

the 'best' planes of the two halves of the molecule are listed in Table 3. As there is no centre of symmetry within the molecule, slightly different values are observed for the two corresponding groups.

The angle between the planes of the *trans*-stilbene moieties 3 and 3' (see Table 3) is 10.2°, in contrast to the value of 0° in the centrosymmetric molecule of the *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). The adjacent naphthyl and phenyl groups, linked by the diazo groups, form angles of 25.5 and 40.5°, respectively. These angles are greater than those found in other azo derivatives, e.g. *trans*-chloroazostilbene (Komeyama, Yamamoto, Nishimura & Hasegawa, 1973) or chloronitrophenylazonaphthol (Whitaker, 1977), 0 and 0.8°, respectively. This may be due to crystal packing forces.

The molecule can be described as quasi centrosymmetric and nearly planar, Fig. 1. The molecule is sufficiently planar to be conjugated with an absorbance maximum at 487 nm in chloroform solution, where it will occur in planar form. The distance from N(1) to N(6) which gives a measure for the length of the conjugated system is 24.65 (2) Å.

The *b* axis projection of the structure (Fig. 2) shows that the molecules are extended along [15,0,2]. The shortest intermolecular atomic distances are N(1)⋯C(33) = 3.567 (3) Å, and C(2)⋯C(19) =

Table 3. Angles (°) between the best planes of the subunits

Subunit	2	3	4	3'	2'	1'
1	18.0	25.5	20.9	15.3	0.6	25.2
2		7.5	3.0	2.7	17.5	43.2
3			4.6	10.2	25.0	50.7
4				5.6	20.4	46.1
3'					14.8	40.5
2'						25.7

Subunits: 1 = C(1)–C(10); 1' = C(27)–C(36); 2 = C(1), C(13), N(2), N(3); 2' = C(24), C(27), N(4), N(5); 3 = C(13)–C(18); 3' = C(21)–C(26); 4 = C(19), C(20), H(19), H(20).

3.507 (3) Å; the intermolecular bonding is entirely of a van der Waals type.

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Structure of 4-Aminopyridinium Dihydrogentetraoxophosphate(V) Monohydrate

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Abstract. C₅H₇N₂⁺·H₂PO₄⁻·H₂O, *M_r* = 210.1, triclinic, *P*1̄, *a* = 8.951 (9), *b* = 7.982 (8), *c* = 7.398 (8) Å, α = 113.47 (5), β = 108.75 (5), γ = 77.18 (5)°, *V* = 456 (2) Å³, *Z* = 2, *D_x* = 1.529 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 2.866 cm⁻¹, *F*(000) = 220, *T* = 293 K, final *R* = 0.032 for 2292 independent observed reflections. This structure points to the formation of an (H₂PO₄·H₂O)_{*n*}⁻ layer polyanion on which the 4-aminopyridinium cations are anchored through hydrogen bonds originating from the amine donor groups. The role of water in the balance of ionic charges is emphasized.

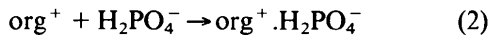
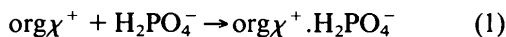
Introduction. The crystal chemistry of alkyl and aryl cations encapsulated between chains or layers of

(H₂PO₄⁻)_{*n*} polyanions is fascinating because it may lead to the crystal engineering of polar materials. The various types of (H₂PO₄⁻)_{*n*} aggregates (= polyanions) observed in many crystal structures reveal the flexibility of the aggregation with respect to the chiral or achiral associated cations (Masse & Durif, 1990) and the possible interaction of the small dipole moments of the H₂PO₄ units with the dipole moments of the organic moieties, which may induce the acentricity of the future packing. The short hydrogen bonds between the H₂PO₄ units which build up the anionic layer structure cannot usually be disjoined by the reactivity of the organic functional groups. The ability of an hydroxyl radical to open the (H₂PO₄⁻)_{*n*} chains has been observed in *N,N*-

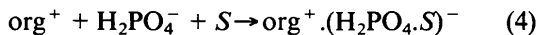
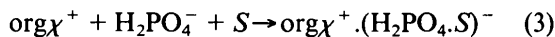
dimethyl-2-hydroxyethylammonium dihydrogen-tetraoxophosphate(V) monohydrate (Bagieu-Beucher & Guitel, 1990). Nevertheless, in this case, the chain structure is maintained by one short hydrogen bond (2.586 Å) instead of two.

