Structure of Disodium Deoxyuridine 5'-Phosphate Pentahydrate

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Abstract

Disodium deoxyuridine 5'-phosphate pentahydrate, $Na_2(C_9H_{11}N_2O_8P).5H_2O$, $C_9H_{11}N_2O_8P^{2-}.2Na^+.5H_2O$, crystallizes in the monoclinic space group $P2_1$ with $a = 7.250$ (4), $b = 35.45$ (2), $c = 7.132$ (4) Å, $\beta = 102.2$ (4)°, $Z = 4$. The Cu $K\alpha$ intensity data were collected photographically and estimated visually. The structure was obtained by the minimum-function method and difference syntheses and refined to an R of 0.089. In both molecules the uracil base has an *anti* conformation ($\chi_{CN} = 57.1$ and 59.9°) with respect to the sugar. The deoxyribose moiety of molecule B shows a typical $C(1')$-*exo* puckering, with $C(1')$ displaced by 0.52 Å from the best plane. The furanose ring conformation of molecule A can be described as $C(2')$-*endo*,$C(1')$-*exo*. Both the molecules have an unusual *trans–gauche* conformation about the exocyclic $C(4')$–$C(5')$ bond with ($\varphi_{OO} = 171.1$, 172.2°; $\varphi_{OC} = -64.7$, $-65.9°$).

Introduction

The structure determination of the title compound (5'-dUMPNa$_2$.5H$_2$O) was undertaken as part of a programme of structural studies on nucleic acid constituents (Viswamitra, Reddy, Lin & Sundaralingam, 1971; Viswamitra, Reddy, James & Williams, 1972; Viswamitra & Seshadri, 1974; Swaminatha Reddy & Viswamitra, 1975). An account of the implications of the conformational parameters of the present structure has been reported (Viswamitra, Seshadri & Post, 1975).

Experimental

The compound, isolated by DNase hydrolysis of DNA from salmon sperm, was obtained from Sigma Chemical Company, USA. Crystals were grown by slow diffusion of acetone into an aqueous solution of the compound. Crystal data were obtained from rotation, Weissenberg and precession photographs taken with Cu $K\alpha$ radiation (Table 1). The density, measured by flotation in carbon tetrachloride and bromoform mixtures, was 1.68 Mg m^{-3}, suggesting $Na_2(C_9H_{11}N_2O_8P).6H_2O$ as the chemical formula in the asymmetric unit ($d_c = 1.70$ Mg m^{-3}). However, detailed structure analysis showed that the correct formula is $Na_2(C_9H_{11}N_2O_8P).5H_2O$. The numbering of the atoms is shown in Fig. 1.

Table 1. *Crystal data of disodium deoxyuridine 5'-phosphate pentahydrate*

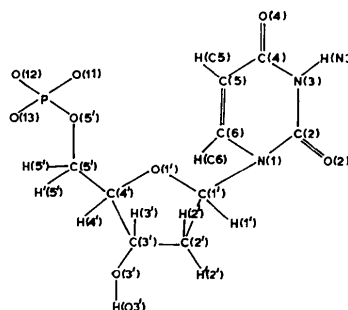|	
Formula	$Na_2(C_9H_{11}N_2O_8P).5H_2O$
M_r	441.9
Crystal system	Monoclinic
a	7.250 (4) Å
b	35.45 (2)
c	7.132 (4)
β	102.2 (4)°
Volume	1791.6 Å^3
Z	4
d_m	1.68 Mg m^{-3}
d_c (5H$_2$O)	1.64
d_c (6H$_2$O)	1.70
Systematic absences	0k0, k odd
Space group	$P2_1$

Fig. 1. Numbering in deoxyuridine 5'-phosphate.

Intensity data

Intensities were collected by the multiple-film equi-inclination Weissenberg technique with Cu $K\alpha$ radiation from a crystal $1\cdot3 \times 0\cdot3 \times 0\cdot3$ mm. Intensities from 2139 unique reflections were estimated visually with pre-calibrated graded intensity strips. Lorentz–polarization and spot-shape corrections were applied and the intensities scaled to absolute values by a Wilson plot. No absorption correction was applied ($\mu r = 0\cdot55$).

Structure determination and refinement

The structure was initially obtained by the application of Patterson and minimum-function methods, and later independently by direct methods with programs developed by Dr G. M. Sheldrick; it was refined by full-matrix least squares. The final R with anisotropic thermal parameters was 0·089. The H atoms of the molecules were fixed wherever possible according to their expected geometry. The computations were performed on the IBM 360/44 computer at the Indian Institute of Science, Bangalore, and on the Cambridge University computer.

