suggestive, but the number density is difficult to estimate, and the point needs further work.

(ii) A strong triplet of reflexions is observed in the X-ray diffraction pattern of the silk of *Apis Mellifera* (Atkins, 1967), although it is 'reversed' – the off-equatorial reflexions are at smaller values of *d* than the truly equatorial one. Atkins's interpretation of his diffraction pattern is a packing of four stranded ropes. The presence of the triplet strongly suggests that the silk must contain structural features involving straight and tilted segments (and probably gap and overlap regions), as is proposed in this paper. It seems very likely that a model involving single molecules, or at most, dimers, will be found for that structure as well.

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The Crystal and Molecular Structure of α-5-Acetyl-2′-deoxyuridine

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The title compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 16{\cdot}40\,(1)$, $b = 10{\cdot}34\,(1)$, $c = 7{\cdot}01\,(1)$ Å, $Z = 4$. The structure was refined to $R = 3{\cdot}95\%$ for 1535 observed counter amplitudes. The pyrimidine ring is essentially planar with the acetyl group inclined at 13° to it. There is evidence of conjugation between the pyrimidine and acetyl moieties. The sugar takes up the C(2′)-*endo* conformation and the arrangement about C(4′)–C(5′) is *trans–gauche*. The glycosidic torsion angle O(1′)–C(1′)–N(1)–C(6) is −12° (*anti* conformation), with the angle between the pyrimidine and sugar planes 76°.

Introduction

The group of analogues of the nucleic acid base thymine, the 5-substituted uracils, and the corresponding nucleosides have recently aroused considerable interest with regard to antiviral activity (Muraoka, Seto & Ueda, 1970; Muraoka, Takada & Ueda, 1970; Muraoka & Ueda, 1973) and also the possibility of replacement of thymine in bacteriophage DNA (Pietrzykowska & Shugar, 1967) and bacterial DNA (Piechowska & Shugar, 1965).

During the preparation of one such deoxynucleoside, 5-acetyl-2′-deoxyuridine, by a modified Hilbert–Johnson procedure, two anomers were obtained. It is usual for the naturally occurring β-anomer to predominate under the reaction conditions used (Winkley & Robbins, 1968; Kotick, Szantay & Bardos, 1969; Gupta & Bubbar, 1971), but in this case the overwhelming product displayed the typical NMR characteristics of an α-anomer. The ORD spectrum of the *p*-toluoylated nucleoside was, however, ambiguous.

In order to confirm the anomeric nature of this major product unequivocally, its crystal structure has been determined. Only comparatively few α-nucleoside crystal structures are known (Sundaralingam, 1971; Armstrong, Dattagupta, Eckstein & Saenger, 1976) and the present analysis yields some interesting stereochemical comparisons with these and related molecules.

Experimental

Suitable crystals were obtained by recrystallization from methanol. A crystal 0·4 × 0·4 × 0·5 mm was used for all X-ray measurements (mounted about *z*). Photographs indicated orthorhombic symmetry. Systematic absences corresponded to space group $P2_12_12_1$. The final cell dimensions were measured on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The ω-scan technique was employed with a stepping interval of 0·01° and a step time of 1 s. For layers *hk*0–*hk*2, $\Delta\omega$ was taken as 1·4°, and for the higher layers, a variable scan range was employed; $\Delta\omega$ was calculated from $(A + B \sin \mu/\tan \theta')°$, where $2\theta'$ is the azimuth angle, and A and B were assigned the values 1·0 and 0·5 respectively. Backgrounds for all reflexions were measured for 30 s at the end of each scan. After each layer, three standard reflexions on the zero layer were remeasured to monitor the stability of the system. There was no systematic variation of intensity with time. 1762 reflexions were scanned, of which 1535 $[I > 2{\cdot}5\sigma(I)]$ were used in the structure analysis.

Crystal data

$C_{11}H_{14}N_2O_6$, $M_r = 270{\cdot}4$, orthorhombic, $a = 16{\cdot}40\,(1)$, $b = 10{\cdot}34\,(1)$, $c = 7{\cdot}01\,(1)$ Å, $U = 1188{\cdot}7$ Å^3, $Z = 4$, $D_c = 1{\cdot}51$ g cm^{-3}, $F(000) = 568$. Systematic absences: *h*00, *h* odd; 0*k*0, *k* odd; 00*l*, *l* odd. Space group $P2_12_12_1$. Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo } K\alpha) = 0{\cdot}80$ cm^{-1}.