Four chemical reactions have been used to develop this crystal engineering:

$(\text{H}_2\text{PO}_4^-)_n$ layers or chains



$(\text{H}_2\text{PO}_4 \cdot \text{S})_n^-$ aggregates



$\text{org}\chi^+$ = chiral cation, org^+ = achiral cation, S = solvent.

The reactions (1) and (3) lead to crystals with acentric frameworks. The reaction (2) may generate acentric crystalline frameworks if org^+ is a bearer of a dipole moment. The reactions (3) and (4) result in solvent capture with formation of large anionic aggregates. This capture depends on the positive charge distribution in the organic cation. The charge is balanced through the hydrogen bonds originating from the functional groups. The positions of the H donor groups induce the solvent capture in order to obtain a maximum surrounding of the organic cation.

The main motivation of this crystal structure investigation is to prove that the chemical reaction (4) occurs rather than (2) with the 4-aminopyridinium cation and, therefore, a unique $(\text{H}_2\text{PO}_4^-)_n$ layer subnetwork cannot be formed.

Experimental. Crystals of 4-aminopyridinium dihydrogen-tetraoxophosphate monohydrate are easily prepared by slow evaporation at room temperature of an aqueous solution of H_3PO_4 and 4-aminopyridine in the stoichiometric ratio. Stout colorless triclinic prisms are obtained; crystal size: $0.72 \times 0.44 \times 0.44$ mm; density not measured; Philips PW1100 diffractometer, graphite monochromator. Unit-cell refinement with 24 reflections ($10 < \theta < 18^\circ$); ω scan, scan width 1.20° , scan speed $0.03^\circ \text{ s}^{-1}$; total background measuring time 10 s. 2779 reflections collected ($3 < \theta < 40^\circ$); $h, \pm k, \pm l, h_{\text{max}} = 12, k_{\text{max}} = 11, l_{\text{max}} = 10$; two orientation and intensity reference reflections (0,12,0 and $0, \bar{1}2, 0$) measured every 4 h showed no significant variation; 2369 reflections obtained after averaging Friedel pairs ($R_{\text{int}} = 0.011$); Lorentz and polarization corrections, no absorption correction. Crystal structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); H atoms located by difference Fourier syntheses; anisotropic

Table 1. Atomic positions and B_{eq} (Å²) for the title compound; e.s.d.'s are given in parentheses

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	B_{eq}
P	0.50599 (4)	0.22356 (5)	0.78018 (5)	2.081 (6)
O(1)	0.4836 (2)	0.3951 (1)	0.7189 (2)	3.54 (3)
O(2)	0.6614 (1)	0.1062 (2)	0.7255 (2)	3.64 (3)
O(3)	0.5326 (1)	0.2810 (1)	1.0068 (1)	2.95 (2)
O(4)	0.3672 (1)	0.1136 (1)	0.6502 (2)	2.72 (2)
O(W)	0.7604 (1)	0.0655 (1)	0.1936 (2)	2.88 (2)
N(1)	0.1298 (2)	0.2444 (2)	0.0958 (2)	3.10 (3)
N(2)	-0.0248 (2)	0.7545 (2)	0.4542 (2)	3.23 (3)
C(2)	-0.0266 (2)	0.3017 (2)	0.0617 (2)	2.97 (3)
C(3)	-0.0821 (2)	0.4688 (2)	0.1785 (2)	2.69 (3)
C(4)	0.0248 (2)	0.5873 (2)	0.3388 (2)	2.37 (3)
C(5)	0.1885 (2)	0.5212 (2)	0.3712 (2)	2.84 (3)
C(6)	0.2352 (2)	0.3524 (2)	0.2484 (2)	3.13 (3)

full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights; final refinements with 2292 reflections corresponding to $I > 3\sigma_I$; final $R = 0.032$ ($wR = 0.035$), $S = 0.315$; $(\Delta/\sigma)_{\text{max}} = 0.0$; max. peak height in the final difference Fourier map = $0.31 \text{ e } \text{Å}^{-3}$. Secondary extinction not refined. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol IV, Table 2.2B). Enraf-Nonius (1977) *SDP* used for all calculations on a MicroVAX II computer. Crystal structure representations drawn using *STRUPLO84* (Fischer, 1985).

