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Acta Cryst. (1991). **C47**, 153–156

Structure of 2'-Deoxycytidinium Dihydrogenphosphate

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(Received 14 November 1989; accepted 28 March 1990)

Abstract. $C_9H_{14}N_3O_4^+ \cdot H_2PO_4^-$, $M_r = 325.2$, orthorhombic, $P2_12_12_1$, $a = 9.742(1)$, $b = 7.0773(6)$, $c = 19.327(3)$ Å, $V = 1332.5(3)$ Å³, $Z = 4$, $D_x = 1.62$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.99$ cm⁻¹, $F(000) = 680$, $T = 290$ K, $R = 0.030$ for 1193 observed reflections. The crystals are isostructural with those of cytidinium dihydrogenphosphate and also contain the characteristic infinite sugar...phosphate chains in which the dihydrogenphosphate anions are hydrogen bonded (*via* their POH donors) to O(3') and O(5') of neighboring nucleosides. In the absence of the O(2') group, the O(5')H donor forms a much stronger hydrogen bond with O(2) along the chain. Parallel to the sugar...phosphate chains there are also analogous nucleobase...phosphate hydrogen-bonded chains in which the phosphate anion accepts two hydrogen bonds [N(4)H(41)...O and N(3)H⁺...O] from one cytosinium cation and one bond [N(4)H(42)...O] from the next cation in the chain. The 2'-deoxyribose conformation is ²E [$P = 167.5(7)^\circ$, $\tau_m = 36.4(5)^\circ$], the glycosidic torsion angle χ is *anti* [$33.7(4)^\circ$] and the side chain is *gauche*⁺ [$\gamma = 48.9(4)^\circ$].

Introduction. The first information on the synthesis and physico-chemical properties of phosphate salts of nucleosides was reported by Wiewiórowski *et al.* (1986) who described the dihydrogenphosphate salt of cytidine. The conclusions drawn by these authors were generally confirmed when the crystal structure of cytidinium dihydrogenphosphate (CydH⁺·H₂PO₄⁻) became available recently (Jaskólski, 1989), revealing that the dihydrogenphosphate anion uses both its POH donors to form ---O(3')...H—OP(O₂)O—H...O(5')--- hydrogen bonds with the ribose residues of two adjacent cytidinium units leading to infinite ribose...phosphate chains in which the

hydrogen bonds mimic the ester bonds of a real polynucleotide chain. The organization of the ions in that structure suggested a possible retention of this arrangement even on replacement of ribose by 2'-deoxyribose. However, attempts to synthesize the analogous 2'-deoxycytidinium dihydrogenphosphate salt (dCydH⁺·H₂PO₄⁻) revealed a more complicated situation. In the case of cytidine, CydH⁺·H₂PO₄⁻ seems to be the only stoichiometry with which the ions crystallize even when there is a large excess of cytidine (Bratek-Wiewiórowska, Popenda, Malinowska & Wiewiórowski, 1990). In contrast, 2'-deoxycytidine reacts with orthophosphoric acid to preferentially form a hemi salt, (dCyd)₂H⁺·H₂PO₄⁻, even from solutions in which the dCyd:H₃PO₄ molar ratio is 1:1.5. It is possible that two dCyd nucleosides share a single proton and form a homoconjugated cation with three hydrogen bonds operating within its base pair, since such cationic cytosine...H⁺...cytosine or cytosine—H⁺...cytosine base pairs have been described previously (*e.g.* Marsh, Bierstedt & Eichhorn, 1962; Tamura, Sato & Hata, 1973; Kistenmacher, Rossi, Caradonna & Marzilli, 1979; Kistenmacher, Rossi, Chiang, Caradonna & Marzilli, 1980; Westhof, Rao & Sundaralingam, 1980; Gdaniec, Brycki & Szafran, 1988) and are believed to represent a strong association similar to that present in Watson-Crick C—G base pairs. Furthermore, the crystal of neutral 2'-deoxycytidine (Young & Wilson, 1975) has two molecules in the asymmetric unit which form a C—C base pair through a doublet of N(4)H...N(3) hydrogen bonds. In contrast, neutral cytidine crystallizes without formation of base pairs (Furberg, Petersen & Rømming, 1965). The 1:1 salt, dCydH⁺·H₂PO₄⁻, crystallizes only when orthophosphoric acid is in at least 1.8-fold excess (Bratek-Wiewiórowska, Popenda, Malinowska &

Wiewiórowski, 1990). The present paper reports the X-ray structure of this crystal.