Results and discussion

The final positional parameters of the heavy atoms are listed in Table 2* and those of the H atoms in Table 3. Bond lengths and angles involving heavy atoms are given in Tables 4 and 5, respectively, and those involving H atoms in Table 6. The average e.s.d.'s in bond distances are $\sigma(P-O) = 0\cdot012$, $\sigma(C-N,O,C) = 0\cdot02$ Å; those of the bond angles vary from 0·6 to 1·8°.

Molecular geometry and conformation

The relative orientation of the base with respect to the sugar is *anti*, the glycosidic torsion angles being 57·1 and 59·9° for molecules A and B respectively. These are slightly higher than the 43·0° in 5'-UMPBa (Shefter & Trueblood, 1965) [C(2')-*endo* puckering]. This could be due to the crystalline environment and metal coordination. The three known cases having the acid 5'-nucleotide form, namely 5'-dCMP (Viswamitra *et al.*, 1971), 5'-GMP (Murayama, Nagashima &

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34966 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Shimizu, 1969) and 5'-AMP (Kraut & Jensen, 1963), have smaller χ_{CN} angles, whereas the metal complexes of nucleotides exhibit larger χ_{CN} angles. This has been pointed out earlier by Sundaralingam (1973).

Table 2. *Fractional coordinates* $(\times 10^4)$ *of the heavy atoms with e.s.d.'s in parentheses*

	x	y	z
Molecule A			
P	1231 (6)	5683 (0)	7837 (5)
O(11)	−612 (18)	5497 (3)	6894 (14)
O(12)	2012 (18)	5615 (3)	9978 (16)
O(13)	1248 (16)	6095 (2)	7285 (16)
O(5')	2682 (17)	5485 (3)	6840 (16)
C(5')	2975 (28)	5086 (4)	6998 (25)
C(4')	4079 (25)	4957 (3)	5800 (21)
C(3')	3211 (25)	5000 (4)	3594 (25)
O(3')	4496 (17)	5203 (3)	2791 (15)
C(2')	2909 (28)	4603 (4)	2912 (24)
C(1')	4345 (23)	4371 (3)	4440 (21)
O(1')	4569 (16)	4562 (3)	6245 (14)
N(1)	3737 (21)	3981 (3)	4613 (18)
C(2)	4781 (30)	3686 (3)	4191 (19)
O(2)	6240 (21)	3727 (3)	3707 (16)
N(3)	4036 (22)	3333 (3)	4304 (19)
C(4)	2447 (28)	3260 (4)	4890 (24)
O(4)	1925 (21)	2922 (3)	4995 (21)
C(5)	1424 (30)	3574 (4)	5338 (31)
C(6)	2164 (28)	3926 (4)	5233 (24)
Molecule B			
P	5015 (6)	2499 (1)	1679 (5)
O(11)	5572 (17)	2091 (2)	1509 (16)
O(12)	2808 (17)	2575 (3)	939 (16)
O(13)	5937 (16)	2670 (3)	3651 (15)
O(5')	5955 (16)	2701 (3)	163 (15)
C(5')	5783 (27)	3114 (3)	−41 (24)
C(4')	7048 (26)	3243 (4)	−1207 (24)
C(3')	9112 (29)	3189 (4)	−275 (21)
O(3')	9982 (21)	2985 (3)	−1595 (17)
C(2')	9977 (28)	3582 (4)	134 (27)
C(1')	8488 (27)	3814 (4)	−1390 (24)
O(1')	6619 (16)	3635 (3)	−1562 (16)
N(1)	8316 (19)	4208 (3)	−749 (17)
C(2)	8715 (26)	4494 (3)	−1799 (25)
O(2)	9219 (19)	4444 (3)	−3294 (16)
N(3)	8658 (22)	4856 (3)	−1090 (20)
C(4)	8099 (26)	4936 (4)	496 (21)
O(4)	8003 (24)	5273 (3)	937 (20)
C(5)	7607 (27)	4622 (4)	1469 (23)
C(6)	7816 (28)	4280 (4)	900 (26)
Na(1)	7529 (11)	5587 (2)	3548 (10)
Na(2)	9984 (10)	6597 (2)	2346 (9)
Na(3)	757 (10)	7612 (2)	4748 (10)
Na(4)	5001 (11)	6510 (2)	3802 (11)
W(1)	550 (21)	5932 (2)	2841 (19)
W(2)	5427 (17)	6041 (3)	1703 (17)
W(3)	6064 (18)	5936 (3)	6597 (20)
W(4)	8671 (17)	7192 (3)	2490 (18)
W(5)	2143 (19)	6666 (3)	283 (20)
W(6)	2783 (17)	6628 (3)	5398 (15)
W(7)	8367 (17)	6564 (3)	5169 (19)
W(8)	7115 (19)	6501 (3)	−444 (17)
W(9)	9687 (18)	7259 (3)	7220 (18)
W(10)	5001 (20)	7214 (3)	3397 (18)

