Migrating hydrogen in 2,4,6-triaminopyrimidin-ium(1+)_x hydrogen trioxofluorophosphate(−)_x monohydrate/2,4,6-triaminopyrimidin-ium(2+)_{1−x} trioxofluorophosphate(2−)_{1−x} monohydrate (0.0 < x < 0.73) with changing temperature

Irena Matulková,^a Jan Fábry,^{b*} Ivan Němec,^a Ivana Císařová^a and Přemysl Vaněk^b

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^aFaculty of Science, The Charles University, Hlavova 2030/8, 128 43 Praha 2, Czech Republic, and ^bInstitute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Praha 8, Czech Republic. *Correspondence e-mail: fabry@fzu.cz

The data of the title structure of 2,4,6-triaminopyrimidin-ium(1+)_x hydrogen trioxofluorophosphate(1−)_x monohydrate/2,4,6-triaminopyrimidin-ium(2+)_{1−x} trioxofluorophosphate(2−)_{1−x} monohydrate (0.0 < x < 0.73), with the sum formula C₄H₁₁FN₅O₄P, were collected in 10 K intervals between 290 and 150 K, as well as at 100 K. The most interesting feature is the presence of a moderate though still strong O—H...N/O...H—N hydrogen bond. Its bridging H atom was found to be disordered over two positions in the temperature interval 290–220 K, with the larger occupation towards the O atom. The occupation in the latter position decreased with decreasing temperature, though not monotonously. At 210 K and below, the difference electron-density maps showed just one maximum which was closer to the N atom. Though difference scanning calorimetry (DSC) revealed no anomaly in the interval 303–93 K, the dependence of the length of the unit-cell axes *b* and *c* on temperature showed a kink in the slope at about 190 K. The N...O distance of the mentioned hydrogen bond or the occupational parameter of the electron density of the disordered H atom indicate less pronounced anomalies for the temperatures 270 and 230 K. The cation and the anion, as well as the water molecules, form layers which are parallel to (10 $\bar{1}$) and which are interconnected by O—H...N (in the interval 290–220 K), N—H...O and O—H...O hydrogen bonds of moderate strength. The layers are arranged into centrosymmetric double layers in which the F atoms are directed outwards. The layers are interconnected by water–acid O—H...O hydrogen bonds, weak N—H...F interactions and π -electron ring... π -electron ring interactions. The dependence of P—F bond lengths on bonding properties of the trioxofluorophosphate or hydrogen trioxofluorophosphate anions is discussed. It has been recognized that a carbon-bonded F atom avoids participation in a hydrogen-bond pattern; however, this property seems to be also common to fluorine bonded to P, As and S, especially if an oxygen ligand is also present in a molecule. The deposited material contains an overview of the determined structures with trioxofluorophosphate or hydrogen trioxofluorophosphate anions.

1. Introduction

The aim of the present work was the preparation of a structure which was hoped would be isostructural with bis(2,4,6-triaminopyrimidin-ium) phosphite heptahydrate. The preparation of the latter compound (Kodrlová, 2007) was motivated by the search for novel materials with nonlinear optical properties. Its crystal structure has been deposited with the

Table 1

An overview of structures with a migrating H atom in O...O and N...O hydrogen bonds due to temperature changes.

Reference	Compound	Probe	$T_{\min}$ – $T_{\max}$ (K)	Refcodes for $T_{\min}/T_{\max}$ structures
Bond				
$T_{\min}$ (K)	$D\cdots H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D\cdots H\cdots A$ (°)
$T_{\max}$ (K)	$D\cdots H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D\cdots H\cdots A$ (°)
O...H...O				
Olovsson <i>et al.</i> (2001)	<i>a</i>	Neutron	30–295	KHDCMT02/KHDCMT01
O2–H1...O6				
30	1.268 (12)	1.185 (12)	2.437 (2)	167 (1)
295	1.214 (15)	1.259 (15)	2.453 (2)	166 (1)
Olovsson <i>et al.</i> (2002)	<i>a</i>	Neutron	30–295	KHDCMT02/KHDCMT01
O2–H1...O6				
30	1.268 (12)	1.185 (12)	2.437 (2)	167 (1)
295	1.214 (15)	1.259 (15)	2.453 (2)	166 (1)
Wilson (2001)	<i>b</i>	Neutron	150–335	CRBAMP05/CRBAMP18
O5–H7...O4				
150	1.177 (8)	1.232 (7)	2.400 (5)	170.1 (8)
335	1.214 (15)	1.226 (13)	2.430 (9)	169.7 (12)
Parkin <i>et al.</i> (2004)	<i>b</i>	X-ray	150–350	CRBAMP26/CRBAMP30
O5–H7...O4				
150	1.1756 (9)	1.2546 (8)	2.4198 (12)	169.42 (5)
350	1.2182 (12)	1.2156 (11)	2.4257 (16)	170.64 (7)
Wilson <i>et al.</i> (2001)	<i>b</i>	Neutron	150–350	CRBAMP19/CRBAMP25
O5–H7...O4				
150	1.168 (4)	1.252 (4)	2.411 (2)	169.8 (4)
350	1.210 (7)	1.217 (8)	2.420 (5)	171.5 (6)
Thomas <i>et al.</i> (2009)	<i>c</i>	Neutron	100–280	DBEZLM07/DBEZLM12
O2–H12...O1				
100	1.113 (11)	1.372 (11)	2.435 (6)	156.9 (8)
280	1.13 (3)	1.39 (3)	2.468 (14)	155.0 (18)
Thomas <i>et al.</i> (2009)	<i>c</i>	X-ray	100–293	DBEZLM13/DBEZLM19
O2–H12...O1				
100	1.15 (2)	1.33 (2)	2.4486 (14)	159 (2)
293	1.25 (3)	1.26 (3)	2.4641 (18)	158 (2)
Thomas <i>et al.</i> (2010)	<i>d</i>	Neutron	40–300	QUQCUB/QUQCUB03
O2–H5...O1				
40	1.009 (7)	1.645 (7)	2.652 (5)	175.2 (6)
300	1.29 (3)	1.33 (3)	2.624 (17)	177 (3)
Thomas <i>et al.</i> (2010)	<i>d</i>	X-ray	100–300	QUQCUB04/QUQCUB06
O8–H19...O7				
100	1.10 (3)	1.54 (3)	2.6368 (15)	176 (3)
300	1.24 (3)	1.40 (4)	2.633 (2)	177 (3)
Wilson (2002)	<i>e</i>	Neutron	20–300	ACSALA05/ACSALA07
O1–H8...O2				
20	1.017 (7)	1.625 (7)	2.641 (4)	177.0 (7)
300	1.07 (3)	1.56 (3)	2.626 (15)	175 (2)
O...H(split)...O				
Wilson <i>et al.</i> (2006)	<i>f</i>	Neutron	100–298	CLBZAP05/CLBZAP04
O1–H1...O2				
100	0.997 (6)	1.595 (6)	2.588 (4)	173.9 (6)
298	1.011 (15)	1.600 (15)	2.608 (7)	174.6 (15)
O2...H1A...O1				
100	0.83 (5)	1.81 (6)	2.588 (4)	156 (6)
298	0.79 (4)	1.84 (5)	2.608 (8)	164 (5)

