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The Molecular and Crystal Structure of Disodium Uridine-3′-phosphate Tetrahydrate

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Crystals of the disodium salt of uridine-3′-phosphate tetrahydrate have the space group $P2_12_12$, with $a=6{\cdot}746$, $b=39{\cdot}653$, $c=6{\cdot}483$ Å, $Z=4$. The structure was determined by Patterson superposition and Fourier methods using three-dimensional Mo $K\alpha$ data collected by the ω-scan technique on a Picker automated four-circle diffractometer. All hydrogen atoms in the structure have been located from difference Fourier syntheses. The final R value is 0·043 for 2426 observed reflexions. The torsional angle about the glycosidic bond N(1)–C(1′) is 45·1°, corresponding to the *anti* conformation. The ribose conformation can be described as C(2′)-*endo*, C(3′)-*endo*, with C(2′) and C(3′) displaced by 0·683 and 0·147 Å [$\sigma(r)=0{\cdot}006$ Å] from the plane defined by C(4′)–O(1′)–C(1′). The conformation about the C(4′)–C(5′) bond is the commonly observed *gauche–gauche* with $\varphi_{OO}=-77{\cdot}4°$ and $\varphi_{OC}=42{\cdot}9°$. The pyrimidine ring is not strictly planar. The exocyclic atoms O(2) and O(4) are displaced in opposite directions from the mean base plane by −0·057 and 0·078 Å respectively. Each of the phosphate oxygen atoms, except O(3′) in the ester linkage, participates in forming three hydrogen bonds. The Na(1) ion has an octahedral coordination of six oxygen atoms, all from water molecules. The Na(2) ion has a capped octahedral coordination of seven neighbours, two of which are phosphate oxygen atoms. The sodium polyhedra share faces as well as corners. All the available hydrogen atoms participate in hydrogen bonding. Both the carbonyl oxygen atoms of the base participate in hydrogen bonding, giving rise to an infinite chain of nucleotide molecules parallel to the a axis. These chains are stacked against the sodium coordination polyhedra as alternate channels in the structure.

Introduction

The molecular structures of mononucleotides are of considerable interest for any model-building studies of nucleic acids. At present, three mononucleotide structures related to uridine have been reported: barium uridine-5′-phosphate (Shefter & Trueblood, 1965), cyclic uridine-3′,5′-phosphate (Coulter, 1969), and cyclic uridine-2′,3′-phosphate (Saenger & Eckstein, 1970). Also, several nucleoside structures have been reported with uracil as a base (Voet & Rich, 1970; Arnott, 1970; Sundaralingam, 1969). This paper presents a complete crystal and molecular structure determination of a disodium salt of uridine-3′-phospate [hereafter referred to as UMP(3′)], a monomer unit of ribonucleic acids. The chemical structure, with the conventional numbering scheme of atoms, is given in Fig. 1.

Experimental

The crystals were grown by slow diffusion of acetone into water solutions containing disodium salts of uridine-2′-3′-monophosphate (mixed isomers). Needle-shaped crystals, 4 to 5 mm long, grew in about two to three weeks. Preliminary X-ray photography of several of these crystals showed that they were all of one type, later identified (from the crystal-structure analysis) as the 3′-isomer.

Rotation, Weissenberg and precession photographs taken with Cu $K\alpha$ radiation showed that the crystals belong to the orthorhombic system with space group $P2_12_12$. The density of the crystals, 1·689 g.cm^{-3}, as measured by the flotation method using a mixture of carbon tetrachloride and bromoform, showed that four molecules of water are associated with one Na_2UMP-(3′) molecule in the asymmetric unit. The crystal data are given in Table 1.

Table 1. *Crystal data for disodium salt of uridine-3′-phosphate tetrahydrate*

Molecular formula	$C_9H_{11}N_2O_9P.2Na.4H_2O$
M.W.	440·2
System	Orthorhombic
a	6·746 (2) Å
b	39·653 (12)
c	6·483 (2)
V	1734·3 Å^3
Z	4
d_{obs}	1·689 g.cm^{-3}
d_{calc}	1·686 g.cm^{-3}
μ Mo $K\alpha$	2·58 cm^{-1}
Systematic absences	$h00$, h odd $0k0$, k odd
Space group	$P2_12_12$

Three-dimensional intensity data were collected with a crystal of size 1·01 × 0·2 × 0·1 mm using Mo $K\alpha$ radiation with a graphite monochromator on a Picker four-circle computer-controlled diffractometer, em-

