



Synthesis and crystal structure of 4-fluorobenzylammonium dihydrogen phosphate, $[\text{FC}_6\text{H}_4\text{CH}_2\text{NH}_3]\text{H}_2\text{PO}_4$

Ali Rayes,^a Ahlem Dadi,^a Najla Mahbouli Rhouma,^b Francesco Mezzadri^c and Gianluca Calestani^{c*}

Received 21 October 2016
Accepted 10 November 2016

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; organic inorganic hybrid materials; hydrogen bonds.

CCDC reference: 1516161

Supporting information: this article has supporting information at journals.iucr.org/e

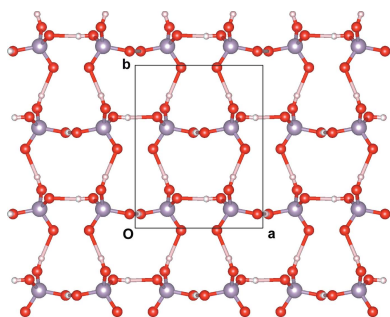
^aUnité de Recherche, Catalyse et Matériaux pour l'Environnement et les Procédés, URCMEP, (UR11ES85), Faculté des Sciences de Gabès, Campus Universitaire, 6072 Gabès, Tunisia, ^bLaboratoire des Sciences des Matériaux et d'Environnement, Faculté des Sciences, Université de Sfax, BP 1171, Route de Soukra, 3018 Sfax, Tunisia, and ^cDipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17A, I-43124 Parma, Italy. *Correspondence e-mail: gianluca.calestani@unipr.it

The asymmetric unit of the title salt, $[p\text{-FC}_6\text{H}_4\text{CH}_2\text{NH}_3]^+\cdot\text{H}_2\text{PO}_4^-$, contains one 4-fluorobenzylammonium cation and one dihydrogen phosphate anion. In the crystal, the H_2PO_4^- anions are linked by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to build corrugated layers extending parallel to the ab plane. The $\text{FC}_6\text{H}_4\text{CH}_2\text{NH}_3^+$ cations lie between these anionic layers to maximize the electrostatic interactions and are linked to the H_2PO_4^- anions through $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a three-dimensional supramolecular network. Two hydrogen atoms belonging to the dihydrogen phosphate anion are statistically occupied due to disorder along the $\text{OH}\cdots\text{HO}$ direction.

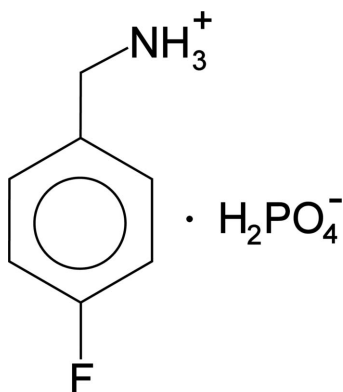
1. Chemical context

A hybrid compound is a material that involves both organic and inorganic components blended in the solid state on the molecular scale. Such materials allow the combination of the intended properties of both the organic and inorganic components when they self-assemble in the crystal. The resulting properties do not simply consist of the sum of the individual contributions, since they also strongly depend on the nature of the interactions established by the different components within the structure. The nature of the interactions has been used to divide organic–inorganic hybrid materials into two different classes, both of them being of technological interest. In class I, organic and inorganic components are connected together through strong chemical covalent or iono-covalent bonds; in class II, the two components are assembled by weaker interactions, such as hydrogen bonds and/or van der Waals and Coulombic interactions.

In particular, in considering hybrid systems belonging to class II, derivatives from orthophosphoric acid (H_3PO_4) are often associated with functionalized organic molecules (amines or amides) to produce organic–inorganic materials with potentially forceful hydrogen-bonding interactions between donor (D) and acceptor (A) components. Among these hybrid phosphates, the dihydrogen phosphates have received great interest over recent years. Indeed, these compounds can be considered the most stable organic phosphates and also the first to be studied in more detail. They have a technological interest in many realms, such as magnetism, electricity, optics and in biomaterials research (Adams, 1977; Hearn & Bugg, 1972).