Cambridge Crystallographic Data Centre under deposition number CCDC 1509706. The ability to form mixed crystals with substituted $[\text{PO}_3\text{F}]^{2-}$ and $[\text{HPO}_3]^{2-}$ anions has been observed in a few cases (Fábry *et al.*, 2012, and references therein), as well as in a recently prepared series of bis(guanidinium) trioxofluorophosphate/phosphite salts in the ratios 1:0, 3:1, 1:1, 1:3 and 0:1 (Matulková *et al.*, 2017). Searches in the Inorganic Crystal Structure Database (2016) and the Cambridge Structural Database (CSD; Groom *et al.*, 2016) revealed that no other mixed phosphites and trioxofluorophosphates had been included in either of these databases since 2012.

It turned out that the obtained title structure differs from the phosphite; however, it shows features which are still worthy of discussion. Most importantly, the structure analysis revealed an interesting O...N hydrogen bond between the base and the acid molecule in which the disordered bridging H atom migrates from the O atom towards the N atom with decreasing temperature.

There are precedents regarding migration of bridging H atoms from donor to acceptor atoms with changing temperature, both in structures with O...O and O...N hydrogen bonds. Table 1 lists examples where the migration of the H atom has been observed for such hydrogen bonds. It is of interest that there is a relatively small number of such examples. It is even more surprising because the problem of the localization of the H atom in such an environment, especially for N...H...O hydrogen bonds, is a hot topic in pharmacology (*e.g.* Childs *et al.*, 2007). The CSD yielded about 200 hits for an H atom situated towards the centre between O and N atoms (the N–H and O–H distances were allowed to be situated in the interval 1.2–1.5 Å). In these structures, migration of the bridging H atom due to changing temperature may be present.

The ability of an H atom to be situated between the donor and acceptor atoms, *i.e.* in a possible transition state during the migration of an H atom, has been observed for rather strong hydrogen bonds (Gilli & Gilli, 2009). Such bonds tend to occur in structures where the difference $\Delta\text{p}K_a = \text{p}K_a(\text{base}) - \text{p}K_a(\text{acid})$ is close to 0 (Gilli *et al.*, 2009). The value $\text{p}K_a$ is correlated with the occurrence of a structure where the base and acid components are not ionized, thus forming a cocrystal ($\text{p}K_a < 0$), or ionized forming a salt ($\text{p}K_a > 3$) (Childs *et al.*, 2007). It is difficult to predict the form in which the acid and base are present for $0 < \Delta\text{p}K_a < 3$.

Changing pressure may also trigger migration within hydrogen bonds, as happens in oxalic acid dihydrate, where the H atom migrates from the protonated acid to the water molecule with increasing pressure. This phenomenon was observed by X-ray diffraction experiments and density functional theory

Table 1 (continued)

Reference	Compound	Probe	$T_{\min}$ – $T_{\max}$ (K)	Refcodes for $T_{\min}/T_{\max}$ structures
N···H···O				
Steiner <i>et al.</i> (2001)	<i>g</i>	Neutron	20–200	RAKQAV/GADGUN05
N1···H1···O1				
20	1.206 (6)	1.309 (7)	2.506 (2)	170.4 (6)
200	1.304 (13)	1.229 (14)	2.525 (6)	170.6 (10)
Cowan <i>et al.</i> (2003)	<i>h</i>	Neutron	20–296	WISNAN01/WISNAN02
N1–H3···O4				
20	1.206 (3)	1.326 (3)	2.5219 (17)	169.6 (3)
296	1.302 (4)	1.240 (4)	2.532 (2)	169.4 (3)
Cowan <i>et al.</i> (2005)	<i>i</i>	Neutron	15–296	DINICA11/DINICA12
N1–H5···O4				
15	1.213 (4)	1.311 (5)	2.523 (2)	176.4 (4)
296	1.307 (6)	1.218 (6)	2.525 (3)	177.8 (6)
Cowan <i>et al.</i> (2005)	<i>j</i>	Neutron	15–296	DINICA13/DINICA15
N1–D2···O4				
15	1.151 (3)	1.388 (3)	2.537 (3)	175.8 (3)
296	1.457 (4)	1.108 (4)	2.564 (3)	177.7 (5)
Seaton <i>et al.</i> (2013)	<i>k</i>	X-ray	80–173	TICYIP03/TICYIP
N2–H1···O1				
80	1.31 (3)	1.23 (3)	2.5303 (14)	171 (2)
173	1.44 (3)	1.11 (3)	2.5424 (14)	171 (2)