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ploying an ω scan. The scan speed was 1°.min^{-1} over a range of 0·7°, and the time spent on each background was 10 sec. Data were collected to a limit of $(\sin\theta)/\lambda_{\max}=$ 0·70, which is slightly in excess of the number of reflexions available in the copper sphere. A set of three standard reflexions 380, 390, and 3,10,0 measured at intervals of 30 reflexions, showed the crystals to be extremely stable to X-rays, the intensity drop of the standards at the end of the data collection being only 0·7%. Lorentz–polarization corrections were applied, but no absorption correction was made. A reflexion was considered to be unobserved if the intensity was smaller than 1·5 times its standard deviation. On this basis out of 2953 reflexions collected, only 2426 were considered observed.

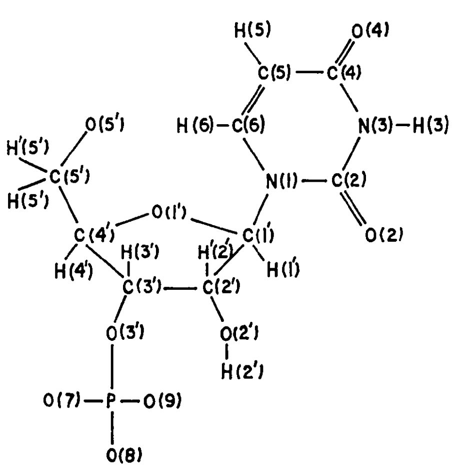

Fig. 1. Numbering scheme for the uridine-3′-phosphate molecule.

Structure determination and refinement

The position of the phosphorus atom (0·25, 0·076, 0·062) was determined from the Harker sections of a three-dimensional sharpened Patterson map computed using $F_o^2 \,.\, 1/\mathrm{Lp}$ as coefficients for this summation. A three-dimensional symmetry minium map (Simpson, Dobrott & Lipscomb, 1965) computed on the basis of the phosphorus position showed two sets of mirror-related positions for the phosphate oxygen atoms. The spurious mirror at $x=\frac{1}{4}$, made it difficult to determine the orientation of the molecule unambiguously. A judicious choice of the phosphate oxygen peaks was made, and a series of symmetry minimum function maps were computed, each successive map being based on the coordinates of an additional oxygen atom. The minimum maps obtained in this fashion with coordinates of both the phosphorus and the phosphate oxygen atoms had about 28 significant peaks, and a model made on this basis revealed practically the entire molecule. As there was still some spurious symmetry present, the complete structure was obtained in successive F_o electron density maps, first with the phosphate and ribose atoms and then including the base, sodium, and water oxygen atoms in succession. To start with, the sodium ions and water oxygen atoms were treated alike and later distinguished from their electron-density peak heights. Five water oxygen peaks were found, three in general positions, and two located on twofold axes,