Conformation of the deoxyribose moiety

The least-squares planes for the deoxyribose moiety are listed in Table 7. The best four-atom plane for molecule B contains $O(1')-C(4')-C(3')-C(2')$. $C(1')$ shows a maximum deviation from this plane of 0.502 Å on the side opposite to $C(5')$, compared to 0.017 Å for $C(2')$. The furanose ring, therefore, has a typical $C(1')$-
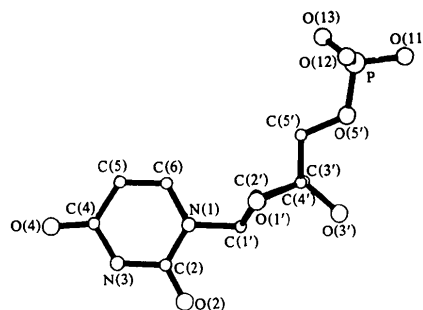
Fig. 2. dUMP viewed perpendicular to the plane of the uracil base, showing the $C(1')$-exo puckering of the deoxyribose moiety for molecule B.

exo envelope conformation (Fig. 2). This conformation has also been reported for guanosine dihydrate (Thewalt, Bugg & Marsh, 1970).

Table 8 shows that there are two equally good four-atom planes for the furanose ring of molecule A, defined by $C(1')-C(3')-C(4')-O(1')$ and $C(2')-C(3')-C(4')-O(1')$. The puckering of the deoxyribose moiety of A is predominantly $C(2')$-endo; when referred to the three-atom plane, $C(2')$ and $C(1')$ are displaced by 0.265 and 0.215 Å respectively. Therefore, the furanose ring conformation can be described as $C(2')$-endo,$C(1')$-exo, as can be seen from the torsion angles around the sugar bonds (Table 8). The furanose ring of molecule A has the typical twist conformation.

Conformation about $C(4')-C(5')$

The torsion angles φ about $C(4')-C(5')$, which determine the geometry of the phosphate group relative

Table 3. Fractional coordinates ($\times 10^4$) of the H atoms with e.s.d.'s in parentheses

	x	y	z
Molecule A			
H(5')	1847 (28)	4971 (4)	6689 (25)
H'(5')	3532 (28)	5030 (4)	8217 (25)
H(4')	5110 (25)	5106 (3)	6026 (21)
H(3')	2115 (25)	5128 (4)	3283 (25)
H(2')	1717 (28)	4529 (4)	2887 (24)
H'(2')	3159 (28)	4577 (4)	1735 (24)
H(1')	5451 (23)	4358 (3)	4059 (21)
H(N3)	4668 (22)	3135 (3)	3956 (19)
H(C5)	306 (30)	3542 (4)	5676 (31)
H(C6)	1562 (28)	4127 (4)	5593 (24)
Molecule B			
H(5')	6084 (27)	3224 (3)	1122 (24)
H'(5')	4589 (27)	3174 (3)	−606 (24)
H(4')	6878 (26)	3107 (4)	−2295 (24)
H(3')	9271 (29)	3058 (4)	829 (21)
H(2')	10005 (28)	3658 (4)	1345 (27)
H'(2')	11147 (28)	3595 (4)	−102 (27)
H(1')	8871 (27)	3814 (4)	−2512 (24)
H(N3)	9024 (22)	5047 (3)	−1757 (20)
H(C5)	7135 (27)	4658 (4)	2526 (23)
H(C6)	7614 (28)	4085 (4)	1642 (26)

