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Structure of Cytosinium Dihydrogenmonophosphate

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Abstract. $C_4H_6N_3O^+.H_2PO_4^-$, $M_r = 209{\cdot}10$, monoclinic, $P2_1/a$, $a = 6{\cdot}931$ (7), $b = 17{\cdot}992$ (8), $c = 6{\cdot}520$ (3) Å, $\gamma = 97{\cdot}97$ (7)°, $V = 805$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}725$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}347$ mm^{-1}, $F(000) = 432$, $T = 293$ K, final $R = 0{\cdot}027$ for 2108 independent observed reflections. Layers of $H_2PO_4^-$ anions perpendicular to the b axis alternate with layers of $C_4H_6N_3O^+$ cations. The phosphate groups are linked by hydrogen bonds to form a two-dimensional network. The cytosine groups are interconnected with the phosphoric planes through three hydrogen bonds along **b** and are joined themselves by another hydrogen bond along the mirror a. The plane of the cytosine ring is approximately perpendicular to the layers. A parallel stacking of the base rings appears with an interplanar distance of 3·3 Å in each cytosine layer.

Introduction. It seems that interactions between various kinds of phosphoric acids and nucleic acids have not yet been well investigated. The only compound known in this domain is the adeninium phosphate $C_5H_6N_5^+.H_2PO_4^-$ (Langer & Huml, 1979) prepared from a purine base, adenine. In the present work, we describe another compound resulting from the interaction between monophosphoric acid and a pyrimidine base, cytosine.

Experimental. Crystals of cytosinium dihydrogenmonophosphate are easily prepared by slow evaporation at room temperature of an aqueous solution of H_3PO_4 and cytosine in stoichiometric ratio. Large colorless prisms up to 1 cm long are obtained. Density not measured. Prism fragment: 0·24 × 0·24 × 0·35 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $0k0$, $k = 2n$; $h0l$, $h = 2n$. 22 reflections ($10 < \theta < 14°$) for refining unit-cell dimensions; ω scan. Scan width: 1·20°, scan speed variable between 0·02 and 0·04° s^{-1}, total background measuring time: between 14 and 28 s. 2258 non-zero reflections measured ($3 < \theta < 35°$), $\pm h$, k, l, $h_{max} = 10$, $k_{max} = 28$, $l_{max} = 10$. Two intensity ($3\bar{4}2$ and $0,10,1$) and two orientation ($\bar{3}42$ and $34\bar{2}$) reference reflections: no significant variation. Lorentz and polarization corrections, no absorption correction. Crystal structure solved by direct methods (*MULTAN*77; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Unit weights. Final refinement with the complete set of unique reflections (2108). Final $R = 0{\cdot}027$, $wR = 0{\cdot}031$, $S = 0{\cdot}398$, max. $\Delta/\sigma = 0{\cdot}08$. Max. peak height in the final difference Fourier map: 0·308 e Å^{-3}. Extinction not refined. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX. The crystal-structure representations were drawn using *STRUPLO*84 (Fischer, 1985).

Discussion. Table 1 reports the final atomic coordinates.* Fig. 1 is a projection of the whole atomic arrangement down the c axis, while Fig. 2 is the projection of a structural detail down the b axis. The main interatomic distances and bond angles are listed in Table 2.

The structure can be described as layers of $H_2PO_4^-$ groups spreading in planes $y \sim 0$ and 0·5 alternating with layers of $C_4H_6N_3O^+$ groups at $y \sim 0{\cdot}25$ and 0·75 (Fig. 1).

Each $H_2PO_4^-$ group is connected by hydrogen bonds with three neighbours across centres of symmetry, to build a two-dimensional network illus-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52252 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates and B_{eq} values* (Å^2)

E.s.d.'s are given in parentheses.

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
P	0·25935 (5)	0·00668 (2)	0·28928 (5)	2·059 (5)
O(1)	0·3424 (2)	0·07527 (5)	0·4014 (2)	2·63 (2)
O(2)	0·1177 (2)	−0·03537 (6)	0·4082 (2)	3·10 (2)
O(3)	0·1595 (2)	0·02686 (6)	0·0721 (2)	2·79 (2)
O(4)	0·4237 (2)	−0·04938 (6)	0·2562 (2)	2·98 (2)
N(1)	0·2940 (2)	0·34193 (6)	0·3495 (2)	2·41 (2)
C(2)	0·3334 (2)	0·27072 (7)	0·4132 (2)	2·03 (2)
O	0·4158 (2)	0·25477 (6)	0·5861 (2)	3·00 (2)
N(3)	0·2758 (2)	0·21654 (5)	0·2677 (2)	1·92 (2)
C(4)	0·6941 (2)	0·26882 (7)	0·0700 (2)	1·83 (2)
N(4)	0·6485 (2)	0·32377 (6)	0·9414 (2)	2·56 (2)
C(5)	0·1609 (2)	0·30668 (7)	0·0110 (2)	2·22 (2)
C(6)	0·7102 (2)	0·14068 (7)	0·1548 (2)	2·35 (2)