Notes: (a) potassium hydrogen maleate, (b) urea/phosphoric acid, (c) dibenzoylmethane, (d) 4-dimethylaminobenzoic acid/3,5-dinitrobenzoic acid/hemikis(4,4'-bipyridine), (e) 2-(acetyloxy)benzoic acid, (f) 4-chlorobenzoic acid, (g) 4-methylpyridine pentachlorophenol, (h) benzene-1,2,4,5-tetracarboxylic acid/4,40-bipyridyl (1:2), (i) pyridine/3,5-dicarboxylic acid, (j) pyridine/3,5-dicarboxylic acid (deuterated), (k) 2-aminobenzoic acid/4-phenylpyridine. Remarks: (i) For the structure determination by Wilson *et al.* (2006), the occupational parameters of H1 were 0.911 (12) and 0.754 (20) at 100 and 298 K, respectively, and *vice versa* 0.089 (12) and 0.246 (20) for atom H1A at 100 and 298 K. (ii) In the X-ray determination at 300 K by Thomas *et al.* (2010), the bridging H atom was denominated as H11.

(DFT) calculations (Casati *et al.*, 2009), as well as by IR spectroscopic methods (Bhatt *et al.*, 2016). As for N···H···O hydrogen bonds, there are indications that a similar proton transfer provoked by exerted pressure takes place in the 1:1 adduct of squaric acid and 4,4'-bipyridine (Martins *et al.*, 2009).

In some ferroelastic crystals, jumps of the bridging H atom between the donor and acceptor atoms are concomitant with ferroelastic switching (Wadhawan, 2000). To the best of our knowledge, this phenomenon is limited to moderately strong O···O hydrogen bonds (Gilli & Gilli, 2009) in *n*-alkylammonium dihydrogen phosphates/arsenates (*e.g.* Fábry *et al.*, 1997), in H₃BO₃ (Wadhawan, 1978) and in 2,10-undecadione-urea (1:9) (Brown & Hollingsworth, 1995).

The present structure analysis has revealed once more (see Krupková *et al.*, 2002) that an F atom bonded to a P atom forms considerably weaker hydrogen bonds than an O atom. A similar phenomenon has been commented on for C–F bonded fluorine by Shimoni & Glusker (1994), Dunitz & Taylor (1997), Prescott (2001) and Dunitz (2004), however, to the best of our knowledge, not for P–F-, As–F- or S–F-bonded F atoms.

2. Experimental

2.1. Synthesis and crystallization

Crystals of the title compound were prepared from a 50 ml water solution of 0.30 g of 2,4,6-triaminopyrimidine (commercial product from TCI, 98%) with 0.24 g of H₂PO₃F in a 2:3 molar ratio. H₂PO₃F was prepared by the exchange of 0.55 g of water-diluted (NH₄)₂PO₃F·H₂O through a column with cation-exchanging resin (Amberlite) in the H-cycle and immediately added to the solution of 2,4,6-triaminopyrimidine dropwise. The volume of the eluted solution of H₂PO₃F was about 50 ml. [(NH₄)₂PO₃F·H₂O was prepared according to the method described by Schülke & Kayser (1991) and the product was recrystallized in water.] Yellow transparent crystals of the title compound, about 0.5 mm in size with prominent cleavage, appeared within one month (see supporting information for a photograph of the specimen used).

2.2. Refinement

The diffraction data of the sample were collected first at 290 K and then at temperature intervals of 10 K down to 190 K. Afterwards, the sample was measured at 150 K and then at 180, 170, 160 and 100 K.

For each experiment, all the H atoms were discernible in the difference electron-density maps. The aryl H atom was constrained by the conditions C–H = 0.93, 0.94 and 0.95 Å for the temperature intervals 290–240, 230–190 and 180–150 K, as well as 100 K, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aryl H atoms for each temperature.

The positional parameters of the water H atoms were restrained by the distance restraints O–H = 0.84, 0.85 and 0.86 Å for the temperature intervals 290–240, 230–190 and 180–150 K, as well as 100 K, respectively. For all these cases, the elasticities (Müller *et al.*, 2006) applied were 0.02 Å, while $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ for water H atoms.

The positional parameters of the primary and secondary amine H atoms were refined freely, except for the migrating H atoms between atoms N1 and O3 (Fig. 1 and Fig. S1 in the supporting information), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ for the primary and secondary amine H atoms for each temperature.

For each temperature, the positional parameters of the migrating H atom were fixed in their as-found positions in the difference electron-density maps (Fig. 2 and Fig. S2 in the supporting information). This H atom was split over two positions corresponding to H1N1 and H1O3 in the temperature intervals 290–250 K and 230–220 K (Fig. 1 and Fig. S1 in the supporting information). The isotropic displacement parameters of H1N1 and H1O3 were refined as being equal, with varying occupational parameters, the sum of which equalled to 1.

Table 2

Experimental details.

For all determinations: $M_r = 243.1$, monoclinic space group $C2/c$ with $Z = 8$, crystal size (mm) $0.31 \times 0.21 \times 0.11$. Diffractometer was a Bruker D8 VENTURE Kappa DUO PHOTON 100 CMOS with Mo $K\alpha$ radiation; a multi-scan absorption correction was applied using *SADABS* (Bruker, 2016). H atoms were treated by a mixture of independent and constrained refinement.

