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Structure of Calcium Thymidine 5'-Phosphate Dihydrate, Ca²⁺.C₁₀H₁₃N₂O₈P²⁻.2H₂O

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Abstract. $M_r = 396.3$, monoclinic, $P2_1$, $a = 12.821$ (5), $b = 11.050$ (2), $c = 5.543$ (1) Å, $\beta = 98.95$ (3)°, $V = 775.7$ (4) Å³, $Z = 2$, $D_x = 1.697$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.56$ mm⁻¹, $F(000) = 412$, $T = 298$ K, final $R = 0.030$ for 2146 observed reflections. The molecule has a C(4')-*exo* (E_4) sugar associated with an *anti* glycosidic bond rotation [torsion angle O(4')–C(1')–N(1)–C(6) = 65.7 (4)°]. The conformations about the C(4')–C(5') and C(5')–O(5') bonds are *trans–gauche* [torsion angle C(3')–C(4')–C(5')–O(5') = −60.4 (3)°] and *trans* [torsion angle C(4')–C(5')–O(5')–P = −153.5 (2)°], respectively. All available H atoms participate in hydrogen bonding.

Introduction. The crystal structure of calcium thymidine 5'-phosphate hexahydrate has been reported (Trueblood, Horn & Luzzati, 1961). We have found another crystalline form of calcium thymidine 5'-phosphate and subjected it to X-ray analysis. This study is part of a series of crystallographic investigations of nucleic acid constituents.

Experimental. Crystals grown from water/2-methyl-2,4-pentanediol solution by vapor diffusion, colorless plates, crystal 0·04 × 0·20 × 0·40 mm used for data collection, Rigaku AFC-5 diffractometer, graphite-monochromator; lattice parameters refined by least-squares method (22 reflections, $29 < 2\theta < 40°$); intensities measured up to $2\theta = 60°$ ($\sin\theta/\lambda \le 0.704$ Å⁻¹), ω scan ($2\theta \le 30°$), ω–2θ scan ($2\theta > 30°$), 3 standard reflections, no variation, 2363 independent reflections, h 0–15, k 0–12, $l = -6$–6, no absorption correction; structure solved by *MULTAN* (Main, Hull, Lessinger,

Germain, Declercq & Woolfson, 1978), Ca and the phosphate group located from E map, the other non-H atoms from weighted Fourier, H atoms from difference Fourier; structure refined by block-diagonal least-squares method, anisotropic temperature factors for non-H atoms, isotropic temperature factors for H atoms, $\sum w\Delta^2$ minimized, $\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$ for $|F_c| \ge 3\sigma(F_o)$, $w = 0$ for $|F_c| < 3\sigma(F_o)$ or $|\Delta| \ge 3\sigma(F_o)$, $\sigma(F_o) = |\sigma_1^2(F_o) + 0.00020|F_o|^2|^{1/2}$, $\sigma_1(F_o)$ is e.s.d. based on counting errors (Grant, Killean & Lawrence, 1969),* $R = 0.030$ for 2146 reflections ($w \ne 0$), $R_w = 0.033$, $S = 1.05$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Refined atomic coordinates are given in Table 1. A perspective view of the molecule is shown in Fig. 1. Bond distances and angles are listed in Table 2.

The deoxyribose ring adopts a C(4')-*exo* puckering. The pseudorotation coordinates of the five-membered ring (Sato, 1983) are $\Pi = 36.8$ (3), $\Phi = 151.5$ (5)°. A pucker quite similar to this has been observed in 5-acetyl-2'-deoxyuridine (Barr, Chananont, Hamor, Jones, O'Leary & Walker, 1980), but C(4')-*exo* puckers are rather exceptional in the crystal structures of nucleosides and nucleotides so far observed. The sugar is associated with an *anti* base. The glycosidic torsion