Table 1. *Fractional atomic coordinates and thermal parameters* (*both* × 10^4)

Estimated standard deviations for coordinates are in parentheses. Isotropic temperature factors are in the form $T = \exp[-2\pi^2U(2 \sin \theta/\lambda)^2]$. Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	1845 (1)	1644 (2)	3435 (3)	237	194	412	18	17	5
C(2)	1557 (1)	399 (2)	3202 (4)	262	219	415	−18	−4	26
O(2)	831 (1)	156 (2)	3104 (4)	276	304	782	−69	−10	4
N(3)	2150 (1)	−541 (2)	3085 (3)	319	167	467	−21	−3	−7
C(4)	2992 (1)	−363 (2)	3086 (3)	302	249	332	25	10	15
O(4)	3436 (1)	−1312 (2)	2961 (4)	397	274	658	91	51	7
C(5)	3246 (1)	980 (2)	3272 (3)	252	256	347	−19	7	3
C(7)	4111 (1)	1410 (2)	3324 (4)	260	413	421	−36	23	−28
O(7)	4270 (1)	2519 (2)	3838 (4)	337	451	1019	−133	89	−215
C(8)	4771 (2)	515 (3)	2737 (6)	261	660	761	44	18	−224
C(6)	2651 (1)	1900 (2)	3461 (3)	271	197	397	−36	−11	−7
C(1′)	1208 (1)	2682 (2)	3740 (4)	248	210	463	17	27	−11
C(2′)	779 (1)	3055 (2)	1900 (4)	211	246	511	−9	−39	−9
C(3′)	1342 (2)	4101 (2)	1091 (4)	339	244	410	−19	−27	12
O(3′)	2020 (1)	3557 (2)	99 (3)	424	405	502	−76	130	−87
C(4′)	1673 (2)	4752 (2)	2886 (4)	263	205	475	−13	−17	−24
C(5′)	1204 (2)	5947 (2)	3519 (4)	358	210	560	23	8	−24
O(5′)	1433 (2)	7031 (2)	2386 (4)	620	219	698	−63	−113	53
O(1′)	1598 (1)	3800 (2)	4404 (3)	401	215	440	28	−55	−41

	x	y	z	U		x	y	z	U
H[N(3)]	1967 (17)	−1387 (29)	2892 (43)	283	H2[C(2′)]	714 (23)	2256 (37)	1034 (52)	483
H1[C(8)]	4649	162	1316	1000	H[C(3′)]	1090 (19)	4700 (30)	359 (44)	309
H2[C(8)]	4796	−289	3719	1000	H[O(3′)]	1888 (29)	2944 (44)	−709 (75)	681
H3[C(8)]	5346	1022	2751	1000	H[C(4′)]	2221 (21)	4949 (33)	2714 (50)	445
H[C(6)]	2801 (20)	2825 (30)	3644 (46)	337	H1[C(5′)]	1342 (23)	6174 (36)	4751 (61)	521
H[C(1′)]	826 (20)	2290 (31)	4664 (48)	345	H2[C(5′)]	629 (24)	5827 (33)	3322 (55)	494
H1[C(2′)]	258 (25)	3371 (38)	2291 (60)	632	H[O(5′)]	1119 (28)	7001 (42)	1376 (70)	645

Structure determination

The structure was solved by direct methods (Germain & Woolfson, 1968) with the *CRYSTALS* system (Carruthers, 1975). An E map based on 219 reflexions revealed the positions of all 19 C, N and O atoms. The atomic parameters (coordinates and isotropic temperature factors) were refined by least squares and a difference synthesis then allowed 11 of the 14 H atoms to be located. The three H atoms on C(8) could only be located approximately, and were placed in idealized positions, such that C(8)—H, C(7)—H and H—H were 1·08, 2·103 and 1·764 Å respectively. In the final cycles of refinement, coordinates and anisotropic temperature factors were refined for the heavier atoms, and coordinates and isotropic temperature factors for the H atoms. Refinement was terminated when all calculated shifts were $<0{\cdot}1\sigma$ for C, N and O, and $<0{\cdot}3\sigma$ for H, and R was 3·95%.* The final atomic parameters are listed in Table 1. The weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}0012\,F^2]$, where $\sigma(F)$ is the standard deviation in the observed amplitudes based on counting statistics.