Discussion. Table 1* reports the final atomic coordinates.

The framework consists of 4-aminopyridinium cations sandwiched between chains of H_2PO_4 tetrahedral units bridged by water molecules (Fig. 1). This layer structure can be easily described from an examination of the complete hydrogen-bond scheme (Table 2). Three types of hydrogen bonds are noticed corresponding to the donor-acceptor distances ($D \cdots A$). The short H bonds ($D \cdots A \sim 2.59 \text{ Å}$) keep the cohesion of the H_2PO_4 units in an infinite chain. The medium H bonds (from the water molecules) ($D \cdots A \sim 2.75 \text{ Å}$) bridge the $(\text{H}_2\text{PO}_4^-)_n$ infinite chains to form a layer polyanion $(\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O})_n^-$ (Fig. 2). Three long H bonds ($D \cdots A > 2.75 \text{ Å}$) anchor the 4-aminopyridinium cations onto the anionic layers. Consequently, the positive charge is not fully located on the NH group as in a pyridinium cation. The major part of the positive charge is balanced through $\text{N}(1) \cdots \text{H}(\text{N}1) \cdots \text{O}(\text{W})$ and $\text{N}(2) \cdots \text{H}(\text{N}2) \cdots \text{O}(\text{W})$ hydrogen bonds. The water molecule, twice an H

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53963 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

acceptor from organic cations, contributes largely to the flow of a part of the negative charge associated with the H₂PO₄ unit. So the negative charge is not fully located on the H₂PO₄ unit which accepts only one H bond from the 4-aminopyridinium cation. Since the charge compensation occurs as much, if not more, *via* the water molecules as *via* the H₂PO₄ units then the two entities H₂PO₄ and H₂O do not play independent roles and we have a true polyanion, the formula of which should be written (H₂PO₄·H₂O)_nⁿ⁻. Similar aggregations have been observed with the formation of (H₂PO₄·H₃PO₄)_nⁿ⁻ and (2H₂PO₄·H₃PO₄)_n²ⁿ⁻ polyanions in crystals of

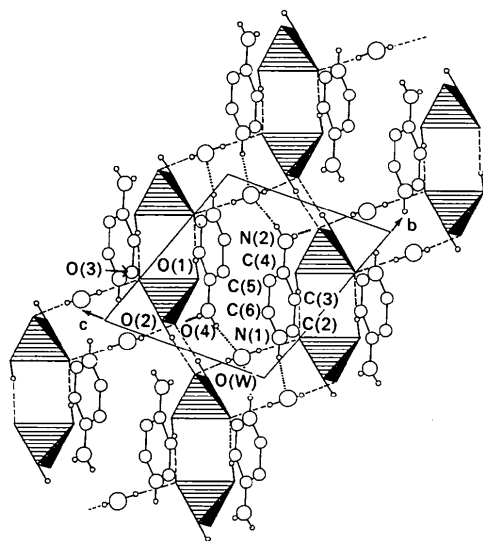


Fig. 1. Atomic arrangement of 4-aminopyridinium dihydrogen-tetraoxophosphate monohydrate, represented in the *bc* projection. The anchorage of organic cations onto the layer polyanion through hydrogen bonds is indicated by dotted lines. The H atoms connected to the C atoms are omitted for the sake of clarity.

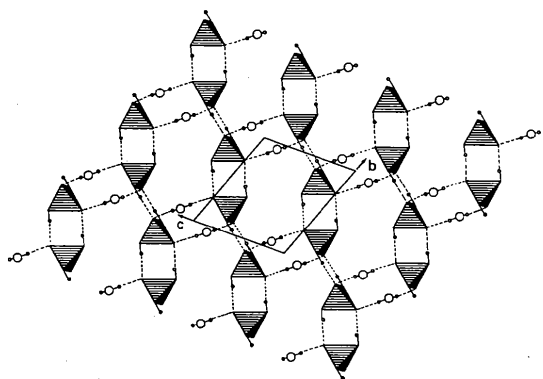


Fig. 2. The layer structure of the polymeric anion (H₂PO₄·H₂O)_nⁿ⁻ in the *bc* projection.