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* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39024 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1)	0·5228 (2)	0·5548 (3)	0·0302 (5)	2·06 (6)
C(2)	0·6145 (2)	0·6138 (3)	−0·0054 (6)	2·52 (7)
N(3)	0·7031 (2)	0·5794 (3)	0·1533 (5)	2·73 (7)
C(4)	0·7054 (2)	0·5045 (3)	0·3564 (5)	2·22 (6)
C(5)	0·6069 (2)	0·4436 (3)	0·3787 (5)	2·14 (7)
C(6)	0·5216 (2)	0·4712 (3)	0·2152 (5)	2·16 (7)
O(2)	0·6165 (2)	0·6884 (3)	−0·1661 (6)	4·55 (8)
O(4)	0·7870 (2)	0·4903 (3)	0·5009 (4)	3·19 (6)
C(7)	0·6056 (3)	0·3522 (4)	0·5758 (6)	3·08 (8)
O(4')	0·3600 (2)	0·6474 (2)	0·0273 (5)	2·98 (6)
C(1')	0·4245 (2)	0·5869 (3)	−0·1246 (5)	2·30 (7)
C(2')	0·3588 (2)	0·4799 (3)	−0·2443 (6)	2·76 (8)
C(3')	0·2503 (2)	0·4946 (3)	−0·1622 (4)	1·75 (6)
C(4')	0·2516 (2)	0·6257 (3)	−0·0764 (5)	1·85 (6)
O(3')	0·1640 (1)	0·4765 (2)	−0·3508 (4)	2·31 (5)
C(5')	0·1862 (2)	0·6520 (3)	0·1194 (5)	2·39 (7)
O(5')	0·0791 (1)	0·6223 (2)	0·0229 (3)	1·74 (4)
P	−0·01614 (5)	0·6914 (1)	0·1309 (1)	1·05 (1)
O(1P)	0·0031 (2)	0·8260 (2)	0·1058 (3)	1·72 (4)
O(2P)	−0·1079 (1)	0·6405 (2)	−0·0459 (3)	1·61 (4)
O(3P)	−0·0134 (2)	0·6558 (2)	0·3942 (3)	1·81 (4)
Ca	−0·02743 (3)	0·5049	−0·3293 (1)	1·09 (1)
O(W1)	−0·0311 (2)	0·3649 (2)	−0·6408 (4)	3·28 (7)
O(W2)	−0·2251 (2)	0·7947 (3)	−0·3867 (6)	4·88 (9)

Table 2. *Molecular dimensions*

Bond distances (Å)

N(1)–C(2)	1·385 (5)		O(4')–C(4')	1·439 (4)
N(1)–C(6)	1·382 (5)		C(1')–C(2')	1·541 (5)
N(1)–C(1')	1·454 (5)		C(2')–C(3')	1·538 (5)
C(2)–N(3)	1·378 (5)		C(3')–C(4')	1·524 (5)
C(2)–O(2)	1·217 (5)		C(3')–O(3')	1·413 (4)
N(3)–C(4)	1·394 (5)		C(4')–C(5')	1·500 (5)
C(4)–C(5)	1·453 (5)		C(5')–O(5')	1·432 (4)
C(4)–O(4)	1·225 (5)		O(5')–P	1·631 (2)
C(5)–C(6)	1·342 (5)		P–O(1P)	1·518 (3)
C(5)–C(7)	1·490 (6)		P–O(2P)	1·517 (2)
O(4')–C(1')	1·434 (4)		P–O(3P)	1·507 (3)

Bond angles (°)