Computations were carried out on the Birmingham University ICL 1906A computer with *CRYSTALS* (Carruthers, 1975) and *SHELX* (Sheldrick, 1975), together with ancillary programs written by Dr J. J. Guy and TAH.

Results and discussion

The stereochemistry of the nucleoside is illustrated in Fig. 1, which also shows the atom numbering. Molecular dimensions are in Table 2. Estimated standard deviations for bond lengths, bond angles and torsion angles are *ca* 0·003 Å, 0·2° and 0·3° respectively. The results of mean-plane calculations are in Table 3.

Table 2. *Molecular dimensions*

(*a*) Bond lengths (Å)

N(1)—C(2)	1·381 (3)	C(6)—N(1)	1·347 (3)
C(2)—O(2)	1·220 (3)	N(1)—C(1′)	1·513 (3)
C(2)—N(3)	1·376 (3)	C(1′)—C(2′)	1·519 (4)
N(3)—C(4)	1·393 (3)	C(2′)—C(3′)	1·530 (3)
C(4)—O(4)	1·225 (3)	C(3′)—O(3′)	1·428 (3)
C(4)—C(5)	1·456 (3)	C(3′)—C(4′)	1·527 (3)
C(5)—C(7)	1·488 (3)	C(4′)—C(5′)	1·522 (3)
C(7)—O(7)	1·230 (3)	C(5′)—O(5′)	1·424 (3)
C(7)—C(8)	1·482 (2)	C(4′)—O(1′)	1·455 (3)
C(5)—C(6)	1·369 (3)	O(1′)—C(1′)	1·401 (3)
N(3)—H[N(3)]	0·94 (3)	O(3′)—H[O(3′)]	0·88 (5)
C(6)—H[C(6)]	1·00 (3)	C(4′)—H[C(4′)]	0·93 (3)
C(1′)—H[C(1′)]	0·99 (3)	C(5′)—H1[C(5′)]	0·92 (4)
C(2′)—H1[C(2′)]	0·96 (4)	C(5′)—H2[C(5′)]	0·96 (4)
C(2′)—H2[C(2′)]	1·03 (4)	O(5′)—H[O(5′)]	0·88 (5)
C(3′)—H[C(3′)]	0·91 (3)		

(*b*) Bond angles (°); all standard deviations 0·2°

C(6)—N(1)—C(2)	121·3	C(8)—C(7)—O(7)	120·6
C(6)—N(1)—C(1′)	122·4	C(5)—C(6)—N(1)	124·1
C(2)—N(1)—C(1′)	116·2	N(1)—C(1′)—O(1′)	108·4
N(1)—C(2)—N(3)	115·1	N(1)—C(1′)—C(2′)	112·3
N(1)—C(2)—O(2)	122·2	C(2′)—C(1′)—O(1′)	106·5
N(3)—C(2)—O(2)	122·8	C(1′)—C(2′)—C(3′)	102·4
C(2)—N(3)—C(4)	127·3	C(2′)—C(3′)—O(3′)	111·8
N(3)—C(4)—C(5)	114·2	C(2′)—C(3′)—C(4′)	102·8
N(3)—C(4)—O(4)	118·9	O(3′)—C(3′)—C(4′)	107·3
O(4)—C(4)—C(5)	126·9	C(3′)—C(4′)—C(5′)	114·7
C(4)—C(5)—C(7)	124·0	C(3′)—C(4′)—O(1′)	105·9
C(4)—C(5)—C(6)	117·9	O(1′)—C(4′)—C(5′)	107·0
C(6)—C(5)—C(7)	118·0	C(4′)—C(5′)—O(5′)	110·1
C(5)—C(7)—O(7)	119·2	C(4′)—O(1′)—C(1′)	110·7
C(5)—C(7)—C(8)	120·2		

(*c*) Selected torsion angles (°); mean estimated standard deviation 0·3°. The sign convention is as defined by Klyne & Prelog (1960).