Experimental. Suitable crystals from water-methanol solution with 1:1.8 molar ratio of dCyd:H₂PO₄, crystal 0.4 × 0.4 × 0.6 mm, Syntex P2₁ diffractometer, graphite monochromator, Mo K α radiation. Cell parameters from least-squares treatment of setting angles of 15 reflections (19.7 < 2 θ < 24.7°). ω :2 θ profiles measured for 1399 unique + $h + k + l$ reflections with 2 θ < 50° [maximum (sin θ)/ λ = 0.595 Å⁻¹] and with 0 ≤ h ≤ 11, 0 ≤ k ≤ 8, 0 ≤ l ≤ 22; profile analysis according to Lehmann & Larsen (1974). Random intensity variation (within 2.7%) of two standard reflections (043, $\bar{5}$ 13) measured every 1.5 h. No absorption correction. 1193 observed reflections with $I \geq 2\sigma(I)$. The structure refinement started from the coordinates of the isostructural CydH⁺.H₂PO₄⁻; function minimized in the full-matrix least-squares refinement: $\sum w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F)$. All non-H atoms refined anisotropically. All H atoms attached to C atoms contributed to F_c at geometrically generated positions recalculated after each refinement cycle. The H atoms attached to the N and O atoms were fixed at the positions deduced from successive ΔF maps calculated throughout the refinement process. The isotropic temperature factors of all H atoms were fixed at $U_{\text{iso}} = 0.05$ Å². The refinement included an empirical isotropic extinction parameter x defined as $F_c' = F_c(1 - xF_c^2/\sin\theta)$, which converged at $x = 1.16(2) \times 10^{-6}$. Final $R = 0.030$, $wR = 0.035$, $S = 3.38$, $(\Delta/\sigma)_{\text{max}} = 0.02$; largest peak in final ΔF map = 0.20, largest trough = -0.21 e Å⁻³. Computer programs: local programs (Jaskólski, 1982) and SHELX76 (Sheldrick, 1976) and PARST (Nardelli, 1983) as implemented in the CRYSRULER package (Rizzoli, Sangermano, Cales-tani & Andreotti, 1986), molecular illustrations drawn using ORTEP (Johnson, 1976) and PLUTO (Motherwell & Clegg, 1978). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic coordinates are listed in Table 1.* Bond distances and angles are given in Table 2 and a thermal-ellipsoid representation of the 2'-deoxycytidinium cation is shown in Fig. 1. The dimensions of the cation are consistent with those found in other cytidinium and 2'-deoxycytidinium salts, particularly in the isostructural cytidinium dihydrogenphosphate (Jaskólski, 1989). The bond

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
P	0.2017 (1)	0.9258 (2)	0.30361 (5)	0.0247 (3)
O(1P)	0.0440 (3)	0.8995 (4)	0.2924 (1)	0.041 (1)
O(2P)	0.2615 (3)	0.9859 (4)	0.2354 (1)	0.0300 (7)
O(3P)	0.2638 (3)	0.7590 (4)	0.3379 (1)	0.0311 (9)
O(4P)	0.2164 (3)	1.1079 (4)	0.3510 (1)	0.0332 (9)
N(1)	0.0129 (3)	0.5806 (5)	0.5797 (1)	0.027 (1)
C(2)	0.0473 (4)	0.7486 (5)	0.6110 (2)	0.026 (1)
O(2)	0.0377 (3)	0.9016 (4)	0.5829 (1)	0.0365 (9)
N(3)	0.0989 (3)	0.7317 (4)	0.6770 (1)	0.026 (1)
C(4)	0.1222 (4)	0.5663 (5)	0.7107 (2)	0.026 (1)
N(4)	0.1755 (3)	0.5681 (5)	0.7730 (2)	0.0335 (9)
C(5)	0.0879 (4)	0.3971 (5)	0.6758 (2)	0.027 (1)
C(6)	0.0339 (4)	0.4095 (6)	0.6115 (2)	0.029 (1)
C(1')	-0.0454 (4)	0.5880 (6)	0.5089 (2)	0.028 (1)
C(2')	0.0621 (4)	0.5625 (6)	0.4526 (2)	0.033 (1)
C(3')	-0.0221 (4)	0.4769 (5)	0.3946 (2)	0.027 (1)
O(3')	-0.0907 (3)	0.6273 (4)	0.3595 (1)	0.0327 (8)
C(4')	-0.1265 (4)	0.3544 (5)	0.4337 (2)	0.027 (1)
O(4')	-0.1385 (3)	0.4367 (4)	0.5020 (1)	0.0328 (8)
C(5')	-0.0904 (4)	0.1462 (6)	0.4393 (2)	0.037 (1)
O(5')	0.0483 (3)	0.1223 (4)	0.4627 (1)	0.043 (1)