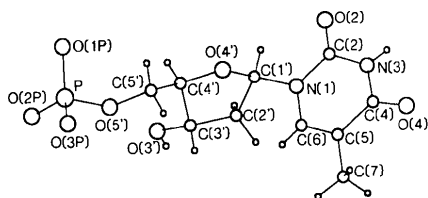|				
C(2)–N(1)–C(6)	121·9 (3)		O(4')–C(1')–C(2')	106·5 (3)
C(2)–N(1)–C(1')	118·6 (3)		C(1')–C(2')–C(3')	104·5 (3)
C(6)–N(1)–C(1')	119·5 (3)		C(2')–C(3')–C(4')	103·1 (3)
N(1)–C(2)–N(3)	114·4 (3)		C(2')–C(3')–O(3')	114·0 (3)
N(1)–C(2)–O(2)	122·6 (3)		C(4')–C(3')–O(3')	109·6 (3)
N(3)–C(2)–O(2)	123·0 (3)		O(4')–C(4')–C(3')	104·2 (3)
C(2)–N(3)–C(4)	126·3 (3)		O(4')–C(4')–C(5')	107·0 (3)
N(3)–C(4)–C(5)	115·7 (3)		C(3')–C(4')–C(5')	115·5 (3)
N(3)–C(4)–O(4)	120·9 (3)		C(4')–C(5')–O(5')	107·3 (3)
C(5)–C(4)–O(4)	123·4 (3)		C(5')–O(5')–P	119·0 (2)
C(4)–C(5)–C(6)	117·7 (3)		O(5')–P–O(1P)	106·5 (1)
C(4)–C(5)–C(7)	119·0 (3)		O(5')–P–O(2P)	98·0 (1)
C(6)–C(5)–C(7)	123·2 (3)		O(5')–P–O(3P)	109·1 (1)
N(1)–C(6)–C(5)	123·4 (3)		O(1P)–P–O(2P)	115·1 (1)
C(1')–O(4')–C(4')	107·3 (3)		O(1P)–P–O(3P)	111·4 (2)
N(1)–C(1')–O(4')	107·1 (3)		O(2P)–P–O(3P)	115·3 (1)
N(1)–C(1')–C(2')	115·6 (3)			

Fig. 1. A perspective view of the molecule, showing the atom numbering.

angle O(4')–C(1')–N(1)–C(6) is 65·7 (4)°, compared with 55·9° found in 5-acetyl-2'-deoxyuridine. It is noticed that these angles are much higher than the value expected for the C(4')-*exo–anti* conformation from the correlation between the glycosidic torsion angle and the sugar puckering, which has been inferred from the structures of oligodeoxynucleotides (Dickerson & Drew, 1981). It is possible that the present structure is strained by the crystal field and, therefore, is deformed from the stable molecular conformation, because it involves several notable sugar–base contacts, *i.e.* O(4')···C(6) [2·915 (4) Å], C(2')···C(6) [3·033 (5) Å], H(C1')···C(2) [2·34 (4) Å] and H(C1')···O(2) [2·19 (4) Å]. On the other hand, the present glycosidic bond rotation can be regarded as normal, when it is compared with the large values observed in various 3',5'-cyclic pyrimidine nucleotides (Sundaralingam, Haromy & Prusiner, 1982), in which the sugars adopt the C(3')-*endo*–C(4')-*exo* conformation similar to the present one. Therefore, it seems more likely that the present structure does reflect a representative conformation for C(4')-*exo* pyrimidine nucleosides. Another uncommon feature of the structure is that the conformation about the C(4')–C(5') bond is *trans–gauche*: C(5')–O(5') is *trans* to C(4')–O(4') and *gauche* to C(4')–C(3'), torsion angle C(3')–C(4')–C(5')–O(5') being −60·4 (3)°. The conformation about the C(5')–O(5') bond is *trans* [torsion angle C(4')–C(5')–O(5')–P = −153·5 (2)°], as usual.

The bond distances of the thymine base are in agreement (within 0·016 Å) with those of thymidine (Young, Tollin & Wilson, 1969), but the pyrimidine ring is appreciably distorted from planarity. Relative to the mean plane through C(4), C(5), C(6) and N(1), which is essentially planar [within 0·003 (3) Å], C(2) and N(3) are displaced by 0·037 (3) and 0·117 (3) Å, respectively, lying on the same side of the plane. The bond distances involved in the sugar moiety are in agreement (within 0·019 Å) with those of a similar conformation found in 5-acetyl-2'-deoxyuridine. The length
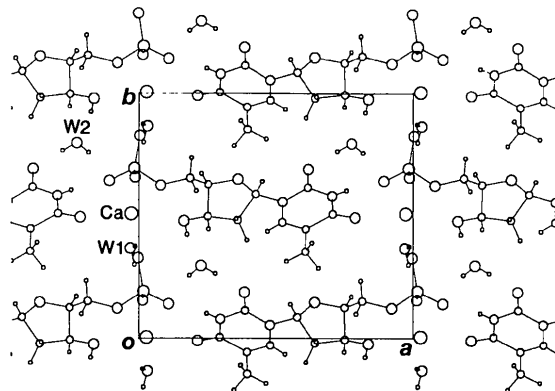
Fig. 2. A projection of the structure viewed along the *c* axis.

of the glycosidic bond is 0·026 Å shorter than that of thymidine. This may be due to the change in the sugar puckering and/or in the glycosidic bond rotation (Lo, Shefter & Cochran, 1975).