C(1′)—C(2′)—C(3′)—C(4′)	−32·8
C(2′)—C(3′)—C(4′)—O(1′)	23·4
C(3′)—C(4′)—O(1′)—C(1′)	−3·9
C(4′)—O(1′)—C(1′)—C(2′)	−17·7
O(1′)—C(1′)—C(2′)—C(3′)	31·7
O(1′)—C(4′)—C(5′)—O(5′)	163·8
C(3′)—C(4′)—C(5′)—O(5′)	−79·1
O(3′)—C(3′)—C(4′)—C(5′)	147·6
O(3′)—C(3′)—C(4′)—O(1′)	−94·7
O(1′)—C(1′)—N(1)—C(6)	−11·7
O(7)—C(7)—C(5)—C(4)	−166·5
O(7)—C(7)—C(5)—C(6)	11·8

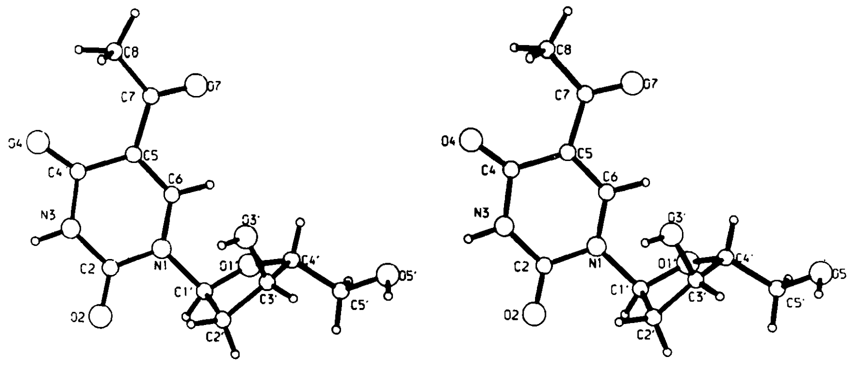

Fig. 1. Stereoscopic view of the molecule along the z axis.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32213 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Packing and hydrogen bonding

The arrangement of the molecules in the unit cell is shown in Fig. 2. Hydrogen bonds are indicated by dashed lines. All intermolecular contacts less than 3·4 Å between C, N and O atoms are listed in Table 4. Also listed are the short intermolecular distances involving the H atoms which take part in the hydrogen bonding.

O(5′) of the deoxyribose residue donates a H atom, forming a hydrogen bond with the carbonyl O(7) of the acetyl group of the molecule at $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$, of length 2·78 Å. The H atom lies close to the donor–acceptor line, the angle H[O(5′)]–O(5′)···O(7) being 16°. O(5′) also acts as an acceptor in a hydrogen bond with N(3) of the molecule related to the standard molecule by a **b** translation. Here O···N is 2·82 Å and H–N···O 6·5°. There is a third hydrogen bond between O(3′) acting as donor, and the carbonyl O(4) of the molecule at $\frac{1}{2}-x$, $-y$, $-\frac{1}{2}+z$, with O(3′)···O(4) 2·86 Å and H–O(3′)···O(4) 8·5°. Thus all the H atoms linked to N and O take part in hydrogen bonding, forming infinite sheets of molecules perpendicular to x. That O(4) takes part in hydrogen bonding, whereas O(2) does not, is a fairly common feature of uracil and uridine crystal structures (Voet & Rich, 1970) and has been attributed to a greater degree of polarization in the 4 position of uracil (Shefter, Kotick & Bardos, 1967). All other contacts correspond to normal van der Waals interactions, although there may be some stacking interactions along z between partially overlapping pyrimidine residues.

Stereochemistry and conformation of the molecule

(*a*) *The pyrimidine base.* The pyrimidine ring is, as expected, essentially planar. Of the substituents, O(4) and C(7) lie close to the plane of the ring, but O(2) and C(1′) are displaced by −0·07 and 0·10 Å respectively. Similar displacements of C(1′) have been found in the crystal structures of a number of nucleosides, *e.g.* 5-fluoro-2′-deoxyuridine (Harris & MacIntyre, 1964), 5-methyluridine (Hunt & Subramanian, 1969), 5-chloro-2′-deoxyuridine (Young & Morris, 1973), and α-5-formyluridine (Armstrong *et al.*, 1976), and may be due to steric effects or to the hybridization of N(1) being intermediate between sp^2 and sp^3. The acetyl group

Table 3. *Mean-plane calculations*

Deviations (Å) of atoms from least-squares planes. Distances marked with an asterisk refer to atoms defining the plane. In the equations of the planes, x, y and z are fractional coordinates relative to the cell axes.