Table 2. Bond distances (Å) and angles (°)

N(1)—C(2)	1.375 (5)	C(3')—O(3')	1.428 (5)
C(2)—O(2)	1.215 (4)	C(3')—C(4')	1.535 (5)
C(2)—N(3)	1.376 (4)	C(4')—C(5')	1.519 (5)
N(3)—C(4)	1.359 (4)	C(5')—O(5')	1.435 (5)
C(4)—N(4)	1.311 (4)	C(4')—O(4')	1.447 (4)
C(4)—C(5)	1.414 (5)	O(4')—C(1')	1.410 (5)
C(5)—C(6)	1.352 (5)	P—O(1P)	1.563 (3)
C(6)—N(1)	1.373 (5)	P—O(2P)	1.503 (2)
N(1)—C(1')	1.483 (4)	P—O(3P)	1.483 (3)
C(1')—C(2')	1.521 (5)	P—O(4P)	1.588 (3)
C(2')—C(3')	1.515 (5)		
C(6)—N(1)—C(2)	121.9 (3)	C(1')—C(2')—C(3')	101.8 (3)
C(6)—N(1)—C(1')	120.1 (3)	C(2')—C(3')—C(4')	102.7 (3)
C(1')—N(1)—C(2)	118.0 (3)	C(2')—C(3')—O(3')	107.9 (3)
N(1)—C(2)—N(3)	115.0 (3)	O(3')—C(3')—C(4')	110.2 (3)
N(1)—C(2)—O(2)	123.7 (3)	C(3')—C(4')—O(4')	106.0 (3)
O(2)—C(2)—N(3)	121.3 (3)	C(3')—C(4')—C(5')	115.4 (3)
C(2)—N(3)—C(4)	125.4 (3)	O(4')—C(4')—C(5')	110.1 (3)
N(3)—C(4)—C(5)	117.5 (3)	C(4')—C(5')—O(5')	110.8 (3)
N(3)—C(4)—N(4)	119.8 (3)	C(4')—O(4')—C(1')	109.9 (3)
O(4)—C(4)—C(5)	122.7 (3)	O(1P)—P—O(2P)	107.1 (1)
C(4)—C(5)—C(6)	118.4 (3)	O(1P)—P—O(3P)	111.6 (2)
C(5)—C(6)—N(1)	121.8 (4)	O(1P)—P—O(4P)	105.4 (1)
N(1)—C(1')—O(4')	107.9 (3)	O(2P)—P—O(3P)	117.3 (2)
N(1)—C(1')—C(2')	113.1 (3)	O(2P)—P—O(4P)	104.0 (1)
O(4')—C(1')—C(2')	106.6 (3)	O(3P)—P—O(4P)	110.6 (1)

distances and angles in the cytosinium moiety agree with the average values compiled by Taylor & Kennard (1982). The pyrimidine ring is planar with $\chi^2 = 33.7$. The C(1') and N(4) substituents are, respectively, 0.002 (4) and 0.014 (3) Å from the pyrimidine plane whereas the deviation of the carbonyl O(2) atom amounts to 0.094 (3) Å. The plane of the exocyclic amino group makes an angle of 4° with the pyrimidine ring. The conformation of the 2'-deoxyribose ring is 2'-endo (²E), slightly deformed towards 2'-endo-3'-exo (²T₃). In terms of pseudo-rotation (Altona & Sundaralingam, 1972), the sugar

* 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 53158 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conformation is characterized by $P = 167.5(7)^\circ$ and $\tau_m = 36.4(5)^\circ$ (Jaskólski, 1984). The glycosidic torsion angle, which describes the relative orientation of the base with respect to the sugar, is in the *anti* region with $\chi = 33.7(4)^\circ$. The torsion angles $O(5')-C(5')-C(4')-C(3')$ (γ) and $O(5')-C(5')-C(4')-O(4')$ [48.9(4) and $-71.0(4)^\circ$, respectively] indicate that the side chain assumes the preferred *gauche*⁺ conformation with the $C(5')-O(5')$ bond rotated *ca* 11° from the ideal staggered orientation towards $C(4')-C(3')$. This deformation is nearly identical to that in