The packing scheme in the crystal is shown in Fig. 2. The ionic groups and the water molecules are located close to each other, and form a layer parallel to the bc plane, as frequently observed in nucleotide crystals. In the present structure, no appreciable base stacking is observed. All available hydrogens participate in hydrogen bonding, i.e. N(3)–H···O(2P) |2·895 (4) Å|, O(3')–H···O(W2) |2·669 (4) Å|, O(W1)–H(1)··· O(3P) |2·700 (4) Å|, O(W1)–H(2)···O(1P) |2·692 (4) Å|, O(W2)–H(1)···O(2P) |2·801 (4) Å|, and O(W2)–H(2)···O(2) |2·788 (5) Å|. The Ca²⁺ ion is surrounded by seven oxygen atoms |O(4), O(3'), O(5'), O(1P), O(2P), O(3P) and O(W1)| at distances ranging from 2·291 (3) to 2·555 (2) Å. Apart from those stated above, there are no notable intermolecular short contacts.

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Structure of Calcium 2'-Deoxyadenosine 5'-Phosphate Pentahydrate, $Ca^{2+}.C_{10}H_{12}N_5O_6P^{2-}.5H_2O$

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Abstract. $M_r = 459.4$, orthorhombic, $P2_12_12_1$, $a = 6.882$ (1), $b = 39.761$ (3), $c = 6.569$ (1) Å, $V = 1797.6$ (2) Å³, $Z = 4$, $D_x = 1.697$ Mg m⁻³, λ(Cu Kα) $= 1.5418$ Å, μ(Cu Kα) $= 4.40$ mm⁻¹, $F(000) = 960$, room temperature, final $R = 0.024$ for 1884 observed reflections. The molecule has a C(4)-exo-O(4')-endo ($^OT_4$) sugar associated with an *anti* glycosidic bond rotation |torsion angle O(4')–C(1')–N(9)–C(8) = 60·9 (3)°|. The conformations about the C(4')–C(5') and C(5')–O(5') bonds are *trans–gauche* |C(3')–C(4')–C(5')–O(5') = −71·3 (2)°| and *trans* |C(4')–C(5')–O(5')–P = 169·1 (1)°|, respectively. All available H atoms participate in intermolecular hydrogen bonds.

Introduction. The crystal structure of the Na salt of 2'-deoxyadenosine 5'-phosphate has been reported (Reddy & Viswamitra, 1975). We have crystallized the Ca salt of the same nucleotide and subjected it to X-ray analysis. This study is part of a series of crystallographic investigations of nucleic acid constituents.

Experimental. Crystals grown from a water/2-methyl-2,4-pentanediol solution by vapor diffusion, colorless plates, D_m not determined, crystal $0.15 \times 0.20 \times 0.20$ mm, Rigaku AFC-5 diffractometer, graphite monochromator, Cu Kα radiation. Lattice parameters refined by least-squares method (25 reflections, $29 < 2\theta < 50°$). $2\theta \le 140°$ ($\sin\theta/\lambda \le 0.609$ Å⁻¹), ω scan ($2\theta \le 30°$), ω–2θ scan ($2\theta > 30°$); h 0 to 8, k 0 to 48, l 0 to 8. 1976 independent reflections. No absorption correction. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms from difference Fourier. Structure refined by block-diagonal least-squares method, anisotropic temperature factors for non-H atoms, isotropic for H atoms; $\sum w\Delta^2$ minimized, $\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$ for $|F_c| \ge 3\sigma(F_o)$, $w = 0$ for $|F_c| < 3\sigma(F_o)$ or $|\Delta| \ge 3\sigma(F_o)$, $\sigma(F_o) = |\sigma_1^2(F_o) + 0.00080|F_o|^2|^{1/2}$, $\sigma_1(F_o)$ is the e.s.d. based on counting errors (Grant, Killean & Lawrence, 1969). $R = 0.024$ for 1884 reflections ($w \ne 0$), $R_w = 0.032$, $S = 1.06$. Atomic scattering factors from *International Tables for X-ray*