Table 2. *Positional parameters and anisotropic thermal parameters of the non-hydrogen atoms* ($\times 10^5$)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	28878 (43)	19794 (7)	52170 (47)	1122 (57)	32 (1)	1212 (59)	−27 (15)	−25 (109)	138 (16)
C(2)	11699 (56)	20706 (9)	41951 (59)	1168 (66)	40 (2)	1259 (76)	47 (20)	−35 (125)	78 (21)
N(3)	14819 (49)	22754 (9)	25061 (53)	1135 (61)	52 (2)	1400 (73)	31 (19)	−215 (120)	168 (22)
C(4)	32726 (59)	23998 (10)	18072 (61)	1251 (70)	44 (2)	1300 (76)	23 (21)	153 (127)	124 (22)
C(5)	49884 (54)	22804 (10)	29110 (61)	1073 (69)	46 (2)	1465 (85)	−74 (21)	200 (141)	197 (23)
C(6)	47352 (52)	20803 (9)	45442 (64)	980 (61)	44 (2)	1442 (79)	−31 (19)	−327 (141)	105 (24)
O(2)	−4817 (41)	19804 (8)	47195 (53)	1047 (51)	68 (2)	2021 (73)	−21 (18)	−149 (117)	279 (22)
O(4)	33038 (49)	25953 (8)	3321 (52)	1706 (65)	70 (2)	1808 (75)	51 (21)	367 (133)	357 (23)
C(1′)	27870 (51)	17334 (8)	68878 (51)	1155 (65)	29 (2)	994 (61)	16 (8)	193 (122)	20 (17)
C(2′)	34214 (53)	13796 (8)	61927 (54)	1103 (64)	28 (2)	1128 (68)	−57 (17)	282 (117)	−23 (17)
C(3′)	40490 (54)	12189 (8)	82424 (55)	1232 (66)	24 (2)	1242 (68)	2 (17)	720 (127)	79 (18)
C(4′)	48704 (62)	15253 (9)	94196 (59)	1648 (78)	36 (2)	1103 (72)	26 (21)	−220 (154)	46 (21)
O(1′)	41382 (44)	18266 (6)	84339 (40)	1739 (62)	33 (1)	1143 (53)	11 (15)	−681 (109)	5 (15)
O(2′)	18860 (44)	12207 (7)	51214 (47)	1424 (58)	53 (2)	1717 (67)	−93 (17)	136 (111)	−199 (19)
O(3′)	22881 (42)	10900 (6)	91783 (46)	1251 (53)	39 (1)	2032 (70)	55 (15)	1185 (113)	215 (17)
C(5′)	71107 (69)	15417 (11)	94604 (93)	1673 (93)	54 (3)	2809 (136)	−24 (25)	−1646 (225)	−34 (33)
O(5′)	78986 (50)	14612 (9)	74801 (72)	1442 (67)	60 (2)	4152 (137)	−8 (20)	1012 (174)	215 (29)
O(7)	1922 (42)	6612 (7)	106347 (50)	1192 (51)	46 (2)	1990 (73)	−106 (15)	393 (122)	82 (19)
O(8)	33965 (48)	8071 (8)	124955 (41)	1674 (64)	75 (2)	945 (55)	102 (21)	−549 (106)	−54 (19)
O(9)	35109 (44)	4859 (7)	92111 (43)	1553 (58)	43 (2)	1364 (57)	57 (16)	140 (104)	−59 (16)
P	23717 (12)	7418 (2)	104686 (12)	975 (14)	29 (0)	732 (15)	−27 (4)	11 (29)	49 (4)
Na(1)	78732 (31)	1960 (4)	46418 (30)	2303 (47)	44 (1)	1882 (40)	95 (11)	284 (87)	−21 (11)
Na(2)	92503 (27)	9319 (5)	66529 (35)	1351 (37)	65 (1)	2578 (53)	−94 (11)	148 (80)	−204 (14)
W(1)	74518 (48)	7817 (8)	35908 (46)	1511 (61)	72 (2)	1588 (65)	75 (22)	4 (124)	23 (20)
W(2)	14661 (46)	3867 (7)	56375 (42)	1945 (67)	51 (2)	1198 (56)	−127 (19)	−32 (117)	−65 (17)
W(3)	72764 (54)	4533 (10)	78731 (50)	1835 (75)	111 (3)	1586 (68)	250 (27)	254 (136)	92 (25)
W(4)	0 (0)	0 (0)	19776 (70)	2569 (124)	48 (3)	1471 (95)	−267 (30)	0 (0)	0 (0)
W(5)	50000 (0)	0 (0)	24606 (88)	2141 (116)	53 (3)	2578 (134)	171 (30)	0 (0)	0 (0)

thus contributing in all four water molecules to the asymmetric unit.

Isotropic block-diagonal least-squares refinement of the structure reduced the residual ($R=\sum||F_o|-|F_c||/\sum|F_o|$) to 0·09. Six cycles of refinement with anisotropic temperature factors and observational weights (de Boer, Zalkin & Templeton, 1968) gave an R value of 0·06. A difference Fourier synthesis at this stage revealed the positions of 11 hydrogen atoms. One more cycle of refinement, with these hydrogen atoms included, decreased the R value to 0·053. A difference Fourier synthesis showed the positions of the remaining eight hydrogen atoms associated with the water molecules. All the hydrogen peak heights were above 0·3 e.Å^{-3}. The above computations were carried out at the University of Alberta using the set of programs of Ahmed, Hall, Pippy & Huber (1966) for the IBM 360/67 computer.