Table 4. Bond distances (Å) involving non-hydrogen atoms

	A	B		A	B		A	B
P—O(11)	1·514 (12)	1·516 (10)	C(4')—O(1')	1·464 (15)	1·431 (16)	N(1)—C(6)	1·322 (27)	1·326 (24)
P—O(12)	1·531 (11)	1·598 (12)	C(3')—O(3')	1·391 (22)	1·433 (23)	C(2)—O(2)	1·189 (27)	1·211 (23)
P—O(13)	1·513 (9)	1·546 (11)	C(3')—C(2')	1·490 (21)	1·533 (23)	C(2)—N(3)	1·373 (19)	1·383 (17)
P—O(5')	1·556 (13)	1·567 (13)	C(2')—C(1')	1·571 (21)	1·589 (23)	N(3)—C(4)	1·331 (26)	1·310 (23)
O(5')—C(5')	1·431 (17)	1·475 (16)	C(1')—O(1')	1·434 (17)	1·478 (22)	C(4)—O(4)	1·265 (18)	1·242 (19)
C(5')—C(4')	1·366 (27)	1·437 (27)	C(1')—N(1)	1·465 (17)	1·485 (18)	C(4)—C(5)	1·410 (25)	1·398 (23)
C(4')—C(3')	1·573 (22)	1·516 (26)	N(1)—C(2)	1·361 (21)	1·328 (19)	C(5)—C(6)	1·366 (23)	1·297 (22)

Table 5. Bond angles (°) involving non-hydrogen atoms

	A	B		A	B		A	B
O(11)—P—O(12)	118·7 (0·6)	113·5 (0·6)	C(2')—C(3')—C(4')	103·6 (1·2)	107·0 (1·3)	C(6)—N(1)—C(1')	117·6 (1·3)	120·7 (1·3)
O(11)—P—O(13)	111·1 (0·6)	112·0 (0·6)	C(2')—C(3')—O(3')	114·7 (1·6)	111·3 (1·6)	N(1)—C(2)—O(2)	122·6 (1·3)	121·9 (1·2)
O(11)—P—O(5')	102·6 (0·6)	102·6 (0·7)	C(4')—C(3')—O(3')	107·4 (1·3)	107·9 (1·2)	N(1)—C(2)—N(3)	116·3 (1·8)	118·4 (1·6)
O(12)—P—O(13)	112·9 (0·6)	116·4 (0·7)	C(1')—C(2')—C(3')	103·8 (1·2)	98·5 (1·3)	O(2)—C(2)—N(3)	121·0 (1·5)	119·6 (1·4)
O(12)—P—O(5')	103·9 (0·6)	104·3 (0·6)	C(2')—C(1')—O(1')	107·9 (1·1)	108·3 (1·2)	C(2)—N(3)—C(4)	124·9 (1·4)	123·7 (1·4)
O(13)—P—O(5')	105·9 (0·7)	106·4 (0·6)	C(2')—C(1')—N(1)	112·7 (1·2)	111·4 (1·2)	N(3)—C(4)—C(5)	116·7 (1·4)	114·5 (1·4)
C(5')—O(5')—P	120·9 (1·2)	118·7 (1·1)	O(1')—C(1')—N(1)	110·5 (1·2)	107·1 (1·4)	N(3)—C(4)—O(4)	119·4 (1·6)	118·1 (1·5)
C(4')—C(5')—O(5')	112·2 (1·5)	108·8 (1·4)	C(1')—O(1')—C(4')	106·4 (1·0)	103·9 (1·2)	O(4)—C(4)—C(5)	123·9 (1·9)	127·4 (1·7)
C(3')—C(4')—C(5')	115·4 (1·4)	113·4 (1·4)	C(2)—N(1)—C(6)	121·4 (1·3)	119·1 (1·2)	C(4)—C(5)—C(6)	118·5 (2·0)	122·0 (1·8)
C(3')—C(4')—O(1')	109·7 (1·0)	111·0 (1·2)	C(2)—N(1)—C(1')	121·0 (1·5)	120·2 (1·4)	C(5)—C(6)—N(1)	121·9 (1·7)	121·9 (1·6)
O(1')—C(4')—C(5')	109·4 (1·3)	105·7 (1·4)						