Table 2. *Interatomic distances (Å) and bond angles (°)*

PO₄ tetrahedron in the H₂PO₄ unit

P	O(1)	O(2)	O(3)	O(4)
O(1)	1.561 (1)	106.27 (8)	110.38 (6)	108.12 (6)
O(2)	2.503 (2)	1.568 (1)	107.38 (6)	108.74 (6)
O(3)	2.515 (2)	2.474 (2)	1.503 (1)	115.55 (7)
O(4)	2.487 (2)	2.502 (2)	2.549 (1)	1.511 (1)

P—O(1)—H(1) = 112 (2) P—O(2)—H(2) = 115(2)
P—P = 4.2466 (4) and 4.3181 (1)

4-Aminopyridinium cation

N(1)—C(2)	1.347 (2)	N(1)—C(2)—C(3)	121.3 (1)
C(2)—C(3)	1.355 (2)	C(2)—C(3)—C(4)	120.0 (1)
C(3)—C(4)	1.413 (2)	C(3)—C(4)—C(5)	117.0 (1)
C(4)—C(5)	1.419 (2)	C(4)—C(5)—C(6)	119.7 (1)
C(5)—C(6)	1.354 (2)	C(5)—C(6)—N(1)	121.6 (1)
C(6)—N(1)	1.345 (2)	C(6)—N(1)—C(2)	120.4 (1)
N(2)—C(4)	1.334 (2)	N(2)—C(4)—C(3)	121.8 (1)
		N(2)—C(4)—C(5)	121.2 (1)

Hydrogen bonds

(O,N)—H...O	(O,N)—H	H...O	(O,N)...O	(O,N)—H...O
N(1)—H(N1)...O(W)	0.89 (2)	1.91 (2)	2.779 (2)	166 (3)
N(2)—H(N2)...O(4)	0.92 (2)	2.05 (2)	2.965 (2)	174 (2)
N(2)—H(2N2)...O(W)	0.83 (2)	2.18 (2)	3.003 (2)	171 (2)
O(1)—H(1)...O(3)	0.74 (2)	1.85 (2)	2.582 (1)	170 (3)
O(2)—H(2)...O(4)	0.79 (2)	1.80 (2)	2.593 (1)	176 (3)
O(W)—H(1W)...O(4)	0.86 (3)	1.91 (3)	2.752 (2)	169 (2)
O(W)—H(2W)...O(3)	0.85 (2)	1.90 (2)	2.748 (2)	177 (2)

H-atom tetrahedral neighbourhood around O(W)

O(W)	H(1W)	H(2W)	H(N1)	H(2N2)
H(1W)	0.84 (3)	106 (2)	107 (2)	105 (2)
H(2W)	1.34 (4)	0.84 (2)	110 (2)	118 (2)
H(N1)	2.31 (3)	2.34 (3)	1.92 (2)	110 (1)
H(2N2)	2.53 (3)	2.68 (3)	3.37 (3)	2.18 (2)

Least-squares plane of the pyridine ring

$$3.650(6)x + 5.89(4)y - 6.72(8)z = 1.265(2)^*$$

Deviations (Å) of atoms used for defining the plane

N(1)	0.004 (1)	C(4)	0.006 (1)
C(2)	-0.001 (2)	C(5)	-0.004 (2)
C(3)	-0.004 (2)	C(6)	-0.001 (2)

Deviations (Å) of atoms excluded from the plane calculation

N(2)	0.033 (1)	H(C2)	0.03 (2)	H(C6)	-0.01 (2)
H(1N2)	0.05 (2)	H(C3)	0.03 (2)		
H(2N2)	-0.04 (2)	H(C5)	-0.01 (2)		

* *x*, *y* and *z* are the crystallographic coordinates referred to the oblique axes *a*, *b* and *c*.

potassium dihydrogen-tetraoxophosphate(V) monophosphoric acid (Philippot, Richard, Roudault & Maurin, 1972), L-histidinium dihydrogen-tetraoxophosphate(V) monophosphoric acid (Blessing, 1986), pyridinium dihydrogen-tetraoxophosphate(V) monophosphoric acid (Masse & Tordjman, 1990) and ethylenediammonium dihydrogen-tetraoxophosphate-pentahydrogenbis[tetraoxophosphate(V)] (Bagieu-Beucher, Durif & Guitel, 1989).