	(I)	(VI)	(XII)	(XVI)
Crystal data				
Chemical formula	$(C_4N_5H_8)_{0.73}(FO_3HP)_{0.73} \cdot (C_4N_5H_9)_{0.27}(FO_3P)_{0.27} \cdot (H_2O)$	$(C_4N_5H_8)_{0.64}(FO_3HP)_{0.64} \cdot (C_4N_5H_9)_{0.36}(FO_3P)_{0.36} \cdot (H_2O)$	$(C_4N_5H_9)(PO_3F)(H_2O)$	$(C_4N_5H_9)(FO_3P)(H_2O)$
Temperature (K)	290	240	180	100
a, b, c (Å)	20.6578 (6), 8.9220 (2), 13.9144 (5)	20.5748 (7), 8.8530 (3), 13.8869 (9)	20.4891 (6), 8.7848 (2), 13.8632 (4)	20.4273 (6), 8.7714 (2), 13.7988 (7)
β (°)	129.181 (1)	128.962 (1)	128.781 (1)	128.623 (1)
V (Å ³)	1987.92 (11)	1966.83 (16)	1945.18 (10)	1931.62 (12)
μ (mm ⁻¹)	0.30	0.30	0.31	0.31
Data collection				
T_{min}, T_{max}	0.913, 0.961	0.918, 0.968	0.912, 0.972	0.909, 0.967
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	8056, 2822, 2091	8371, 2850, 2155	7156, 2796, 2316	10111, 2789, 2477
R_{int}	0.028	0.026	0.020	0.020
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.704	0.704	0.704	0.703
Refinement				
$R[F > 3\sigma(F)], wR(F), S$	0.038, 0.086, 1.83	0.035, 0.082, 1.80	0.034, 0.080, 1.97	0.028, 0.074, 2.16
No. of reflections	2822	2850	2796	2789
No. of parameters	166	166	165	165
No. of restraints	2	2	2	2
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.31, -0.32	0.26, -0.36	0.39, -0.38	0.41, -0.32

Computer programs: *SAINT* (Bruker, 2015), *SIR97* (Burla *et al.*, 2015), *JANA2006* (Petříček *et al.*, 2014), *DIAMOND* (Brandenburg & Putz, 2005) and *PLATON* (Spek, 2009).

The measurement at 240 K yielded one broad maximum only, which was modelled by two H atoms situated at the edges of the smeared electron density. The refinement was otherwise the same as for any of the structures with observed disorder of the migrating H atom.

For the measurements in the interval 210–150 K, there was just one maximum in the difference electron-density map (Fig. 2 and Fig. S2 in the supporting information), which corresponded to the bridging H1N1 atom between atoms N1 and O3 (Fig. 1 and Fig. S1 in the supporting information). The

Figure 1

The title molecules at 290, 240, 180 and 100 K, with anisotropic displacement parameters shown at the 50% probability level.

position of the H atom assigned to this maximum was fixed, while its displacement parameter was refined freely.

The calorimetric experiments were performed on a differential scanning calorimeter PerkinElmer Pyris Diamond DSC (303–93 K) with Cryofill liquid-nitrogen cooling. *PYRIS* software (PerkinElmer Instruments, 2015) was used for control and evaluation. The sample (mass 9.35 mg) was hermetically sealed in an aluminium 30 μ l pan and the scanning rate was 10 K min^{-1} .

Figure 2

(a) The difference electron-density maps without the electron density belonging to the bridging H atom. (b) The residual electron-density maps with the electron density belonging to the bridging H atom. Both maps depict the region between $\text{O3} \cdots \text{N1}$, for the representative structures with indicated temperatures. For (a) and (b), the contours are in 0.05 and 0.02 $\text{e} \text{ \AA}^{-3}$ increments; positive, zero and negative electron densities are indicated by continuous, dotted and dashed lines, respectively. The light-grey, blue and red circles show C1, N1 and O3 atoms, respectively (JANA2006; Petříček *et al.*, 2014).

3. Results and discussion

The title structures, with the sum formula $\text{C}_4\text{H}_{11}\text{FN}_5\text{O}_4\text{P}$, can be considered as mixtures of 2,4,6-triaminopyrimidinium(1+) hydrogen trioxofluorophosphate(1−) monohydrate and 2,4,6-triaminopyrimidinium(2+) trioxofluorophosphate(2−) monohydrate in different proportions which depend on temperature. The most interesting feature is the presence of a moderate though still stronger $\text{O3}—\text{H1O3} \cdots \text{N1}/\text{O3} \cdots \text{H1N1}—\text{N1}$ hydrogen bond (Fig. 1 and Fig. S1 in the supporting information). (For the classification of the hydrogen bonds according to their strengths, see Gilli & Gilli, 2009.) The distribution of the electron density of this bridging H atom undergoes significant changes with decreasing temperature. The anion is fully deprotonated at 210 K and below this temperature.

The right-hand column of Fig. 2, as well as of the deposited Fig. S2, shows residual electron density, with all the atoms included in the calculations. It can be seen from the features of these maps that the structural model has reached the limit of the spherical-atom approximation and that the model, despite its crudeness, explains satisfactorily the basic features of the electron density regarding the migrating H atom.

The values of $\text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a2}}$ of $\text{H}_2\text{PO}_3\text{F}$ at 313 K are about 0.5 and 4.80 (Perrin, 1969), respectively, while the values of $\text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a2}}$ of 2,4,6-triaminopyrimidine at room temperature are 6.86 and 0.95 at 0.1 M ionic strength, respectively (measurement in our laboratory). Thus, the values of $\Delta\text{p}K_{\text{a1}}$ and $\Delta\text{p}K_{\text{a2}}$ are about 6.36 and -3.85 , respectively. This means that according to the $\Delta\text{p}K_{\text{a}}$ rule, the structure with the hydrogen trioxofluorophosphate anion is expected, *i.e.* not the existing low-temperature form of the title structure.

With regard to the localization of the migrating bridging H atom at different temperatures, the representative structures measured at 290, 240, 180 and 100 K were selected for further discussion; the data regarding the remaining structures have been included in the deposited material. Details regarding the crystal data, data collection and refinement for the representative structures are given in Table 2; for the rest of the structure determinations, see Table S1 of the supporting information.