In these compounds, the acidic dihydrogen phosphate anion H_2PO_4^- , through the formation of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, gives rise to various topologies of anionic substructures. In the crystal structure of 2-ammoniumbenzamide dihydrogen phosphate (Belghith *et al.*, 2015), the H_2PO_4^- tetrahedra are associated in pairs, forming centrosymmetric finite units, while in 2,3-dimethylanilinium dihydrogen phosphate (Rayes *et al.*, 2004), they form a network composed of hydrogen-bonded chains. Two-dimensional anionic layers are observed in 4-chloroanilinium dihydrogen phosphate (Dhaouadi *et al.*, 2008) and in 2-methylpiperazinedium dihydrogen phosphate (Choudhury *et al.*, 2000), while in the crystal structure of imidazolium dihydrogen phosphate (Blessing *et al.*, 1986), the H_2PO_4^- anions are linked by hydrogen bonds to form a three-dimensional cage-type network, inside which the cations are trapped. The varieties of the observed arrangements suggest that selected packing architectures can be designed by choosing an appropriate amine.



In order to enrich the knowledge of such kinds of hybrid materials and to investigate the effect of hydrogen bonds on chemical and structural features, we report here synthesis and crystal structure analysis of the novel organic dihydrogen phosphate, $(p\text{-FC}_6\text{H}_4\text{CH}_2\text{NH}_3)^+\cdot\text{H}_2\text{PO}_4^-$.

2. Structural commentary

The title hybrid salt crystallizes in the *Pbcn* space group with one *para*-fluorobenzylammonium cation and one dihydrogen phosphate anion in the asymmetric unit (Fig. 1). Analysis of the P–O bond lengths clearly reveals the double-bond character of the P–O2 interaction [1.492 (4) Å], suggesting at the same time the possible protonation of the remaining O atoms showing longer bonds [P1–O1 = 1.561 (4), P1–O3 = 1.543 (4) and P1–O4 = 1.535 (4) Å]. This is confirmed by the presence of electron density peaks close to these oxygen atoms, compatible in terms of height and distance from hydrogen atoms. However, the refinement showed half occupancy for two of the three hydrogen atoms, in agreement with charge neutrality and geometric considerations (both are disordered over two positions along the $\text{O}-\text{H}\cdots\text{H}-\text{O}$ direction involving the same oxygen atom in two adjacent anions). This explains the shorter P–O3 and P–O4 bond lengths, when compared with P1–O1, revealing at the same time the

Table 1
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1O}\cdots\text{O2}^{\text{i}}$	0.82	1.75	2.569 (5)	172
$\text{O3}-\text{H3O}\cdots\text{O3}^{\text{ii}}$	0.82	1.67	2.483 (5)	168
$\text{O4}-\text{H4O}\cdots\text{O4}^{\text{iii}}$	0.82	1.71	2.523 (5)	174
$\text{N1}-\text{H1A}\cdots\text{O2}^{\text{iv}}$	0.89	1.91	2.785 (6)	169
$\text{N1}-\text{H1B}\cdots\text{O3}^{\text{v}}$	0.89	1.96	2.831 (6)	167
$\text{N1}-\text{H1C}\cdots\text{O4}$	0.89	2.03	2.900 (6)	164

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

composition of the resulting anion as H_2PO_4^- . The organic cation exhibits a regular configuration, with distances and angles in accordance to literature data (Wang *et al.*, 2015; Klapötke *et al.*, 2003).

3. Supramolecular features

The presence in the title compound of a number of donor and acceptor sites leads to the formation of a complex $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding system (Table 1) which, supported by electrostatic and van der Waals interactions, gives rise to the formation of a stable three-dimensional supramolecular network. $\text{O1}-\text{H1O}\cdots\text{O2}$, $\text{O3}-\text{H3O}\cdots\text{O3}$ and $\text{O4}-\text{H4O}\cdots\text{O4}$ hydrogen bonds connect each dihydrogen phosphate unit to an adjacent one, which results in the formation of an infinite two-dimensional corrugated layer of anions extending parallel to the *ab* plane (Fig. 2). In the inorganic supramolecular layers, rings with a graph-set ring motif (Etter, 1990) of $R_4^4(16)$ are found, lying at $z \sim 1/4$ and $3/4$. The 4-fluorobenzylammonium cations are trapped between the anionic layers to maximize the electrostatic interactions and are linked to the H_2PO_4^- anions through $\text{N1}-\text{H1A}\cdots\text{O2}$, $\text{N1}-\text{H1B}\cdots\text{O3}$ and $\text{N1}-\text{H1C}\cdots\text{O4}$ hydrogen bonds, forming $R_3^3(12)$ graph-set motifs with the $\text{O}-\text{H}\cdots\text{O}$ bonds. The cations are anchored on both sides of the H_2PO_4^- anionic layer, resulting in the stacking of an alternating organic–