Table 6. *Bond distances* (Å) *and angles* (°) *involving* H *atoms*

	A	B		A	B		A	B
C(5')—H(5')	0·90 (3)	0·90 (2)	H(5')—C(5')—O(5')	108·6 (1·9)	109·8 (1·5)	H(2')—C(2')—H'(2')	109·5 (2·3)	109·5 (2·5)
C(5')—H'(5')	0·90 (2)	0·90 (3)	H(5')—C(5')—C(4')	108·5 (1·9)	109·6 (1·9)	H(2')—C(2')—C(3')	110·8 (1·9)	112·0 (2·0)
C(4')—H(4')	0·90 (2)	0·90 (2)	H(5')—C(5')—H'(5')	109·5 (2·5)	109·5 (2·4)	H(2')—C(2')—C(1')	111·0 (2·0)	112·1 (2·0)
C(3')—H(3')	0·90 (2)	0·90 (2)	H'(5')—C(5')—O(5')	108·9 (1·7)	109·5 (1·6)	H(1')—C(1')—C(2')	108·7 (1·7)	108·4 (2·0)
C(2')—H(2')	0·90 (3)	0·90 (2)	H'(5')—C(5')—C(4')	109·1 (2·2)	109·6 (1·9)	H(1')—C(1')—O(1')	110·9 (1·5)	112·1 (1·8)
C(2')—H'(2')	0·90 (3)	0·90 (3)	H(4')—C(4')—C(5')	105·5 (1·7)	109·9 (1·9)	H(1')—C(1')—N(1)	106·3 (1·5)	109·5 (1·6)
C(1')—H(1')	0·90 (2)	0·90 (2)	H(4')—C(4')—C(3')	105·3 (1·7)	104·6 (2·0)	H(N3)—N(3)—C(2)	117·6 (1·9)	118·1 (1·8)
N(3)—H(N3)	0·90 (2)	0·90 (2)	H(4')—C(4')—O(1')	111·5 (1·7)	112·5 (1·7)	H(N3)—N(3)—C(4)	117·5 (1·6)	118·2 (1·5)
C(5)—H(C5)	0·90 (3)	0·90 (3)	H(3')—C(3')—C(4')	116·2 (2·1)	112·4 (2·4)	H(C5)—C(5)—C(6)	120·9 (2·1)	119·1 (2·1)
C(6)—H(C6)	0·90 (2)	0·90 (2)	H(3')—C(3')—O(3')	105·8 (1·8)	108·8 (1·9)	H(C5)—C(5)—C(4)	120·6 (1·9)	118·9 (1·9)
			H(3')—C(3')—C(2')	109·4 (1·8)	109·4 (1·7)	H(C6)—C(6)—N(1)	119·0 (2·0)	118·9 (1·9)
			H(2')—C(2')—C(3')	111·0 (2·0)	112·3 (2·1)	H(C6)—C(6)—C(5)	119·1 (2·5)	119·2 (2·3)
			H(2')—C(2')—C(1')	110·7 (1·8)	112·1 (2·0)			

Probable hydrogen bonds and distances (Å)

W(1)—O(12)A	2·732 (18)	W(3)—W(8)	2·908 (18)	W(5)—O(13)B	2·915 (17)	W(9)—O(12)B	2·693 (17)
W(2)—O(12)A	2·938 (17)	W(4)—W(7)	2·974 (17)	W(6)—O(13)A	2·693 (15)	W(10)—O(13)B	2·847 (17)
W(2)—W(8)	2·714 (17)	W(4)—W(10)	2·869 (17)	W(7)—O(13)A	2·839 (16)	N(3)A—O(13)B	2·813 (17)
W(3)—O(11)A	2·838 (17)	W(4)—O(12)B	2·803 (17)	W(7)—W(9)	2·921 (17)	N(3)B—O(11)A	2·799 (18)
W(3)—O(5')A	2·962 (17)						

Table 7. *Deviations* (Å) *of atoms from the least-squares planes through the deoxyribose moiety*

Atoms not used in the calculation of the plane are indicated by asterisks. E.s.d.'s of deviations ~0·02 Å.

	Plane (I)	Plane (II)	Plane (III)
	Molecule A		Molecule B
C(1')	0·415*	0·031	−0·502*
C(2')	−0·036	−0·431*	0·017
C(3')	0·057	−0·029	−0·028
C(4')	−0·059	0·048	0·030
C(5')	−1·184*	−0·879*	1·237*
O(1')	0·038	−0·050	−0·018
r.m.s. (Δ)	0·009	0·007	0·002

Equations of the planes

Plane (I)   0·8888X + 0·0726Y − 0·4525Z =   9·3062
Plane (II)   0·9180X + 0·2436Y − 0·3130Z = 12·7718
Plane (III) −0·2638X + 0·0380Y + 0·9638Z = −2·7802

Table 8. *Torsion angles* (°) *about the furanose ring bonds*

E.s.d.'s ~1·2°.