Fig. 3(a) shows that the occupational parameter of atom H1O3 decreases with decreasing temperature down to 220 K, though not monotonously. It is of interest that in all the structures with an $\text{N} \cdots \text{O}$ hydrogen bond which are listed in Table 1, the migrating H atom moves towards the N atom with decreasing temperature, as happens in the title structure (Table 3 and Table S2 of the supporting information). It is also of interest that the $\text{O3}—\text{H1O3} \cdots \text{N1}/\text{O3} \cdots \text{H1N1}—\text{N1}$ distance [2.5822 (16) Å at room temperature] in the title structure is the longest among the listed $\text{N} \cdots \text{O}$ hydrogen bonds with a migrating H atom (Table 1).

The length of the unit-cell *c* axis turned out to be quite sensitive for detection of the discontinuity at about 190 K (Fig. 3b). Moreover, there is an indication of other anomalies at 230 and 270 K. (The error bars for the *c* axis are too small to be shown in Fig. 3b.) Fig. 3c shows the dependence of the $\text{O3}—$

H1O3...N1/O3...H1N1—N1 distance on temperature. The red connecting lines in Figs. 3(a)–3(c) show concomitant changes for the respective variables at about 270, 230 and 190 K, despite the rather large values of the standard uncertainties. The kink for the dependence of the length of the unit-cell *c* axis on temperature at 190 K seems to be supported by Fig. 4, too, which shows the dependence of the unit-cell *b* axis on temperature. An analogous change in the slope of the dependence of the unit-cell parameters on temperature has been observed by Olovsson *et al.* (2002) in 4-methylpyridine pentachlorophenol, while no signal was recorded by DTA or DSC, similar to the present study.

Figure 3
Dependence (a) of the occupational parameter of atom H1O3, (b) of the length of unit-cell parameter *c* and (c) of the hydrogen-bond O3...N1 distance on temperature in the interval 290–100 K. The red perpendicular lines indicate possible anomalies.

Table 3

Hydrogen-bond interactions (Å, °) in the representative structures measured at 290, 240, 180 and 100 K.

<i>T</i>	Hydrogen bond	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
290	N1—H1N1...O3	0.9670 (12)	1.6255 (11)	2.5822 (16)	169.43 (6)
240		1.0731 (11)	1.5047 (10)	2.5684 (15)	170.07 (6)
180		0.9633 (10)	1.6218 (9)	2.5637 (13)	164.77 (6)
100		0.8488 (8)	1.7207 (8)	2.5640 (11)	172.04 (5)
290	N1...H1O3—O3	0.9784 (11)	1.6064 (12)	2.5822 (16)	174.75 (6)
240		0.9898 (10)	1.5790 (11)	2.5684 (15)	177.78 (6)
180					
100					
290	N2—H1N2...O1 ⁱ	0.866 (16)	1.885 (17)	2.7405 (16)	169.3 (15)
240		0.898 (15)	1.824 (16)	2.7101 (15)	168.6 (15)
180		0.825 (15)	1.860 (15)	2.6784 (14)	171.1 (18)
100		0.858 (13)	1.815 (13)	2.6676 (12)	172.2 (12)
290	N3—H1N3...O2	0.910 (19)	1.993 (18)	2.8984 (17)	173.1 (16)
240		0.903 (17)	1.971 (17)	2.8717 (16)	175.0 (19)
180		0.827 (17)	2.020 (16)	2.8427 (14)	173 (2)
100		0.818 (15)	2.026 (14)	2.8334 (12)	169 (2)
290	N3—H2N3...O1W ⁱⁱ	0.881 (16)	1.976 (16)	2.8448 (17)	169 (3)
240		0.905 (15)	1.931 (15)	2.8265 (15)	170 (2)
180		0.861 (15)	1.962 (15)	2.8099 (14)	168 (3)
100		0.882 (13)	1.931 (13)	2.7985 (12)	168 (2)
290	N4—H1N4...O2 ⁱⁱⁱ	0.919 (18)	2.01 (2)	2.9257 (17)	172 (2)
240		0.905 (17)	2.018 (18)	2.9155 (16)	171 (2)
180		0.881 (17)	2.021 (19)	2.8950 (16)	171 (3)
100		0.887 (14)	2.006 (16)	2.8834 (13)	170 (2)
290	N4—H2N4...F1 ^v	0.82 (2)	2.472 (18)	2.9438 (18)	117.6 (12)
240		0.782 (19)	2.447 (17)	2.9258 (17)	120.8 (12)
180		0.798 (18)	2.462 (17)	2.9109 (15)	116.9 (12)
100		0.798 (16)	2.424 (14)	2.8879 (12)	118.2 (10)
290	N5—H1N5...O1W ^{iv}	0.93 (2)	2.03 (2)	2.919 (2)	159 (2)
240		0.896 (19)	2.05 (2)	2.9090 (19)	159 (2)
180		0.898 (19)	2.02 (2)	2.8939 (19)	163 (2)
100		0.896 (16)	2.03 (2)	2.8884 (15)	159.1 (19)
290	N5—H2N5...O3 ⁱ	0.887 (18)	2.22 (2)	3.0545 (19)	157.5 (17)
240		0.881 (17)	2.175 (19)	3.0191 (17)	160.1 (16)
180		0.903 (17)	2.106 (18)	2.9774 (16)	162.1 (15)
100		0.895 (15)	2.087 (16)	2.9611 (13)	165.3 (12)
290	O1W—H1OW...O2	0.83 (3)	1.94 (2)	2.759 (2)	175 (2)
240		0.84 (2)	1.91 (2)	2.746 (2)	176.6 (19)
180		0.85 (2)	1.89 (2)	2.733 (2)	174.4 (18)
100		0.85 (2)	1.88 (2)	2.7268 (16)	174.7 (14)
290	O1W—H2OW...O1 ⁱⁱ	0.837 (16)	1.866 (16)	2.6873 (15)	166.8 (17)
240		0.855 (15)	1.836 (14)	2.6738 (14)	166.2 (15)
180		0.858 (14)	1.820 (14)	2.6609 (12)	166.3 (14)
100		0.852 (12)	1.823 (12)	2.6567 (10)	165.3 (12)

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

On the other hand, deposited Figs. S3–S5 show no clear anomalies for the respective dependences of the length of lattice parameter *a*, monoclinic angle β and unit-cell volume *V*.