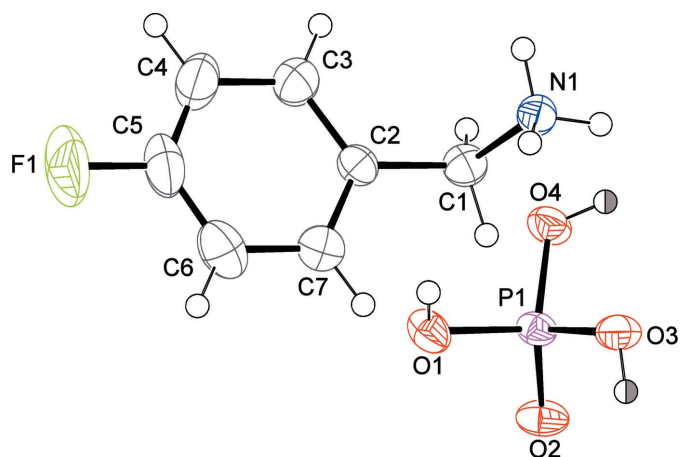


Figure 1
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level. The two half-filled H atoms have a site-occupation factor of 0.5.

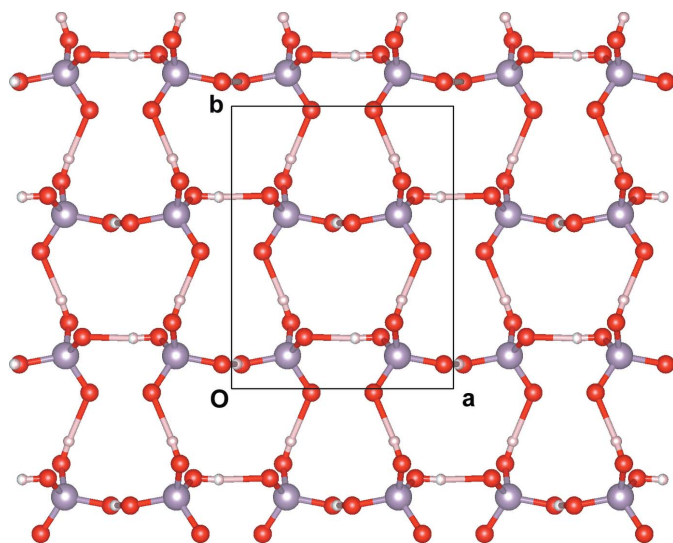


Figure 2
A layer of H_2PO_4^- anions, parallel to the ab plane, formed by hydrogen bonds displaying $R_4^2(16)$ graph-set ring motifs.

inorganic supramolecular network (Fig. 3) along the c axis. Within the organic network, the dipolar character of the 4-fluorobenzylammonium molecule leads to an alternating antiparallel molecular stacking along the a axis that prevents significant π - π interactions between the aromatic rings but promotes van der Waals interactions as the unique intermolecular interactions between the organic molecules.

4. Database survey

A search of the Cambridge Structural Database (Version 5.37; last update February 2016; Groom *et al.*, 2016) for related