	(I)	(II)	(III)	(IV)
N(1)	0·009*		−1·601	−1·383
C(2)	−0·018*			
O(2)	−0·068			
N(3)	0·013*			
C(4)	0·003*			
O(4)	0·028			
C(5)	−0·014*	−0·001*		
C(7)	−0·015	0·004*		
O(7)	0·221	−0·002*		
C(8)	−0·316	−0·001*		
C(6)	0·008*			
C(1′)	0·097		−0·156*	0·013*
C(2′)			0·208*	0·523
C(3′)			−0·184*	−0·012*
O(3′)			−1·582	−1·375
C(4′)			0·094*	0·020*
C(5′)			1·467	1·279
O(5′)			1·469	1·203
O(1′)			0·038*	−0·022*

Equations of planes

(I) $-0{\cdot}1217x + 1{\cdot}1177y - 6{\cdot}9687z = -2{\cdot}2239$
(II) $-1{\cdot}3104x + 3{\cdot}3100y - 6{\cdot}6175z = -2{\cdot}2673$
(III) $13{\cdot}3387x - 5{\cdot}0987y - 2{\cdot}1644z = -0{\cdot}7216$
(IV) $14{\cdot}7545x - 3{\cdot}9576y - 1{\cdot}4723z = 0{\cdot}1836$

Dihedral angles

(I)–(II)	13·2°	(I)–(III)	75·7°

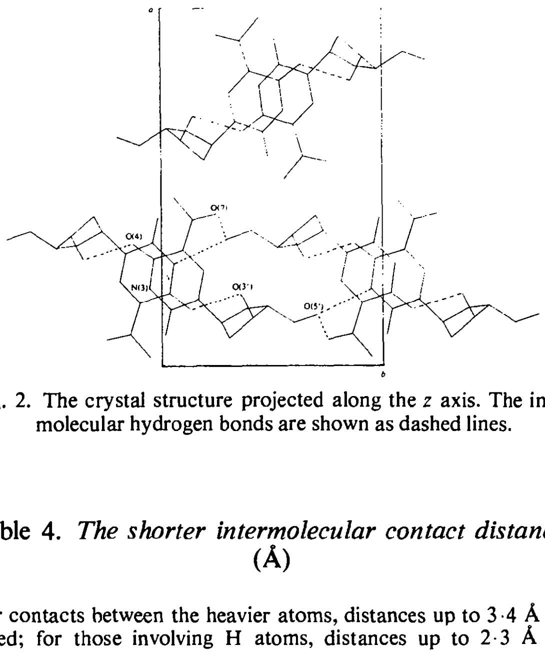

Fig. 2. The crystal structure projected along the z axis. The intermolecular hydrogen bonds are shown as dashed lines.

Table 4. *The shorter intermolecular contact distances* (Å)

For contacts between the heavier atoms, distances up to 3·4 Å are listed; for those involving H atoms, distances up to 2·3 Å are shown.

$\mathrm{O}(5')\cdots\mathrm{O}(7^{\mathrm{i}})$	2·78	$\mathrm{O}(4)\cdots\mathrm{N}(1^{\mathrm{iii}})$	3·22
$\mathrm{O}(5')\cdots\mathrm{N}(3^{\mathrm{ii}})$	2·82	$\mathrm{O}(5')\cdots\mathrm{O}(3'^{\mathrm{iv}})$	3·23
$\mathrm{O}(3')\cdots\mathrm{O}(4^{\mathrm{iii}})$	2·86	$\mathrm{O}(5')\cdots\mathrm{C}(6^{\mathrm{i}})$	3·32
$\mathrm{C}(5')\cdots\mathrm{O}(3'^{\mathrm{iv}})$	3·16	$\mathrm{C}(1')\cdots\mathrm{O}(4^{\mathrm{v}})$	3·33
$\mathrm{C}(4')\cdots\mathrm{O}(3'^{\mathrm{iv}})$	3·17	$\mathrm{O}(5')\cdots\mathrm{C}(7^{\mathrm{i}})$	3·39
$\mathrm{H}[\mathrm{O}(5')]\cdots\mathrm{O}(7^{\mathrm{i}})$	1·95	$\mathrm{H}[\mathrm{O}(3')]\cdots\mathrm{O}(4^{\mathrm{iii}})$	2·00
$\mathrm{O}(5')\cdots\mathrm{H}[\mathrm{N}(3)^{\mathrm{ii}}]$	1·89		