These examples illustrate the formation of (H₂PO₄·S)_nⁿ⁻ aggregates following the chemical reaction (4). The role of the water molecule both in the building of the anionic layer structure and in the charge compensation is expressed through its tetrahedral surrounding of H atoms (Table 2).

The chemistry of salts containing $(\text{H}_2\text{PO}_4^-)_n$ aggregates is close to clathrate chemistry and appears very attractive. Indeed, the controlled formation of $(\text{H}_2\text{PO}_4^-)_n$ or $(\text{H}_2\text{PO}_4\cdot\text{S})_n^-$ aggregates using the previous chemical reactions (1), (2), (3) and (4) is an important step in the crystal engineering of acentric materials having a layer structure for non-linear optical applications.

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Absolute Configuration of Two Bases Co-crystallized with (+)-Tartaric Acid: (R)-1-[3-(4-Chlorophenyl)-3-hydroxy-3-(2-pyridyl)propyl]pyrrolidinium (+)-Tartrate 2-Propanol Hemihydrate and (S)-2-[1-Hydroxy-1-(4-methoxyphenyl)ethyl]pyridinium (+)-Tartrate

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Abstract. (1) $\text{C}_{18}\text{H}_{22}\text{ClN}_2\text{O}^+ \cdot \text{C}_4\text{H}_5\text{O}_6^- \cdot \text{C}_3\text{H}_8\text{O} \cdot \frac{1}{2}\text{H}_2\text{O}$, $M_r = 536.08$, monoclinic, $P2_1$, $a = 13.738$ (3), $b = 15.037$ (5), $c = 7.012$ (2) Å, $\beta = 103.26$ (2)°, $V = 1409.9$ (5) Å³, $Z = 2$, $D_x = 1.260$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.181$ mm⁻¹, $F(000) = 570$, $T = 295$ K, $R = 0.041$, $wR = 0.047$ for 1606 reflections [$I > 3\sigma(I)$]. (2) $\text{C}_{14}\text{H}_{16}\text{NO}_2^+ \cdot \text{C}_4\text{H}_5\text{O}_6^-$, $M_r = 379.37$, monoclinic, $P2_1$, $a = 16.036$ (2), $b = 7.839$ (2), $c = 7.548$ (1) Å, $\beta = 102.97$ (1)°, $V = 924.6$ (5) Å³, $Z = 2$, $D_x = 1.367$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.101$ mm⁻¹, $F(000) = 400$, $T = 295$ K, $R = 0.046$, $wR = 0.055$ for 1613 reflections [$I > 3\sigma(I)$]. The absolute configurations of the bases in (1) and (2) were determined by referring to the known absolute configuration of the co-crystallized (+)-tartrate anion. In both structures the carboxyl groups of the (+)-tartrate anions are *anti*. In both, the molecular packing is dominated by hydrogen bonds including a bifurcated system from the protonated N atoms.

Introduction. Some α -substituted pyridine derivatives exhibit important pharmacological activities and a

few are used in human medicine. A series of such compounds in enantiomerically pure form has been synthesized (Berova, 1987; Bojadziev, Kojić-Prodić & Berova, 1987). For some of them the absolute configuration could not be determined by chemical correlation. The absolute configuration of two selected derivatives, reported in this paper, and their CD measurements were used to determine the chiroptical properties of nine related compounds (Berova, Bojadziev, Bresciani-Pahor, Ivanov, Kojić-Prodić, Rakovska, Ružić-Toroš & Snatzke, 1991).

Experimental. Both samples were crystallized from 2-propanol at ambient temperature. The crystals of (1) were found to include one molecule of solvent and half a molecule of H₂O. Preliminary cell dimensions and space groups were determined from oscillation and Weissenberg photographs with Cu $K\alpha$ radiation; final cell dimensions were refined from diffractometer measurements using 25 reflections with $9 < \theta < 15^\circ$ for (1) and 20 reflections with $10 < \theta < 16^\circ$ for (2). Intensities were measured on an Enraf–Nonius CAD-4F diffractometer in the $\omega/2\theta$ scan mode, $1 + 0.35\tan\theta$, with graphite-mono-

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