities offered