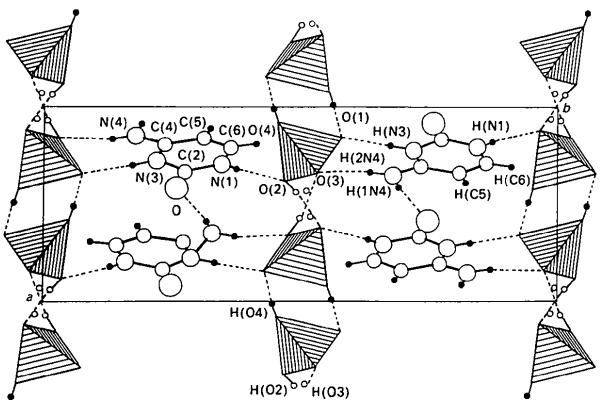

Fig. 1. Projection of the atomic arrangement of cytosinium dihydrogenmonophosphate down the *c* axis. Statistical H atoms are represented by the smallest empty circles. Hydrogen bonds between cytosine groups link one ring (z) to an equivalent one in the lower or upper cell ($z \pm 1$).

trated by Fig. 2. Inside such a layer, P—P distances are rather short (4·023, 4·824 and 4·841 Å). Two of the three H atoms bonded to the phosphate anion *via* O(2) and O(3) are statistical ones. H(4) is entirely involved in hydrogen bonding, but O(1) is not a donor. Consequently, as can be seen in Table 2, the P—O(1) distance (1·507 Å) is significantly shorter than the P—O(H) or P—O(H statistic) distances (1·559 and 1·532 Å).

It is worth noticing that the same type of hydrogen-bond scheme has already been observed in different crystal structures: the aminoguanidinium dihydrogenorthophosphate (Adams, 1977), the 2-carboxyanilinium dihydrogenmonoarsenate (Tordjman, Masse & Guitel, 1988) and the isobutylammonium dihydrogenmonophosphate (Masse, 1989).

The cytosine base occurs as the cytosinium cation $C_4H_6N_3O^+$, the N(3) site having been protonated in the reaction with the orthophosphoric acid.

The base ring atoms are closely coplanar. Their deviations from planarity are given in Table 2. The

Table 2. *Main geometrical features in* $C_4H_6N_3O^+.H_2PO_4^-$

Distances (Å) and bond angles (°) are given with e.s.d.'s in parentheses.

PO_4 tetrahedron

P	O(1)	O(2)	O(3)	O(4)
O(1)	1·507 (1)	112·78 (6)	110·34 (5)	111·08 (6)
O(2)	2·531 (2)	1·533 (1)	110·25 (6)	106·40 (6)
O(3)	2·493 (1)	2·513 (2)	1·531 (1)	105·70 (6)
O(4)	2·528 (1)	2·475 (2)	2·462 (1)	1·559 (1)

Cytosine group

N(1)—C(2)	1·363 (2)	C(2)—N(1)—C(6)	122·9 (1)
C(2)—N(3)	1·380 (2)	N(1)—C(2)—N(3)	115·3 (1)
N(3)—C(4)	1·360 (2)	C(2)—N(3)—C(4)	123·9 (1)
C(4)—C(5)	1·422 (2)	N(3)—C(4)—C(5)	118·2 (1)
C(5)—C(6)	1·343 (2)	C(4)—C(5)—C(6)	118·0 (1)
C(6)—N(1)	1·357 (2)	C(5)—C(6)—N(1)	121·6 (1)
C(2)—O	1·224 (2)	N(1)—C(2)—O	123·3 (1)
C(4)—N(4)	1·306 (2)	N(3)—C(2)—O	121·4 (1)
		N(3)—C(4)—N(4)	119·6 (1)
		C(5)—C(4)—N(4)	122·3 (1)

Hydrogen bonds

	(O,N)—H	H···O	(O,N)···O	∠(O,N)—H···O
N(1)—H(N1)···O(2)	0·73 (2)	2·01 (2)	2·734 (2)	169 (2)
N(3)—H(N3)···O(1)	0·86 (2)	1·84 (2)	2·705 (1)	176 (2)
N(4)—H(1N4)···O	0·89 (2)	2·06 (2)	2·910 (2)	159 (2)
N(4)—H(2N4)···O	0·84 (2)	1·98 (2)	2·817 (2)	170 (2)
O(2)—H(02)···O(2)	0·67 (3)	1·84 (3)	2·501 (2)	172 (4)
O(3)—H(03)···O(3)	0·73 (4)	1·76 (4)	2·476 (1)	167 (5)
O(4)—H(04)···O(1)	0·73 (2)	1·89 (2)	2·611 (1)	178 (2)