Symmetry code

(i)	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	(iv)	$\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$
(ii)	x,	$1+y$,	z	(v)	$\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$
(iii)	$\frac{1}{2}-x$,	$-y$,	$-\frac{1}{2}+z$				

is accurately planar and is inclined at 13° to the pyrimidine ring.

Bond lengths and angles, apart from certain values which will be discussed below, agree closely with averaged values for uracils and uridines (Voet & Rich, 1970). The major deviations occur at C(5), C(6) and N(1). Thus the formal double bond C(5)–C(6) is 0·026 Å longer and C(6)–N(1) is 0·023 Å shorter than the averaged lengths of Voet & Rich, and the endocyclic angle at C(5) is smaller by 2·8° than the averaged value. These differences can be rationalized by postulating conjugation between N(1) and the carbonyl O(7) of the acetyl group. Consistent with this, C(7)–O(7) is slightly greater than a normal C–O(carbonyl) length, although some of this lengthening may be due to the effect of the hydrogen bonding in which O(7) is involved. On the other hand, C(5)–C(7) (1·488 Å) appears to correspond to a pure C(sp^2)–C(sp^2) single bond (Cruickshank, 1962). The N(1)–C(1′) glycosidic bond length is 1·513 Å compared with the 1·476 Å quoted by Voet & Rich. This is larger than would be expected for a C–N bond in which the N atom is essentially sp^2 hybridized. In α-5-formyluridine (Armstrong *et al.*, 1976) and 5-[1-(2′-deoxy-α-D-ribofuranosyl)uracilyl] disulphide (Shefter, Kotick & Bardos, 1967), where conjugation with the substituent at the 5 position also probably occurs, similar, but somewhat smaller, deviations from the averaged values of Voet & Rich are found.

(*b*) *The deoxyribose residue*. The sugar ring adopts the envelope conformation. C(1′), C(3′), C(4′) and O(1′) are coplanar to within ±0·02 Å and C(2′) is displaced by 0·52 Å from the four-atom plane, on the same side as C(5′). The ring, therefore, has the C(2′)-*endo* conformation, ^2E in the nomenclature of Sundaralingam (1971). This appears to be the first example of an α-nucleoside with this type of puckering. The conformation about C(4′)–C(5′) is *trans–gauche*, torsion angles φ_{OO} and φ_{OC} (Shefter & Trueblood, 1965) being 164 and −79°. This is unusual for nucleosides, although a similar conformation occurs in at least one other α-nucleoside (Shefter, Kotick & Bardos, 1967) and one β-nucleoside (Harris & MacIntyre, 1964). In the structure of yeast tRNA$^{\mathrm{Phe}}$ (Jack, Klug & Ladner, 1976), four of the ribose residues have the *trans–gauche* conformation at C(4′)–C(5′), the ring adopting the C(2′)-*endo* pucker, as in the present structure.

Bond lengths and angles are in good agreement with averaged values for the ribose residues of C(2′)-*endo* nucleosides (Saenger & Eckstein, 1970) and with those of the deoxyribose moiety of 5-chloro-2′-deoxyuridine (Young & Morris, 1973) where the sugar ring also has the C(2′)-*endo* conformation. As usual, C(1′)–O(1′) is significantly shorter than C(4′)–O(1′).

(*c*) *The glycosidic link*. The torsion angle O(1′)–C(1′)–N(1)–C(6) is −11·7°, and the conformation about the glycosidic bond is *anti* in the nomenclature of Donohue & Trueblood (1960) and Sundaralingam (1969). For the known α-nucleoside structures (Sundaralingam, 1971) the glycosidic torsion angles are all in the *anti* range but the actual values vary from −30 to −72° (mean *ca* −50°) so that the present structure falls outside this range. In the α-5-formyluridine structure the conformation is quite similar with a torsion angle of −21·6°. The angle between the pyrimidine ring and the mean plane of the deoxyribose ring is 75·7°, similar to those found in other nucleosides (Young, Tollin & Wilson, 1969).