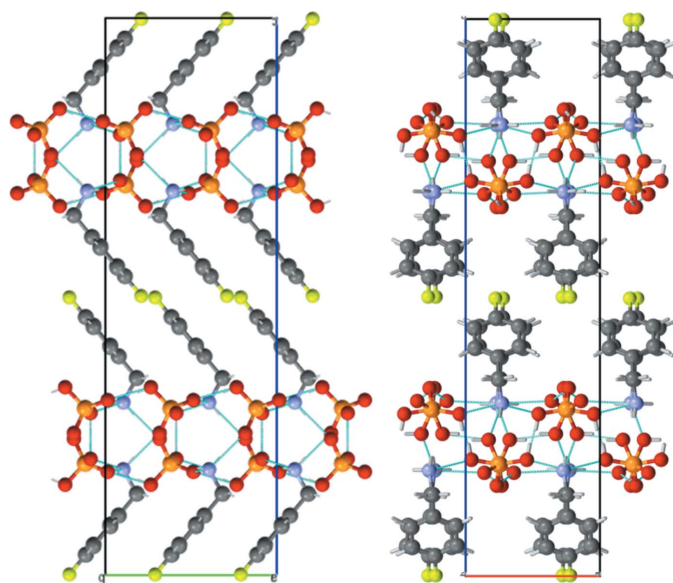


Figure 3
Projections of the $[\text{FC}_6\text{H}_4\text{CH}_2\text{NH}_3]\text{H}_2\text{PO}_4$ structure along the a axis (left) and the b axis (right), showing the alternate stacking of inorganic and organic layers along the c axis.

Table 2
Experimental details.

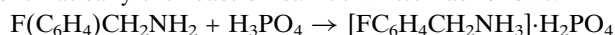
Crystal data	
Chemical formula	$\text{C}_7\text{H}_9\text{FN}^+\cdot\text{H}_2\text{PO}_4^-$
M_r	223.14
Crystal system, space group	Orthorhombic, $Pbcn$
Temperature (K)	294
a, b, c (Å)	7.1630 (8), 9.1309 (10), 29.694 (3)
V (Å ³)	1942.1 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.29
Crystal size (mm)	0.36 × 0.31 × 0.27
Data collection	
Diffractometer	Bruker SMART CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
T_{\min}, T_{\max}	0.813, 0.846
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19365, 1803, 1780
R_{int}	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.077, 0.170, 1.33
No. of reflections	1803
No. of parameters	131
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.52, -0.65

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *VESTA* (Momma & Izumi, 2011).

compounds showed that $[\text{FC}_6\text{H}_4\text{CH}_2\text{NH}_3]\cdot\text{H}_2\text{PO}_4$, is isotopic with 4-chlorobenzylammonium dihydrogen phosphate (Dhaouadi *et al.*, 2005). The main difference concerns the hydrogen atoms of the dihydrogen phosphate anion. These, ordered on two sites in the latter structure, are located over three positions for the title structure, two of which show half occupancy. In spite of this difference, the resulting anionic framework and the linking of the cations are analogous in both cases. A similarly organized anionic layer is formed by self-assembly of H_2PO_4^- units in the structure of octane-1,8-diammonium bis(dihydrogen phosphate) (Mrad *et al.*, 2011). Although the amine used is of different nature, the compound crystallizes in the same space group $Pbcn$ and, approximately similar to the present case, two hydrogen atoms were found to be shared along the O—H—O bonding direction involving two H_2PO_4^- groups. The difference in the organic moiety is reflected in a different anchoring of the cations on the anionic layers, building in this case a three-dimensional hydrogen-bonded network.

5. Synthesis and crystallization

Crystals of the title compound were grown by dissolving in water *p*-fluorobenzylamine (purity 99%, Sigma–Aldrich) and orthophosphoric acid (85%_{w/w}, $d = 1.7 \text{ kg cm}^{-3}$) in a 1:1 molar ratio. The resulting mixture was heated slightly (330 K) under constant stirring for 3 h to obtain a clear solution. Schematically the reaction can be written as follows:



The solution thus obtained was placed in a Petri dish and kept for crystallization at room temperature without disturbance. Single crystals of the title compound, suitable for X-ray diffraction analysis, were obtained after one week (yield 82%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were located in a difference Fourier map and refined as riding, with O—H = 0.82 Å, N—H = 0.89 Å, C—H = 0.93 and 0.97 Å. A rotating model was used for the OH and ammonium groups. The dihydrogen phosphate H atoms were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, those of the ammonium H atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$, and the remaining ones with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Two H atoms were found to be disordered over two positions along the O—H \cdots H—O direction involving the same oxygen atom in two adjacent anions and refined with half occupancy. An outlier (524) was omitted in the last cycles of the refinement.

Acknowledgements

We would like to acknowledge the support provided by the Secretary of State Scientific Research and Technology of Tunisia.