The already mentioned hydrogen bond with the migrating H atom, namely O3—H1O3...N1/O3...H1N1—N1, is situated within the layer which is composed of the cations, the anions and the water molecules (Fig. 5). Within this layer, the water molecule donates its H2OW atom to O1, while it accepts

two hydrogen bonds which are donated by the primary amine H atoms. Altogether there are present primary amine–acid $\text{N}—\text{H}\cdots\text{O}$, secondary amine–acid $\text{N}—\text{H}\cdots\text{O}$, primary amine–water $\text{N}—\text{H}\cdots\text{O}$ and water–acid $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonds within the layer at 210 K and below. At higher temperatures,

Figure 4
The dependence of the length of unit-cell parameter b on temperature.

Figure 5
View of a single layer of the title structure at 100 K. Colour key: C atoms are grey, F green, N blue, O red, P pink and H grey (small circle). Yellow dashed lines show the hydrogen bonds (Brandenburg & Putz, 2005). The ring graph-set motifs are indicated by grey polygons.

Table 4

π – π -electron ring interactions ($\text{\AA}$) in the representative structures measured at 290, 240, 180 and 100 K.

Cg is the centroid of the pyrimidine ring N1/C1/N2/C4/C3/C2.

T (K)	Ring 1	Ring 2	Centroid–centroid distance ($\text{\AA}$)	Note
290	$Cg1$	$Cg1^{iv}$	3.4927 (9)	Within a double layer
240	$Cg1$	$Cg1^{iv}$	3.4905 (9)	Within a double layer
180	$Cg1$	$Cg1^{iv}$	3.4924 (9)	Within a double layer
100	$Cg1$	$Cg1^{iv}$	3.4803 (7)	Within a double layer
290	$Cg1$	$Cg1^{vi}$	3.4763 (10)	
240	$Cg1$	$Cg1^{vi}$	3.4674 (9)	
180	$Cg1$	$Cg1^{vi}$	3.4573 (9)	
100	$Cg1$	$Cg1^{vi}$	3.4397 (8)	

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

i.e. at 220 K and above, there is also present an acid–secondary amine $\text{O}—\text{H}\cdots\text{N}$ hydrogen bond. Atom H2N4 is flanking (Fig. 5), except for a weak $\text{N4}—\text{H2N4}\cdots\text{F1}$ interaction (Table 3 and Table S2 in the supporting information). The very weak interaction of H2N4 may account for a rather short $\text{N4}—\text{H2N4}$ distance in comparison to other $\text{N}—\text{H}$ bond lengths observed in the structure (Table 3 and Table S2 in the supporting information). [For the graph-set motifs (Etter *et al.*, 1990), see the ‘Supramolecular features’ section (§6) in this article.]

So far, only the atomic interactions within the layer have been described. Fig. 6 shows that the layers are parallel to $(10\bar{1})$. The layers are interconnected by weak interactions into a centrosymmetric pair of layers which are characterized by the outward orientations of the $\text{P}—\text{F}$ bonds. There are four double layers across the unit cell. The observed prominent cleavage originates plausibly from the separation of these double layers. (See Fig. S6 in the supporting information, which shows photographs of the measured crystal with the cleavage plane.) Adjacent layers within the double layer are interconnected by $\text{O1W}—\text{H1W}\cdots\text{O2}$ hydrogen bonds (Table 3 and Table S2 in the supporting information), as well as by other π -electron ring $\cdots\pi$ -electron ring interactions (Table 4).

Figure 6
View of the title structure along the monoclinic unit-cell b axis at 100 K. Colour key: C atoms are grey, F green, N blue, O red, P pink and H grey (small circle). Yellow dashed lines show the hydrogen bonds (Brandenburg & Putz, 2005).

Table 5

Hydrogen bonds ($\text{\AA}$, $^\circ$) with fluorine as an acceptor in trioxofluorophosphate and hydrogen trioxofluorophosphate molecules retrieved from the Cambridge Structural Database (Groom *et al.*, 2016).

For the search, the $\text{H}\cdots\text{A}$ nonbonding interval was set at 0.9–2.5 $\text{\AA}$. There were no hits for $\text{O}\cdots\text{H}\cdots\text{F}$ hydrogen bonds.

CSD refcode	Donor	$D\cdots\text{H}$	$\text{H}\cdots\text{A}$	$D\cdots\text{A}$	$D\cdots\text{H}\cdots\text{A}$
Trioxofluorophosphates					
JEHFUY ^a	C	0.970	2.472	3.2470 (17)	136.73 (8)
SAHKET ^b	N	0.860	2.479	3.096 (2)	129 (2)
XAQYEV01 ^c	N	0.859	2.409	2.999 (6)	126.3 (3)
Hydrogen trioxofluorophosphates					
XAQYOF ^d	N	0.86	2.428	2.998 (6)	124 (5)

References: (a) Fábry *et al.* (2006a), room-temperature determination; (b) Fábry *et al.* (2012a); (c) Fábry *et al.* (2012b); (d) Fábry *et al.* (2012c).