Further refinement was carried out on a CDC 3600 computer using a full-matrix least-squares program, *LALS*, by Gantzel, Sparks and Trueblood. The initial R value with all the atoms included (28 heavy atoms + 19 hydrogen atoms) was 0·065. Since a maximum of only 160 parameters could be refined in one cycle, the refinement was carried out in two sets for the heavy atoms, with water oxygen atoms W(4) and W(5) on the twofold axes kept common. The hydrogen atoms were included in these calculations but were not refined. The refinement converged after three cycles to an R value of 0·046. Keeping the heavy-atom parameters fixed, the hydrogen atom positional parameters were refined in three further cycles to an R value of 0·043. A constant isotropic temperature factor of 3·5 Å^2 was used for the hydrogen atoms. The function minimized in the refinement was $\sum w(|F_o|-k|F_c|)^2$, where $w=1/(a+b|F_o|+c|F_o|^2+d|F_o|^3)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), $a=2F_{\min}$, $b=1$, $c=2/F_{\max}$, $d=5/F^2_{\max}$. For hydrogen atoms, the scattering factors of Stewart, Davidson & Simpson (1965) were used, and for other atoms scattering factors were computed using the function developed by Cromer & Waber (1965). A tabulation of the structure amplitudes and phase angles has been filed with 'The Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Canada'. A copy of these data may be obtained free of charge from this source.

Results and discussion

The final atomic parameters of the heavy atoms and their estimated standard deviations are given in Table 2 and the corresponding values for the hydrogen atoms appear in Table 3. The bond lengths and the bond angles are given in Fig. 2. The average C–H, O–H, and N–H bond distances are 0·978, 0·822, 0·746 Å. The average e.s.d.'s in various bond lengths are: σ(P–O) = 0·003 Å, σ(C,N,O–C) = 0·005 Å, and σ(C,N,O–H) = 0·06 Å; the average e.s.d. in bond angles involving heavy atoms is 0·3°. The bond lengths presented in Fig. 2(*a*) are not corrected for thermal motion and in general agree well with those reported previously in similar structures (Voet & Rich, 1970).

Table 3. *Positional parameters of hydrogen atoms* (B = 3·5Å^2)

(× 10^3)

	x	y	z
H(O5′)	827 (9)	161 (1)	694 (9)
H(5′)	760 (9)	137 (1)	16 (9)
H′(5′)	754 (9)	177 (1)	−2 (9)
H(4′)	436 (8)	151 (1)	76 (9)
H(3′)	504 (8)	101 (1)	809 (8)
H′(2′)	467 (9)	139 (1)	543 (9)
H(1′)	143 (9)	172 (1)	748 (9)
H(2′)	239 (8)	107 (1)	434 (9)
H(6)	577 (8)	197 (1)	517 (9)
H(5)	630 (9)	238 (1)	257 (9)
H(3)	52 (8)	229 (1)	189 (9)
H(W1)	619 (8)	77 (1)	315 (9)
H′(W1)	842 (8)	79 (1)	272 (9)
H(W2)	223 (9)	45 (1)	495 (9)
H′(W2)	217 (9)	44 (1)	651 (9)
H(W3)	840 (8)	48 (1)	−121 (8)
H′(W3)	611 (9)	45 (1)	803 (9)
H(W4)	26 (9)	16 (1)	131 (9)
H(W5)	474 (9)	14 (1)	168 (9)