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supporting information

Acta Cryst. (2016). E72, 1812-1815 [https://doi.org/10.1107/S2056989016018090]

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

(I)

Crystal data

$\text{C}_7\text{H}_9\text{FN}^+\cdot\text{H}_2\text{PO}_4^-$

$M_r = 223.14$

Orthorhombic, *Pbcn*

$a = 7.1630$ (8) Å

$b = 9.1309$ (10) Å

$c = 29.694$ (3) Å

$V = 1942.1$ (4) Å³

$Z = 8$

$F(000) = 928$

$D_x = 1.526$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4573 reflections

$\theta = 5.5\text{--}37.8^\circ$

$\mu = 0.29$ mm⁻¹

$T = 294$ K

Prism, colourless

$0.36 \times 0.31 \times 0.27$ mm

Data collection

Bruker SMART CCD
diffractometer

ω scan

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.813$, $T_{\max} = 0.846$

19365 measured reflections

1803 independent reflections

1780 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 1.4^\circ$

$h = -8 \rightarrow 8$

$k = -11 \rightarrow 11$

$l = -35 \rightarrow 35$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.077$

$wR(F^2) = 0.170$

$S = 1.33$

1803 reflections

131 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 11.9717P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.52$ e Å⁻³

$\Delta\rho_{\min} = -0.65$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
P1	0.7518 (2)	0.61709 (14)	0.29940 (4)	0.0247 (3)	
O1	0.7675 (6)	0.7342 (4)	0.33752 (11)	0.0346 (9)	
H1O	0.7332	0.8139	0.3279	0.052*	
O2	0.8598 (5)	0.4862 (4)	0.31440 (13)	0.0328 (9)	
O3	0.8281 (5)	0.6833 (4)	0.25529 (12)	0.0325 (9)	
H3O	0.9425	0.6786	0.2553	0.049*	0.5
O4	0.5439 (5)	0.5863 (4)	0.29115 (12)	0.0336 (9)	
H4O	0.5230	0.5869	0.2640	0.050*	0.5
N1	0.2305 (6)	0.3951 (5)	0.31025 (13)	0.0304 (10)	
H1A	0.1169	0.4344	0.3092	0.046*	
H1B	0.2441	0.3322	0.2876	0.046*	
H1C	0.3158	0.4655	0.3079	0.046*	
C1	0.2552 (9)	0.3166 (6)	0.35386 (16)	0.0334 (12)	
H1D	0.3705	0.2609	0.3531	0.040*	
H1E	0.1530	0.2482	0.3580	0.040*	
C2	0.2606 (8)	0.4220 (6)	0.39291 (16)	0.0297 (11)	
C3	0.0985 (9)	0.4714 (7)	0.4122 (2)	0.0427 (15)	
H3	-0.0159	0.4388	0.4013	0.051*	
C4	0.1037 (11)	0.5698 (8)	0.4480 (2)	0.0541 (19)	
H4	-0.0059	0.6043	0.4610	0.065*	
C5	0.2724 (12)	0.6139 (8)	0.46325 (19)	0.0543 (18)	
C6	0.4362 (11)	0.5685 (8)	0.4453 (2)	0.0558 (19)	
H6	0.5498	0.6013	0.4566	0.067*	
C7	0.4285 (9)	0.4709 (7)	0.4093 (2)	0.0442 (15)	
H7	0.5388	0.4383	0.3961	0.053*	
F1	0.2783 (8)	0.7094 (5)	0.49869 (14)	0.0887 (17)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0248 (6)	0.0201 (6)	0.0293 (6)	0.0016 (5)	-0.0057 (6)	0.0010 (5)
O1	0.043 (2)	0.0255 (18)	0.0348 (19)	0.0029 (18)	-0.0126 (19)	-0.0025 (16)
O2	0.0263 (19)	0.0222 (17)	0.050 (2)	0.0002 (16)	-0.0069 (18)	0.0051 (17)
O3	0.0229 (18)	0.042 (2)	0.0326 (19)	0.0039 (18)	0.0007 (16)	0.0095 (17)
O4	0.0226 (18)	0.048 (2)	0.0299 (19)	-0.0048 (18)	-0.0031 (16)	0.0030 (18)
N1	0.029 (2)	0.032 (2)	0.030 (2)	-0.001 (2)	0.001 (2)	-0.0028 (19)
C1	0.037 (3)	0.027 (3)	0.036 (3)	0.004 (3)	-0.002 (3)	0.002 (2)
C2	0.032 (3)	0.029 (3)	0.028 (2)	-0.001 (2)	-0.003 (2)	0.003 (2)
C3	0.039 (3)	0.050 (4)	0.040 (3)	-0.001 (3)	0.003 (3)	-0.003 (3)