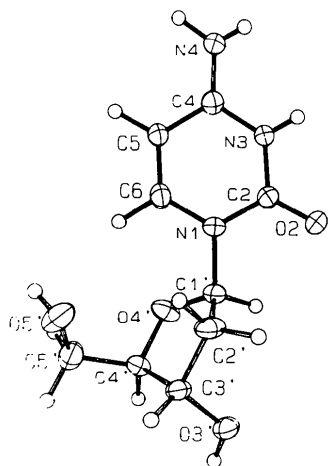


Fig. 1. Thermal-ellipsoid representation of the 2'-deoxycytidinium cation. Non-H-atom ellipsoids are at 50% probability level, H-atom spheres are arbitrarily sized.

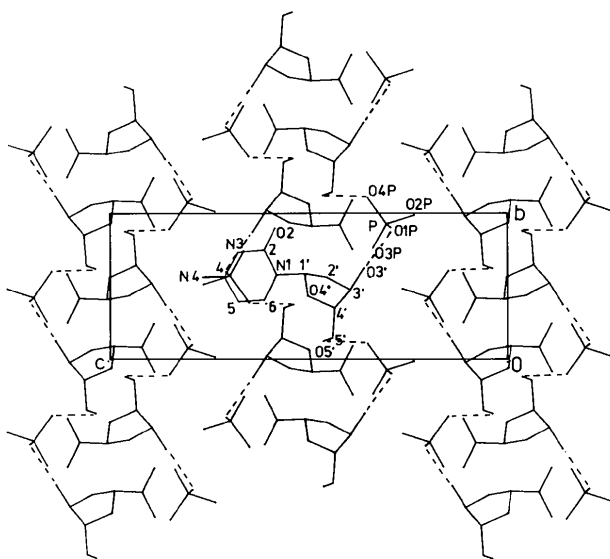


Fig. 2. Projection of the structure down *a*. Except in one cation, the $C(2)-C(6)$ fragment of the pyrimidine system has been omitted to increase clarity. H atoms are not shown. $O-H\cdots O$ hydrogen bonds between the 2'-deoxyribose and phosphate moieties are indicated by broken lines.

Table 3. Geometry of the hydrogen bonds

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$\angle D-H\cdots A$ (°)
$O(1P)-H(1P)\cdots O(3')$	0.93	1.75	2.667 (4)	170
$O(4P)-H(4P)\cdots O(5')$	0.77	1.99	2.712 (3)	156
$N(3)-H(3)\cdots O(2P^{ii})$	0.84	1.83	2.667 (4)	169
$N(4)-H(41)\cdots O(3P^{iii})$	0.97	1.73	2.698 (4)	176
$N(4)-H(42)\cdots O(4P^{iv})$	0.77	2.20	2.939 (4)	163
$O(3')-H(3'O)\cdots O(2P^{iv})$	0.89	1.79	2.671 (4)	167
$O(5')-H(5'O)\cdots O(2')$	0.75	2.06	2.802 (3)	167
$C(5)-H(5)\cdots O(2P^{iii})$	1.08	2.29	3.290 (5)	154

Symmetry codes: (i) $x, 1+y, z$; (ii) $0.5-x, 2-y, 0.5+z$; (iii) $0.5-x, 1-y, 0.5+z$; (iv) $-x, y-0.5, 0.5-z$; (v) $x, y-1, z$.

$CydH^+ \cdot H_2PO_4^-$ (13°). The pattern of the $P-O$ bond lengths in the present dihydrogenphosphate anion is identical to that in $CydH^+ \cdot H_2PO_4^-$ with the two $P-OH$ bonds significantly longer than the other two $P-O$ bonds.