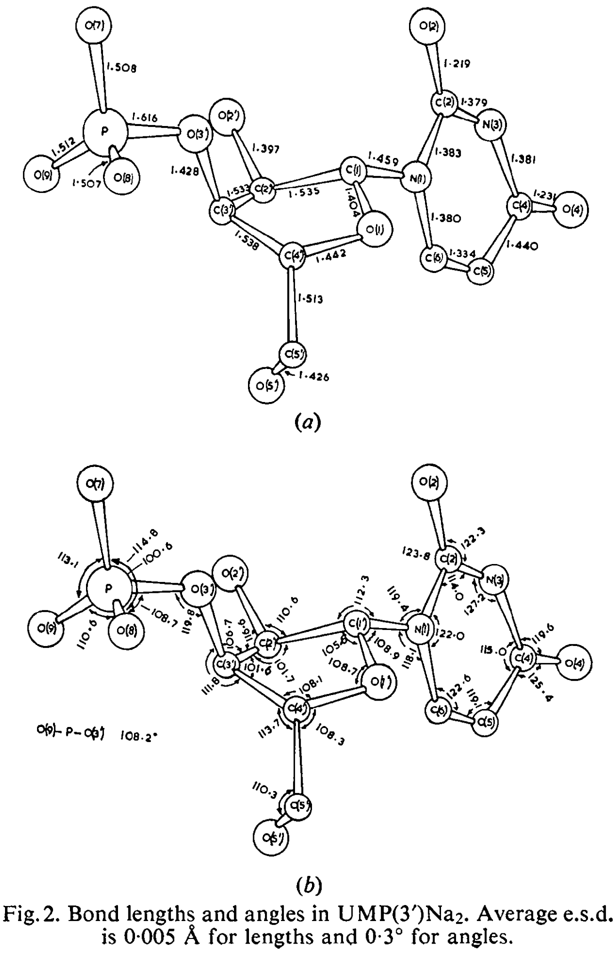

Fig. 2. Bond lengths and angles in UMP(3′)Na$_2$. Average e.s.d. is 0·005 Å for lengths and 0·3° for angles.

Molecular conformation and geometry

Glycosidic bond

The torsional angle describing the relative orientation of sugar and base residues with respect to the glycosidic bond N(1)–C(1′) is 45·1°; it corresponds to the *anti* conformation in the notation of Sundaralingam (1969) and lies within the range of values observed so far in β-pyrimidine nucleosides and nucleotides. In the notation of Arnott (1970) this angle (χ) is 100·4°. The dihedral angle between the plane of the ribose [defined by C(4′)–O(1′)–C(1′)] and that of the base [defined by C(6)–N(1)–C(2)] is 62·5°

Ribose

Least-squares planes for the various four-atom combinations in the ribose ring have been computed, and it was found that the best four-atom plane is defined by C(1′)–C(3′)–C(4′)–O(1′), (Table 4). The displacement of C(2′) from this plane is 0·58 Å on the same side as C(5′), a conformation usually referred to as C(2′)-*endo*, and is commonly observed in nucleosides and nucleotides. However, when referred to the three-atom plane C(1′)–O(1′)–C(4′), C(2′) and C(3′) are displaced on the same side of the plane as is C(5′) by 0·68 and 0·15 Å respectively (Table 4). Since $\sigma(r)$ of C(3′) is of the order of 0·006 Å, it would probably be more apt to describe the conformation as C(2′)-*endo*, C(3′)-*endo*. This conformation, regardless of the nomenclature used to describe it, represents an unusual puckering for five-membered furanose rings in nucleosides and nucleotides (*cf.* Sundaralingam, 1969; Arnott, 1970).

The torsional angles involving the heavy atoms in the ribose ring are given in Table 5(*a*), and those involving ring hydrogen atoms are listed in Table 5(*b*). The conformation about the C(4′)–C(5′) bond is the commonly observed *gauche–gauche* with $\varphi_{OO} = -77{\cdot}4°$ and $\varphi_{OC} = 42{\cdot}9°$. The bond lengths and bond angles in the ribose moiety are generally in good agreement with those of similar nucleotide structures (Sundaralingam & Jensen, 1965).

Table 4. *Least-square planes through the ribose*

	Planes					
	I	II	III	IV	V	VI
C(1′)	−0·536*	0·015	−0·130	−0·317	0·058	0·0
C(2′)	−0·136	−0·583*	−0·154	−0·488	−0·233	−0·683*
C(3′)	−0·203	−0·026	−0·666*	−0·168	−0·451	−0·147*
C(4′)	0·213	0·035	−0·073	0·879*	0·506	0·0
O(1′)	0·060	−0·026	0·301	0·781	0·830*	0·0
C(5′)	1·643*	−1·092*	1·149*	2·301*	1·797*	−1·109
r.m.s.Δ	0·164	0·026	0·185	0·494	0·359	0·0
σr.m.s.Δ	0·006	0·006	0·006	0·006	0·006	0·006

Equations of the planes:

Planes
I $0{\cdot}9473X + 0{\cdot}1010Y - 0{\cdot}3039Z = 1{\cdot}6548$
II $-0{\cdot}7569X - 0{\cdot}0148Y + 0{\cdot}6533Z = 1{\cdot}3776$
III $0{\cdot}7987X + 0{\cdot}4041Y - 0{\cdot}4457Z = 2{\cdot}4190$
IV $0{\cdot}9232X + 0{\cdot}3647Y + 0{\cdot}1214Z = 5{\cdot}1018$
V $0{\cdot}8349X + 0{\cdot}5200Y - 0{\cdot}1804Z = 4{\cdot}2806$
VI $-0{\cdot}7473X + 0{\cdot}0456Y + 0{\cdot}6629Z = 1{\cdot}8684$

* Atoms not included in the calculation of the plane.