	Molecule A	Molecule B
C(4')—O(1')—C(1')—C(2')	−24·1	−31·4
O(1')—C(1')—C(2')—C(3')	30·8	33·3
C(1')—C(2')—C(3')—C(4')	−23·4	−22·3
C(2')—C(3')—C(4')—O(1')	10·3	5·3
C(3')—C(4')—O(1')—C(1')	8·9	16·1

to the sugar, are O(5')—C(5')—C(4')—O(1') = 171·1 and 172·2° and O(5')—C(5')—C(4')—C(3') = −64·7 and −65·9° for molecules A and B respectively. The conformation of the deoxyuridylic acid moiety in both molecules about this bond is therefore *trans–gauche*
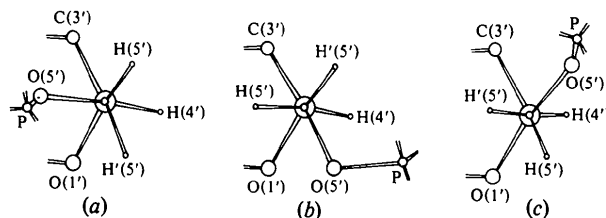

Fig. 3. The three possible staggered conformations about C(4')—C(5') of the phosphate moiety in nucleotides showing the relevant regions in (a) dTMP (*gauche–gauche*), (b) dGMP (*gauche–trans*), (c) dUMP (*trans–gauche*).

(*tg*). This is the first nucleotide to show the *tg* conformation about C(4')—C(5'). Although all three possible conformers (*gg, gt* and *tg*) are found in nucleosides, only the *gg* conformer is observed in nucleotides (Sundaralingam, 1973; Sasisekaran. 1973). Other mononucleotides that exhibit the *gt* conformation are 5'-dGMP (Young, Tollin & Wilson. 1974; Viswamitra & Seshadri, 1974) and 6-azauridine 5'-phosphate (Saenger & Suck, 1973); the latter is not a normal constituent of DNA. Fig. 3 illustrates this geometry along with the other two staggered conformations about this bond, namely *gauche–gauche* and *gauche–trans*.

Phosphate group

The torsion angles about C(5')—O(5') are 170·7 and 168·5° for the two molecules. The dihedral angles about P—O(5') are O(11)—P—O(5')—C(5') = −61·0 and −177·6°, O(12)—P—O(5')—C(5') = 63·2 and 63·7° and O(13)—P—O(5')—C(5') = −177·6 and −59·8° for molecules A and B respectively.

The phosphate O atoms are involved in both hydrogen bonding and metal coordination.

Table 9. *Deviations* (Å) *of atoms from the least-squares plane through the uracil base*

Atoms not used in the calculation of the plane are indicated by asterisks. E.s.d.'s of deviations ~0·02 Å.

N(1)	−0·020	0·001	O(4)	0·024*	−0·019*
C(2)	0·016	−0·029	C(5)	−0·012	−0·036
O(2)	0·038*	−0·029*	C(6)	0·018	0·033
N(3)	−0·010	0·026	r.m.s. (Δ)	0·001	0·004
C(4)	0·008	0·005			

Equations of the planes

Molecule A $0·5036X − 0·0578Y + 0·8620Z = 5·1278$
Molecule B $0·9511X − 0·0504Y + 0·3049Z = 4·3011$

Fig. 4. Sodium coordination polyhedra viewed along c.

Table 10. *Sodium coordination polyhedra* (Å *and* deg)