The reluctance of the F atom to participate in stronger hydrogen bonds is remarkable. It has already been recognized that an F atom attached to a C atom is rarely involved in hydrogen bonding (Shimoni & Glusker, 1994; Dunitz & Taylor, 1997; Prescott, 2001; Dunitz, 2004). Shimoni & Glusker (1994) have shown that the $D\cdots\text{H}\cdots\text{F}$ angles are usually less than 140° . Ammonium trifluoroacetate (Jones, 2010) can be given as a notable example (Dunitz, 2004) of how a C–F-bonded F atom avoids participation in the hydrogen-bond pattern. A similar behaviour was observed for phosphorus-bonded fluorine. A typical example is $(\text{NH}_4)_2\text{PO}_3\text{F}$ (Krupková *et al.*, 2002), where despite the

Figure 7

The dependence of the longest P–O bond length on the P–F bond length in trioxofluorophosphates, as well as in hydrogen trioxofluorophosphates (Origin 6.1; OriginLab, 2000). Key: black squares represent trioxofluorophosphates, which are also bonded by hydrogen bonds; red circles represent hydrogen trioxofluorophosphates, which are also bonded by hydrogen bonds; green triangles represent hydrogen trioxofluorophosphates, with a centred position of the H atoms in the hydrogen bonds; dark-blue triangles represent trioxofluorophosphates, with all the ligands bonded by ionic bonds only; light-blue squares represent trioxofluorophosphates, with all O atoms, but not F atoms, bonded by ionic bonds only. The structures used for this plot are listed in Table S3 of the supporting information.

Table 6

Incidences of selected molecules with fluorine from a search in the Cambridge Structural Database (Groom *et al.*, 2016) and the number of hits/counts with the $D\cdots\text{H}\cdots\text{F}$ hydrogen bond.

The limits for the nonbonded contacts were set at 0.9–2.5 $\text{\AA}$. For the $[\text{PF}_6]^-$ anion, the counts for the $\text{O}\cdots\text{H}\cdots\text{F}$ and $\text{N}\cdots\text{H}\cdots\text{F}$ hydrogen-bond angles ($^\circ$) below 100° have been discarded. The final number of counts were 3739 and 1130, respectively.

Molecule	Hits/counts	Hits/counts with $D\cdots\text{H}\cdots\text{F}$ bond	$D\cdots\text{H}\cdots\text{F}$ range ($^\circ$)
O–H...F			
$[\text{PO}_3\text{F}]^{2-}$	18/27	0/0	–
$[\text{HPO}_3\text{F}]^-$	13/14	0/0	–
$[\text{SO}_3\text{F}]^-$	8/10	0/0	–
$[\text{PF}_6]^-$	16658/26509	636/1146	100.01–179.95
Trifluoroacetate	730/1079	14/18	103.54–147.08
Trifluoroacetic acid	130/209	1/1	134.23
N–H...F			
$[\text{PO}_3\text{F}]^{2-}$	18/27	2/22	126.32–129.35
$[\text{HPO}_3\text{F}]^-$	13/14	1/1	124.23
$[\text{SO}_3\text{F}]^-$	8/10	0/0	–
$[\text{PF}_6]^-$	16658/26509	1497/3746	103.00–180.0
Trifluoroacetate	730/1079	32/37	101.90–160.97
Hydrogen trifluoroacetate	130/209	0/0	–

presence of the tetrahedral cation bearing H atoms, the F atom is not involved in the hydrogen-bond pattern. Table 5 lists selected hydrogen bonds in trioxofluorophosphates and in hydrogen trioxofluorophosphates. Considering this feature, the presence of quite a weak $\text{N}\cdots\text{H}\cdots\text{F}$ interaction in each of the title structures is usual (Table 3 and Table S2 of the supporting information).

This avoidance of C–F- and P–F-bonded F atoms being involved in hydrogen bonding can be generalized to include other fluorine-containing molecules (Table 6). Table 6 also shows that the $D\cdots\text{H}\cdots\text{F}$ angles tend to be more acute than happens usually in $\text{O}\cdots\text{H}\cdots\text{O}$ or $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds; see Jeffrey (1995), Desiraju & Steiner (1999) and Shimoni & Glusker (1994). The highly symmetric $[\text{PF}_6]^-$ anion, which contains no oxygen, is exceptional in this respect. Its behaviour can be attributed to the fact that it does not contain O atoms, which are given preference as acceptors, as well as to steric reasons. Whatever orientation was adopted by this anion, an F atom would be directed towards an H atom offered by a cation.

An interesting related structure is $\text{KAsF}_5(\text{OH})$ (Peterková *et al.*, 1998), where moderate $\text{O}\cdots\text{H}\cdots\text{F}$ hydrogen bonds (Gilli & Gilli, 2009) are present, with $\text{O}\cdots\text{H}\cdots\text{F}$ hydrogen-bond angles between 160 and 170° , despite the presence of the ligand O atoms, which, however, are not given preference in the hydrogen-bond pattern in this structure.

Fig. 7 shows the interdependence of the P–F bond lengths on the longest P–O distances in the trioxofluorophosphate or hydrogen trioxofluorophosphate units which were retrieved from the Cambridge Structural Database [version 5.37 (November 2015) with addenda upto February 2016; Groom *et al.*, 2016] and the Inorganic Crystal Structure Database (2016). [Fig. 7 is an update of Fig. 8 from the article by Fábry *et al.*

(2012). The data and references for Fig. 7 are given in Table S3 of the supporting information.] Fig. 7 shows that the structures with trioxofluorophosphates and hydrogen trioxofluorophosphates form rather distinct patterns. Interestingly, the structures with symmetrical hydrogen bonds are situated just between the regions with the hydrogen trioxofluorophosphates and trioxofluorophosphates, and the title structure determinations fit this tendency. The fact that the P–F bond lengths tend to be shorter in the hydrogen trioxofluorophosphates than in the trioxofluorophosphates can be explained by the conservation of the bond-valence sum of the central P^V atom in the structures (see Brown, 2002).