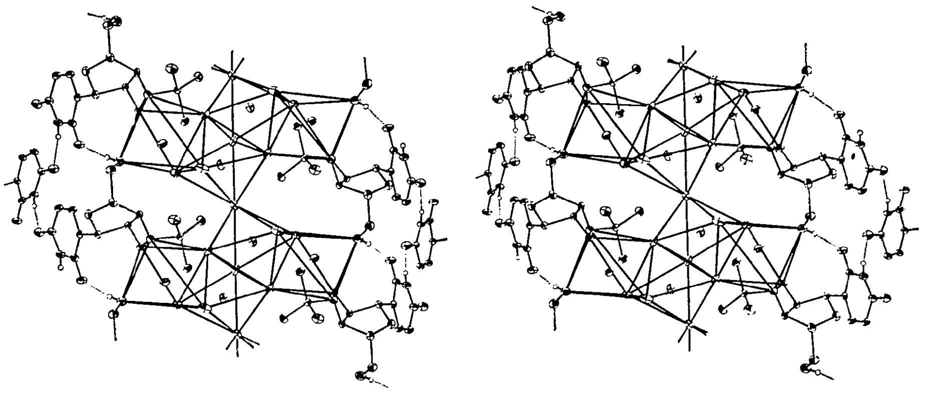

Fig. 3. Stereoscopic view of the Na coordination polyhedra as seen down the *c* axis. Only the hydrogen bonds involving the base and ribose moieties are shown. This drawing was done using the program *ORTEP* (Johnson, 1965).

Table 5. *Torsional angles*

(*a*) Involving heavy atoms in ribose

C(4′)–O(1′)–C(1′)–C(2′)	−27·5°
O(1′)–C(1′)–C(2′)–C(3′)	+38·0
C(1′)–C(2′)–C(3′)–C(4′)	−32·6
C(2′)–C(3′)–C(4′)–O(1′)	+18·0
C(3′)–C(4′)–O(1′)–C(1′)	5·8

(*b*) Involving hydrogen atoms in ribose

H(1′)–H′(2′)	+172·0
H′(2′)–H(3′)	−44·4
H(3′)–H(4′)	−77·5

Base

The least-squares plane through the uracil ring atoms is given in Table 6. The pyrimidine ring is not strictly planar (plane I). The displacements of exocyclic atoms O(2) (−0·057 Å) and O(4) (0·078 Å) are in opposite directions, probably due to their hydrogen bonding with the neighbouring molecules on opposite sides of the ring plane. The bond lengths and bond angles agree well with those previously reported.

Table 6. *Least-square planes for base*

	Plane I	Plane II
N(1)	0·017 Å	0·034* Å
C(2)	−0·004	−0·004
N(3)	−0·017	−0·033*
C(4)	0·025	0·007
C(5)	−0·012	−0·012
C(6)	−0·008	0·008
O(2)	−0·057*	−0·053*
O(4)	0·078*	0·045*
C(1′)	−0·118*	−0·083*
r.m.s. *Δ*	0·015	0·008
σ r.m.s. *Δ*	0·006	0·007

Equations of the planes

Plane I $0·0703X+0·8020Y+0·5932Z=8·1470$

Plane II $-0·0644X+0·7946Y+0·6037Z=8·1192$

* Atom not included in the calculation of the plane.

The base–base interactions in this structure are edge to edge (Figs. 3 & 4) rather than the familiar 'base stacking' type documented by Bugg, Thomas, Sundaralingam & Rao (1971). This hydrogen-bonding scheme gives rise to infinite ribbons of approximately coplanar bases (Fig. 5) running parallel to the *a* axis. Although the edge-to-edge bonding pattern here does not resemble Watson–Crick base pairing, it is interesting to note that each base utilizes both of its carbonyl oxygen atoms as H-bond acceptors as well as its imino nitrogen atom [N(3)] as an H-bond donor.

The phosphate

The phosphate group is in the characteristic staggered conformation with respect to the ester bond C(3′)–O(3′). The torsional angles are: C(3′)–O(3′)–P–O(7) 165·6°, C(3′)–O(3′)–P–O(8) 73·6°, and C(3′)–O(3′)–P–O(9) 46.6°.