Na(1)—O(4)B	2·257 (16)		Na(1)—O(3')A	2·545 (14)
Na(1)—W(2)	2·408 (13)		Na(1)—W(1)ᴵ	2·649 (17)
Na(1)—O(11)A	2·500 (12)		Na(1)—W(3)	2·891 (17)
O(4)B—Na(1)—O(11)A	125·4 (0·5)		W(1)—Na(1)—O(3')A	156·8 (0·5)
O(4)B—Na(1)—O(3')A	80·6 (0·5)		W(1)—Na(1)—O(4)B	78·1 (0·6)
W(2)—Na(1)—O(11)A	139·3 (0·5)		W(3)—Na(1)—O(11)A	63·0 (0·4)
W(2)—Na(1)—O(3')A	79·8 (0·4)		W(3)—Na(1)—O(11)A	87·1 (0·4)
W(2)—Na(1)—O(4')B	93·9 (0·5)		W(3)—Na(1)—O(4)B	167·3 (0·6)
W(2)—Na(1)—W(1)	92·3 (0·5)		W(3)—Na(1)—W(1)	113·2 (0·4)
O(11)A—Na(1)—O(3')A	113·7 (0·5)		W(3)—Na(1)—W(2)	80·5 (0·4)
W(1)—Na(1)—O(11)A	86·5 (0·5)			
Na(2)—W(4)	2·325 (12)		Na(2)—W(7)	2·538 (16)
Na(2)—W(5)ᴵ	2·376 (17)		Na(2)—W(8)	2·576 (13)
Na(2)—W(1)ᴵ	2·407 (13)		Na(2)—W(6)ᴵ	2·646 (12)
W(4)—Na(2)—W(1)	160·2 (0·6)		W(8)—Na(2)—W(4)	82·8 (0·4)
W(5)—Na(2)—W(1)	94·4 (0·5)		W(8)—Na(2)—W(5)	93·7 (0·5)
W(5)—Na(2)—W(4)	105·3 (0·5)		W(8)—Na(2)—W(6)	173·7 (0·5)
W(7)—Na(2)—W(1)	86·0 (0·5)		W(8)—Na(2)—W(7)	100·0 (0·5)
W(7)—Na(2)—W(4)	75·3 (0·5)		W(6)—Na(2)—W(1)	80·9 (0·4)
W(7)—Na(2)—W(5)	166·2 (0·5)		W(6)—Na(2)—W(4)	100·1 (0·4)
W(7)—Na(2)—W(6)	75·6 (0·4)		W(6)—Na(2)—W(5)	90·8 (0·5)
W(8)—Na(2)—W(1)	94·4 (0·4)			
Na(3)—O(4)Aᴵᴵᴵ	2·274 (17)		Na(3)—O(13)Bᴵⱽ	2·436 (13)
Na(3)—W(9)ᴵᴵ	2·419 (15)		Na(3)—O(3')Bⱽ	2·566 (13)
Na(3)—W(4)ᴵᴵ	2·462 (12)			
O(4)A—Na(3)—W(9)	77·3 (0·5)		W(9)—Na(3)—W(4)	85·2 (0·5)
O(4)A—Na(3)—O(13)B	134·0 (0·6)		W(9)—Na(3)—O(3')B	149·9 (0·5)
O(4)A—Na(3)—W(4)	85·8 (0·5)		O(13)B—Na(3)—W(4)	139·9 (0·5)
O(4)A—Na(3)—O(3')B	78·3 (0·5)		O(13)B—Na(3)—O(3')B	111·7 (0·5)
W(9)—Na(3)—O(13)B	97·9 (0·5)		W(4)—Na(3)—O(3')B	75·7 (0·5)
Na(4)—W(6)	2·118 (16)		Na(4)—W(10)	2·513 (13)
Na(4)—W(2)	2·301 (14)		Na(4)—W(3)	2·839 (14)
Na(4)—W(7)	2·436 (14)		Na(4)—W(5)	2·950 (15)
W(6)—Na(4)—W(2)	133·5 (0·5)		W(10)—Na(4)—W(2)	129·8 (0·2)
W(6)—Na(4)—W(3)	83·9 (0·5)		W(10)—Na(4)—W(3)	141·8 (0·5)
W(6)—Na(4)—W(5)	86·9 (0·5)		W(10)—Na(4)—W(5)	74·5 (0·4)
W(7)—Na(4)—W(2)	93·2 (0·5)		W(10)—Na(4)—W(7)	86·8 (0·5)
W(7)—Na(4)—W(3)	71·0 (0·4)		W(3)—Na(4)—W(2)	83·4 (0·4)
W(7)—Na(4)—W(5)	142·2 (0·6)		W(5)—Na(4)—W(2)	75·5 (0·4)
W(7)—Na(4)—W(6)	123·9 (0·5)		W(5)—Na(4)—W(3)	140·3 (0·4)

Symmetry code: (I) x + 1, y, z; (II) x − 1, y, z; (III) x̄, y + ½, z̄ + 1; (IV) x̄ + 1, y + ½, z̄ + 1; (V) x̄ + 1, y + ½, z.

Uracil base

The uracil base is essentially planar (Table 9). The C(2)—O(2) and C(4)—O(4) lengths in both molecules indicate their double-bond character. Therefore, the bases of both the molecules exist in the same diketo tautomeric form.