It was observed in ionic compounds with trioxofluorophosphate that the anion can be involved in a bonding pattern *via* all its ligand atoms or exceptionally by all the O atoms, while the F atom is excluded from close bonding interactions. [The criterion for the consideration of a trioxofluorophosphate ligand as bonded was a bonding distance shorter than the sum of the van der Waals radii. This condition is visualized by *Mercury* (Macrae *et al.*, 2008).] These exceptional structures (see also deposited Table S3) are SnPO₃F (Berndt, 1974), Hg₂PO₃F (Weil *et al.*, 2004) and Ag₂PO₃F (Weil *et al.*, 2007). Thus, a lower ability of a P–F-bonded F atom to be involved in bonding to its neighbours is observed even in ionic compounds, though important differences from hydrogen bonding should be emphasized. The directionality observed in the hydrogen bonds which is manifested by relatively low *D*–H...F angles seems to be absent in ionic compounds. Fig. 7 shows that ionic compounds with trioxofluorophosphates, where all the ligands are involved in ionic bonds, tend to contain the longest P–F distances in contrast to the P–F distances in the three ionic substances, where the F atom is loosely involved in the bonding pattern.

Fig. 7 also shows some dubious outliers. When viewed from the left, these outliers are Na₂Mn(HPO₃F)F₃ (Armstrong *et al.*, 2013; ICSD code 424942; red circle), (NH₄)₃Fe(PO₃F)₂F₂ (Keates *et al.*, 2013; ICSD code 425616; black square), and two hits for the independent molecules in bis[*N*-hydroxy-1-(pyridin-2-yl)ethanimine](1,2-difluorodiphosphato)nickel acetonitrile solvate hydrate (Dermitzaki *et al.*, 2014; CSD refcode VOGQUF; black squares). The outlier on the right is [(CH₃)₂NH₂](HPO₃F) (Samuel *et al.*, 2001; ICSD code 110589; red circle). The leftmost blue triangle corresponds to K₂PO₃F (Robinson, 1958) and clearly indicates that this structure determination does not meet today's standards. The reason for some dubious structure determinations may follow from partial substitution of [PO₃F]^{2−} by [PO₄]^{3−} due to the low stability of [PO₃F]^{2−} which converts to [PO₄]^{3−}.

Quantum chemical calculations can offer a deeper insight into the problem of the bonding properties of fluorine. Therefore, it is useful to remember the article by Spackman & Maslen (1985), who pointed to the fact that chemical bonding between two atomic nuclei can be achieved not only by a build-up of electron density between them, but also by a deficit of electron density outside the nuclei. Spackman & Maslen (1985) have provided evidence by calculations involving the F₂ molecule. Such a depletion of electron density is

called a σ -hole and explains halogen bonding, while fluorine turned out to be the worst halogen-bond donor among the halogens (*e.g.* Clark *et al.*, 2007). However, the presence of a σ -hole in a bonded F atom has been reported for pentafluorophenyl 2,2'-bithiazole (Pavan *et al.*, 2013) or fluorobenzene (Jelsch & Guillot, 2017). The presence of a σ -hole in the structures listed in Table 5 would explain the weak ability of fluorine to take part in N–H...F or O–H...F hydrogen bonds in which F is bonded to C, P and As atoms. It would also explain the observed *D*–H...F angles in such hydrogen bonds (see also Shimoni & Glusker, 1994). In general, the ability of a halogen atom to act as a hydrogen-bond acceptor and halogen-bond donor would be an interrelated property which is worthy of comparison.

4. Chemical context

The crystal structures of 2,4,6-triaminopyrimidinium(1+) hydrogen trioxofluorophosphate(1−) monohydrate/2,4,6-triaminopyrimidinium(2+) trioxofluorophosphate(2−) monohydrate contain moderate N1–H1N1...H1O3–O3 hydrogen bonds. The bridging H atom, which is disordered over two positions at 220 K and above, migrates with decreasing temperature towards atom N1. The F atom does not participate in the hydrogen-bond pattern of the structure.

5. Database survey

The Cambridge Structural Database (Version 5.37 of November 2015, with addenda up to February 2016) has been used (Groom *et al.*, 2016), as well as the Inorganic Crystal Structure Database (2016) (Version 2016-1).

6. Supramolecular features

The primary and secondary amine groups of the title base often form *R*₂²(8) graph-set motifs (Etter *et al.*, 1990) easily with suitable anions. One such suitable anion is the title one, and more specifically its O atoms (Fig. 5).

On a local scale, the graph-set motifs are independent of temperature, though the role of atoms N1 and O3 is temperature dependent. The graph-set motifs within the layer are as follows:

*R*₂²(8): N1–H1N1...O3–P1–O2...H1N3–N3–C1 (at all measured temperatures);

*R*₂²(8): N1...H1O3–O3–P1–O2...H1N3–N3–C1 (at 220 K and above);

*R*₂²(8): N2–H1N2...O1ⁱ–P1ⁱ–O3ⁱ...H2N5–N5–C4;

*R*₂³(8): N3–H2N3...O1Wⁱⁱ–H2OWⁱⁱ...O1ⁱ...H1N2–N2–C1;

*R*₃³(12): N4–C2–C3–C4–N5–H1N5...O1W^{iv}–H2OW^{iv}...O1ⁱⁱⁱ–P1ⁱⁱⁱ–O2ⁱⁱⁱ...H1N4.

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

7. Conclusions

The title structure is remarkable for features which have been investigated relatively rarely, *i.e.* for the presence of an $N\cdots H\cdots O$ hydrogen bond in which the bridging H atom migrates with changing temperature. The distance $O3\cdots H1O3\cdots N1/O3\cdots H1N1-N1$ in the title structure with the migrating H atom (Table 3 and deposited Table S2) is the longest one among similar cases (Table 1).

A usually observed reluctance of the C—F-bonded F atom to act as a hydrogen-bond acceptor (Dunitz & Taylor, 1997; Dunitz, 2004; Shimoni & Glusker, 1994) can be generalized to include other molecules, such as $[HPO_3F]^-$, $[PO_3F]^{2-}$ and $[SO_3F]^-$, which also contain oxygen ligands. The bonding properties of $[PO_3F]^{2-}$ or $[HPO_3F]^-$ are sensitive to their environment, as it is manifested by Fig. 7.

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