C4	0.063 (5)	0.061 (4)	0.039 (4)	0.013 (4)	0.009 (3)	-0.006 (3)
C5	0.082 (5)	0.048 (4)	0.033 (3)	0.003 (4)	-0.006 (4)	-0.010 (3)
C6	0.060 (5)	0.060 (4)	0.047 (4)	-0.011 (4)	-0.013 (4)	-0.009 (3)
C7	0.042 (3)	0.050 (4)	0.041 (3)	0.007 (3)	-0.004 (3)	-0.003 (3)
F1	0.127 (4)	0.084 (3)	0.055 (2)	0.002 (3)	-0.010 (3)	-0.039 (2)

Geometric parameters (Å, °)

P1—O2	1.492 (4)	C1—H1E	0.9700
P1—O4	1.535 (4)	C2—C3	1.371 (8)
P1—O3	1.543 (4)	C2—C7	1.372 (8)
P1—O1	1.561 (4)	C3—C4	1.391 (9)
O1—H1O	0.8200	C3—H3	0.9300
O3—H3O	0.8200	C4—C5	1.352 (11)
O4—H4O	0.8200	C4—H4	0.9300
N1—C1	1.491 (6)	C5—C6	1.354 (11)
N1—H1A	0.8900	C5—F1	1.367 (7)
N1—H1B	0.8900	C6—C7	1.393 (9)
N1—H1C	0.8900	C6—H6	0.9300
C1—C2	1.508 (7)	C7—H7	0.9300
C1—H1D	0.9700		
O2—P1—O4	113.9 (2)	H1D—C1—H1E	108.0
O2—P1—O3	112.5 (2)	C3—C2—C7	119.2 (5)
O4—P1—O3	106.3 (2)	C3—C2—C1	120.7 (5)
O2—P1—O1	107.1 (2)	C7—C2—C1	120.2 (5)
O4—P1—O1	108.1 (2)	C2—C3—C4	120.6 (6)
O3—P1—O1	108.8 (2)	C2—C3—H3	119.7
P1—O1—H1O	109.5	C4—C3—H3	119.7
P1—O3—H3O	109.5	C5—C4—C3	118.2 (7)
P1—O4—H4O	109.5	C5—C4—H4	120.9
C1—N1—H1A	109.5	C3—C4—H4	120.9
C1—N1—H1B	109.5	C4—C5—C6	123.4 (6)
H1A—N1—H1B	109.5	C4—C5—F1	118.4 (7)
C1—N1—H1C	109.5	C6—C5—F1	118.2 (7)
H1A—N1—H1C	109.5	C5—C6—C7	117.7 (7)
H1B—N1—H1C	109.5	C5—C6—H6	121.2
N1—C1—C2	111.4 (4)	C7—C6—H6	121.2
N1—C1—H1D	109.4	C2—C7—C6	121.0 (6)
C2—C1—H1D	109.4	C2—C7—H7	119.5
N1—C1—H1E	109.4	C6—C7—H7	119.5
C2—C1—H1E	109.4		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1O \cdots O2 ⁱ	0.82	1.75	2.569 (5)	172
O3—H3O \cdots O3 ⁱⁱ	0.82	1.67	2.483 (5)	168

O4—H4O···O4 ⁱⁱⁱ	0.82	1.71	2.523 (5)	174
N1—H1A···O2 ^{iv}	0.89	1.91	2.785 (6)	169
N1—H1B···O3 ^v	0.89	1.96	2.831 (6)	167
N1—H1C···O4	0.89	2.03	2.900 (6)	164

Symmetry codes: (i) $-x+3/2, y+1/2, z$; (ii) $-x+2, y, -z+1/2$; (iii) $-x+1, y, -z+1/2$; (iv) $x-1, y, z$; (v) $x-1/2, y-1/2, -z+1/2$.