As the crystals are isostructural with $CydH^+ \cdot H_2PO_4^-$, the network of hydrogen bonds is generally based on the same principle. In particular, the structure still contains hydrogen-bonded sugar \cdots phosphate chains in which the $H_2PO_4^-$ anion is a donor (through its $PO-H$ groups) to $O(5')$ and $O(3')$ on two (*b*-translation-related) 2'-deoxyribose residues. The hydrogen bonds along such a chain mimic the $O(3')-P-O(5')$ ester bonds in the backbone of a real polynucleotide chain (Fig. 2). Owing to the lack of the $O(2')H$ function, the sugar \cdots phosphate backbone cannot have an $O(2')-H\cdots O(3P)$ bond on the 3'-end of the sugar and is no longer reinforced by the direct $O(5')-H\cdots O(2')$ link between adjacent residues. Instead, the $O(5')H$ donor forms a much stronger hydrogen bond with $O(2)$ of the base fragment of the same adjacent nucleoside (Table 3). In $CydH^+ \cdot H_2PO_4^-$ this $O(5')-H\cdots O(2)$ bond was a (weak) component of a bifurcated hydrogen bond. On its 'base end' the cation also interacts with the anion (at $0.5-x, 1-y, 0.5+z$) forming another hydrogen-bonded chain running along *b* in the same way as in $CydH^+ \cdot H_2PO_4^-$ [not shown in Fig. 2, but compare with Fig. 2 of Jaskólski (1989)]. The role of the dihydrogenphosphate anion is reversed in this chain as it *accepts* one hydrogen bond [$N(4)H(41)\cdots O(3P)$] from one cation and two bonds [$N(4)H(42)\cdots O(4P)$ and $N(3)^+-H(3)\cdots O(2P)$] from its *b*-translated equivalent (Table 3). It was observed by Viswamitra, Reddy, Lin & Sundaralingam (1971) that the latter scheme of phosphate \cdots nucleobase pairing, where the base uses the *exo* amino $HN-H$ function and the N^+-H protonation site to bind a single phosphate residue, is characteristic of the cytidine and adenosine (Sundaralingam, 1966) nucleosides. In the structure of 2'-deoxycytidinium 5'-phosphate monohydrate (Viswamitra, Reddy, Lin & Sundaralingam, 1971), which also crystallizes in the $P2_12_12_1$ space group,

the nucleotide units related by a 2_1 screw axis parallel to **b** form an infinite hydrogen-bonded chain in which the $-\text{O}(5')-\text{[PO}_3\text{H]}^-$ phosphate group is a hydrogen donor to $\text{O}(3')$ of another molecule.

Thanks are due to Professor Maciej Wiewiórowski for his interest in this work and to Mgr Marek Figlerowicz for preparing the crystals. This work was partly supported by Project RPBP 01.6 (Polish Academy of Sciences).

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Acta Cryst. (1991). **C47**, 156–159

Conformational Comparison of 1,2-Dimethyl-6-oxo-1,6-dihydro-3,4'-bipyridine-5-carbonitrile Free Base and its Hydrobromide Monohydrate Salt

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(Received 24 January 1990; accepted 10 April 1990)

Abstract. $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$ (I), $M_r = 225.25$, monoclinic, $P2_1/c$, $a = 11.713$ (4), $b = 7.891$ (3), $c = 12.154$ (4) Å, $\beta = 92.27$ (4)°, $V = 1123$ (1) Å³, $Z = 4$, $D_x = 1.333$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.082$ mm⁻¹, $F(000) = 472$, $T = 293$ K, $R = 0.063$ for 2579 reflections. 5-Cyano-1,2-dimethyl-6-oxo-1,6-dihydro-3,4'-bipyridinium bromide monohydrate, $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}^+\text{Br}^-\cdot\text{H}_2\text{O}$ (II), $M_r = 324.18$, orthorhombic, $Pbca$, $a = 7.2893$ (8), $b = 18.955$ (3), $c = 19.814$ (3) Å, $V = 2738$ (1) Å³, $Z = 8$, $D_x = 1.573$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu =$

2.972 mm⁻¹, $F(000) = 1312$, $T = 293$ K, $R = 0.086$ for 2292 reflections. The twist angle around the bipyridine C(1)—C(1)' bond is 66.6 (2) and 44.1 (8)° for the free base (I) and its salt (II), respectively. The larger C(3)'—N(4)'—C(5)' pyridine ring angle [121.8 (5)°] in the salt structure compared with the corresponding value for the free base [116.1 (1)°] suggests that N(4)' is a protonation site. The water molecule in the salt structure (II) is disordered with occupancy refined to 0.6 and 0.4.

Introduction. A new class of bipyridine derivatives which act as positive cardiac inotropic agents have been developed for the treatment of congestive heart failure (Endoh, Yamashita & Taira, 1982). Biological tests reveal that one of the series, milrinone (6-oxo-

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