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Hydrogen Bonding in the Crystalline State. $CaHPO_4$ (Monetite), $P\bar{1}$ or $P1$? A Novel Neutron Diffraction Study*

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1749 independent reflexions, measured on a single-crystal neutron diffractometer ($\lambda = 1{\cdot}217$ Å), were used for refining the crystal structure of $CaHPO_4$ in both space groups $P\bar{1}$ ($R = 0{\cdot}0283$) and $P1$ ($R = 0{\cdot}0286$). In the $P\bar{1}$ model a proton lies on a symmetry centre forming a symmetric hydrogen bond (2·459 Å) and another is statistically distributed between two centrosymmetric positions; in the $P1$ models the first proton is slightly off the centre and the second is either ordered or disordered. By crystal–chemical considerations on the refinements, and taking into account a heat capacity anomaly at about 280 K together with very weak effects of piezoelectricity and of generation of the second optical harmonic at room temperature, the existence of a low-temperature ordered ($P1$) phase and a high-temperature disordered ($P\bar{1}$) phase is suggested; diffraction data would come from a crystal in the disordered phase with a small fraction of the ordered one. A peculiar version of the KKM effect is shown by the difference maps. X-ray and neutron diffraction refinements are compared statistically.

Introduction

$CaHPO_4$ (monetite) has been the subject of several crystallographic (MacLennan & Beevers, 1955; Jones & Cruickshank, 1961; Curry, Denne & Jones, 1968; Denne & Jones, 1971; Dickens, Bowen & Brown, 1972), spectroscopic (Blinc & Hadži, 1960; Petrov, Šoptrajanov, Fuson & Lawson, 1967) and other physicochemical studies (Egan & Wakefield, 1964).

The structural model refined in space group $P\bar{1}$ ($Z = 4$) by Dickens *et al.* (1972), with X-ray data ($R = 0{\cdot}031$), implies that H(1)† is on an inversion centre, forming a symmetric hydrogen bond $O(7)\cdots O(7') = 2{\cdot}458$ (2) Å [type *A* (Currie & Speakman, 1970) or symmetry-restricted (SR) hydrogen bond (Catti & Ferraris, 1974)]; H(2) forms the hydrogen bond $O(1)\cdots O(5')^{ii} = 2{\cdot}565$ (1) Å, and the third independent hydrogen atom, H(3), is disordered over two centrosymmetric positions and is involved in the hydrogen bond $O(6)\cdots O(8')^{ii} = 2{\cdot}669$ (1) Å which is also an edge of the coordination polyhedron of Ca(2′) (Fig. 1). [101] chains of P(2) coordination tetrahedra, linked *via* the hydrogen bonds involving H(1) and H(3) are present in the structure; the P(1) tetrahedra are connected to these chains by the third hydrogen bond.

However, according to Denne & Jones (1971) 'Professor W. G. Perdok found that monetite gave the weakest positive piezoelectric effect yet detected with his Giebe & Scheibe apparatus'; such an effect was also reported by the same authors for the isostructural (Ferraris & Chiari, 1970) $CaHAsO_4$ (weilite). At that time, they proposed a $P1$ model with H(3) ordered and H(1) in an asymmetric position; however, the quality and quantity of their neutron diffraction data did not allow

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† Atoms are numbered according to Denne & Jones (1971); Dickens *et al.* (1972) interchanged H(1) and H(2). A prime denotes an atom in a centrosymmetric (or quasi-centrosymmetric) position for the $P\bar{1}$ (or $P1$) model. Roman numerals represent the translations: (i) $-\mathbf{c}$; (ii) $+\mathbf{a}+\mathbf{b}+\mathbf{c}$; (iii) $+\mathbf{b}+\mathbf{c}$; (iv) $+\mathbf{b}$; (v) $+\mathbf{c}$; (vi) $-\mathbf{b}$; (vii) $+\mathbf{a}+\mathbf{c}$.