An interesting feature of the phosphate group is that each of the phosphate oxygen atoms, except O(3′) involved in the ester linkage, participates in forming three hydrogen bonds as acceptors with water and hydroxyl oxygen atoms as donor atoms. O(8) forms hydrogen bonds with hydroxyl oxygen O(2′) and with oxygen atoms *W*(1) and *W*(2); O(7) hydrogen-bonds with water oxygen atoms *W*(4), *W*(3), and *W*(1), and O(9) hydrogen bonds to *W*(2), *W*(3), and *W*(5). The hydrogen bonding around the oxygen atoms of the phosphate group is shown in Fig. 6.

In addition to their hydrogen bonds, the phosphate oxygen atoms O(7) and O(3′) are coordinated to the Na(2) ion. Note that in BaUMP(5′) (Shefter & Trueblood, 1965, NaIMP(5′) (Rao & Sundaralingam, 1969) and in barium ribose 5′-phosphate (Furberg & Mostad, 1962) the metal ions are only indirectly attached to the phosphate oxygen atoms through water bridges. Direct coordination of the phosphate oxygen atoms to the metal ion is rare in nucleotide structures; the present compound and calcium thymidylate (Trueblood, Horn & Luzatti, 1961) comprise the only two known

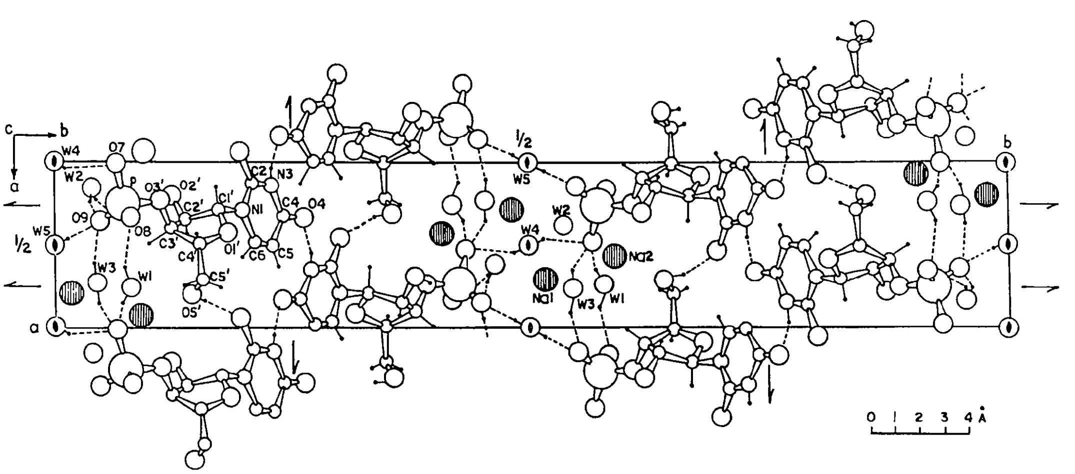

Fig.4. Molecular packing diagram viewed down the *c* axis. Dotted lines indicate hydrogen bonds. (Not all hydrogen bonds are indicated, for the sake of clarity.)