Sodium-ion coordination

There are four crystallographically independent Na ions in the structure, of which three have nearly octahedral coordination and one has five nearest neighbours. Na(2) and Na(4) are completely surrounded by water O atoms. The corners of the Na(1) octahedra are occupied by O(11)A, O(3')B, W(1), W(2) and W(3) atoms at distances ranging from 2·408 to 2·891 Å. Na(2) is completely surrounded by water O atoms, W(1), W(4), W(5), W(6), W(7) and W(8), at distances ranging from 2·325 to 2·646 Å. Na(3) has only five neighbours, O(4)A, W(9), W(4), O(13)B, O(3')B, in the range 2·419 to 2·566 Å. In 5'-dGMP one of the Na atoms also has only five neighbours. Na(4) is again surrounded by the water O atoms W(6), W(2), W(7), W(10), W(3) and W(5). Na ions coordinated only by water O atoms are also present in 3'-UMPNa₂ and 5'-dAMPNa. Details of the Na octahedra are given in Table 10 and Fig. 4.

Molecular packing

The packing of the molecules is shown in Figs. 5 and 6. The molecules pack as infinite chains along b which are stacked along a. There is no overlap of bases belonging to the two molecules.

Hydrogen bonding

The N(3)A and N(3)B atoms of the bases are hydrogen bonded to the phosphate O(13)B and O(11)A atoms which are at 2·813 and 2·799 Å respectively. The water molecules form hydrogen
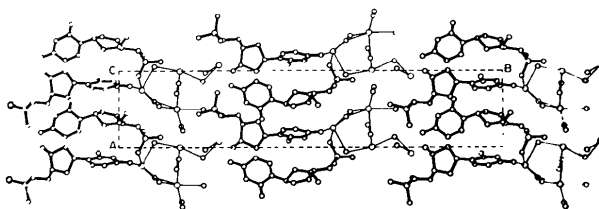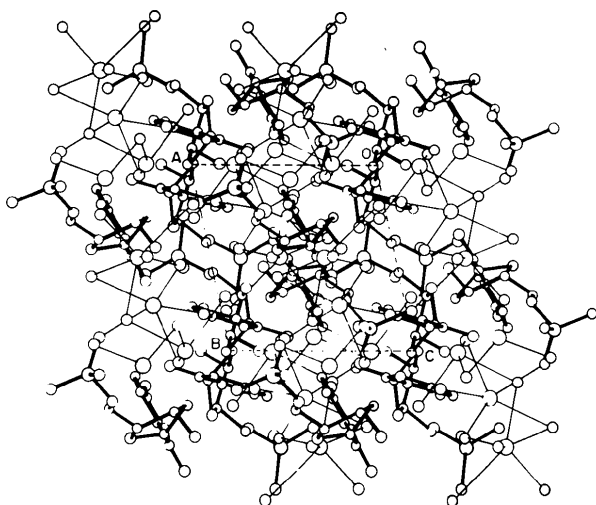

Fig. 5. A c-axis view of the structure of dUMP.

Fig. 6. The packing diagram of dUMP viewed along b.

bonds between themselves. $W(4)$ is hydrogen bonded to $W(7)$ and $W(8)$ at 2·974 and 2·869 Å respectively. There is a hydrogen bond between $W(7)$ and $W(9)$. $W(8)$ forms bonds with $W(2)$ and $W(3)$. Thus each water has at least three neighbours at distances in the range 2·25 to 2·95 Å.

Conclusion

Uracil base is not a normal constituent of double-helical DNA. If the unusual features we have found are its most preferred structure then its absence in the normal double-helical DNA may have a structural basis. However, the existence of dUMP in the double-helical DNA of transducing phage for *Bacillus subtilis* has been reported (Takahashi & Marmur, 1963). X-ray pictures of such uracil-containing DNA seem to be similar to those of thymine–DNA (Langridge & Marmur, 1964). A reshaping of the dUMP molecule to fit normally into DNA-like dTMP cannot, therefore, be ruled out. The *trans–gauche* conformation about $C(4')-C(5')$ found in the present structure is of relevance to the nature of the phosphate-sugar backbone structure in the side-by-side models of DNA recently proposed as an alternative to the double-helical

structure (Sasisekaran & Pattabiraman, 1976; Rodley, Scobie, Bates & Lewitt, 1976). Further structural studies on other forms of dUMP as well as detailed theoretical-energy calculations of its various preferred conformations would be of assistance in this respect.

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