Least-squares plane of the cytosine group and deviations of ring atoms from it (Å); X,Y,Z are the coordinates (Å) referred to the orthogonal axes **a**,**b**,**c***

Plane equation: $0{\cdot}9514X + 0{\cdot}0561Y - 0{\cdot}3027Z - 1{\cdot}3160 = 0$

Deviations of atoms used for defining the plane

N(1)	−0·017	C(4)	0·000
C(2)	−0·008	N(4)	0·006
O	0·032	C(5)	0·023
N(3)	−0·033	C(6)	−0·004

Deviations of atoms excluded from the plane calculation

H(N1)	−0·037	H(2N4)	−0·028
H(N3)	−0·025	H(C5)	0·085
H(1N4)	−0·034	H(C6)	−0·007

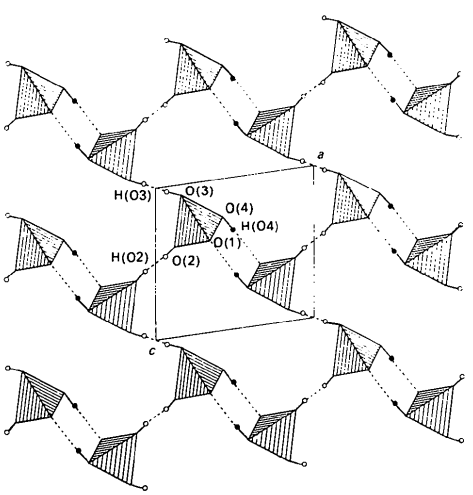

Fig. 2. Projection of the two-dimensional network of the phosphate groups down the *b* axis.

cytosine ring is inclined 87° to the *ac* plane, namely almost perpendicular to the phosphate layers. Comparing the geometrical characteristics of the base rings in this structure (Table 2) and in the cytosine molecule (McClure & Craven, 1973), the effect of protonation of N(3) can be defined thus: an increase of the distances C(2)—N(3) and N(3)—C(4) by about 0·02 Å, an increase of the angle C(2)—N(3)—C(4) by about 4·5° and a decrease of the angles N(1)—C(2)—N(3) and N(3)—C(4)—C(5) by 4·5°. Similar deviations have been observed by Mandel (1977) in the structural analysis of cytosine hydrochloride.

Each cytosine cation is connected to two $H_2PO_4^-$ ions by three hydrogen bonds nearly situated in its plane and perpendicular to the anionic layers: N(1)—H(N1)···O(2), N(3)—H(N3)···O(1) and N(4)—H(2N4)···O(3).

The cytosine groups join themselves by weaker hydrogen bonds from the ammonium N(4) towards the carbonyl oxygen O, so as to form infinite chains running on both sides of the mirror *a*. Thus N(4) participates twice in the cohesion of the structure *via* its H atoms: H(1N4) links the cytosinium ions together along the [(**a**/2) + **c**] direction, while H(2N4) links the $C_4H_6N_3O^+$ cation to the $H_2PO_4^-$ anion along the **b** direction.

In the nucleic acids domain, it is known that, besides the hydrogen bonding, the base stacking also contributes to the stabilization of the structure. In this compound the cytosine rings stack in a direction which is inclined about 18° to the *a* axis. Adjacent base rings are related by the glide plane *a* with an interplanar spacing of 3·30 Å and a dihedral angle between them of 6·5°. Partial overlap of such adjacent rings occurs in each cytosine layer perpendicular to the *b* axis. This type of base packing is uncommon in the crystal structures of compounds containing protonated pyrimidines (Bugg, Thomas, Sundaralingam & Rao, 1971; Mandel, 1977).

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Structure of 2-Acetoxy-10-hydroxy-3-methoxy-10-phenyl-9(10*H*)-anthracenone

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Abstract. $C_{23}H_{18}O_5$, $M_r = 374{\cdot}40$, triclinic, $P\bar{1}$, $a = 12{\cdot}210\ (3)$, $b = 10{\cdot}557\ (3)$, $c = 8{\cdot}832\ (1)$ Å, $\alpha = 96{\cdot}39\ (2)$, $\beta = 121{\cdot}15\ (2)$, $\gamma = 103{\cdot}99\ (2)°$, $V = 906{\cdot}3\ (5)$ Å^3, $Z = 2$, $D_m = 1{\cdot}38$, $D_x = 1{\cdot}372$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}04$ cm^{-1}, $F(000) = 392$, $T = 293$ K, final $R = 0{\cdot}051$ for 3205 unique observed reflections. The anthracenone tricyclic system is nonplanar being bent about the C(9)···C(10) vector; the dihedral angle between the two halves is 11·1 (3)°. The acetoxy and methoxy groups are found in the expected 2- and 3-positions of the anthracenone system. The molecules form dimers by hydrogen bonding between the hydroxyl group and the 'ether' O atom of the acetoxy group; the O···O distance is 2·870 (2) Å and the O—H···O angle is 155 (2)°.

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