Table 7. *Sodium coordination polyhedra*

Na(1)	-*W*(3)	2·365 (4) Å
Na(1)	-*W*(4) (x+1, y, z)	2·376 (4)
Na(1)	-*W*(1)	2·437 (4)
Na(1)	-*W*(2) (−x+1, −y, z)	2·440 (3)
Na(1)	-*W*(5)	2·522 (4)
Na(1)	-*W*(2) (x+1, y, z)	2·620 (4)
W(1)	-*W*(3)	3·069 (5)
W(1)	-*W*(2) (x+1, y, z)	3·398 (4)
W(1)	-*W*(5)	3·589 (4)
W(1)	-*W*(4) (x+1, y, z)	3·696 (4)
W(2)(x+1, y, z)	-*W*(4) (x+1, y, z)	2·993 (5)
W(2)(x+1, y, z)	-*W*(3)	3·187 (5)
W(2)(x+1, y, z)	-*W*(2) (−x+1, −y, z)	3·649 (6)
W(2)(−x+1, −y, z)	-*W*(4) (x+1, y, z)	2·993 (5)
W(2)(−x+1, −y, z)	-*W*(5)	3·504 (3)
W(2)(−x+1, −y, z)	-*W*(3)	3·730 (5)
W(4)(x+1, y, z)	-*W*(5)	3·388 (1)
W(3)	-*W*(5)	3·799 (6)
W(3)	-Na(1)-*W*(4)(x+1, y, z)	152·6 (1)°
W(3)	-Na(1)-*W*(1)	79·4 (1)
W(3)	-Na(1)-*W*(2)(−x+1, −y, z)	101·8 (1)
W(3)	-Na(1)-*W*(5)	119·9 (1)
W(3)	-Na(1)-*W*(2)(x+1, y, z)	79·3 (1)
W(4)(x+1, y, z)	-Na(1)-*W*(1)	100·3 (1)
W(4)(x+1, y, z)	-Na(1)-*W*(2)(−x+1, −y, z)	76·8 (1)
W(4)(x+1, y, z)	-Na(1)-*W*(5)	87·5 (1)
W(4)(x+1, y, z)	-Na(1)-*W*(2)(x+1, y, z)	73·4 (1)
W(1)	-Na(1)-*W*(2)(−x+1, −y, z)	176·1 (1)
W(1)	-Na(1)-*W*(5)	92·7 (1)
W(1)	-Na(1)-*W*(2)(x+1, y, z)	84·4 (1)
W(2)(−x+1, −y, z)	-Na(1)-*W*(5)	89·8 (1)
W(2)(−x+1, −y, z)	-Na(1)-*W*(2)(x+1, y, z)	92·2 (1)
W(5)	-Na(1)-*W*(2)(x+1, y, z)	159·7 (1)
Na(2)	-O(2′) (x+1, y, z)	2·336 (4) Å
Na(2)	-O(5′)	2·350 (4)
Na(2)	-*W*(1)	2·402 (4)
Na(2)	-*W*(3)	2·450 (4)
Na(2)	-O(3′) (x+1, y, z)	2·697 (4)
Na(2)	-*W*(2) (x+1, y, z)	2·710 (4)
Na(2)	-O(7) (x+1, y, z+1)	2·867 (4)
O(2′)(x+1, y, z)	-O(5′)	3·238 (5)
O(2′)(x+1, y, z)	-*W*(1)	3·600 (4)
O(2′)(x+1, y, z)	-O(3′) (x+1, y, z)	2·694 (4)
O(2′)(x+1, y, z)	-*W*(2) (x+1, y, z)	3·336 (4)
O(5′)	-*W*(1)	3·702 (5)
O(5′)	-*W*(3)	4·027 (5)
O(5′)	-O(3′) (x+1, y, z)	3·485 (5)
W(1)	-*W*(3)	3·069 (5)
W(1)	-*W*(2) (x+1, y, z)	3·398 (4)
W(3)	-*W*(2) (x+1, y, z)	3·187 (5)
W(3)	-O(3′) (x+1, y, z)	4·308 (5)
O(3′)(x+1, y, z)	-*W*(2) (x+1, y, z)	3·654 (4)
O(2′)(x+1, y, z)	-Na(2)-O(5′)	87·4 (1)°
O(2′)(x+1, y, z)	-Na(2)-*W*(1)	98·9 (1)
O(2′)(x+1, y, z)	-Na(2)-*W*(3)	158·5 (1)
O(2′)(x+1, y, z)	-Na(2)-O(3′)(x+1, y, z)	64·3 (1)
O(2′)(x+1, y, z)	-Na(2)-*W*(2)(x+1, y, z)	82·4 (1)
O(5′)	-Na(2)-*W*(1)	102·4 (1)
O(5′)	-Na(2)-*W*(3)	114·0 (1)
O(5′)	-Na(2)-O(3′)(x+1, y, z)	87·1 (1)
O(5′)	-Na(2)-*W*(2)(x+1, y, z)	169·1 (1)
W(1)	-Na(2)-*W*(3)	78·5 (1)
W(1)	-Na(2)-O(3′)(x+1, y, z)	160·6 (1)
W(1)	-Na(2)-*W*(2)(x+1, y, z)	83·1 (1)
W(3)	-Na(2)-O(3′)(x+1, y, z)	113·4 (1)
W(3)	-Na(2)-*W*(2)(x+1, y, z)	76·1 (1)
O(3′)(x+1, y, z)	-Na(2)-*W*(2)(x+1, y, z)	85·0 (1)

cases. No qualitative reason can be given for this since the two compounds are 5′ and 3′ phosphates respectively, and also differ in that the ribose portion of the thymidylate ion is 2′-deoxy whilst the 2′-hydroxyl function exists in the present compound.

The bond lengths and bond angles in the phosphate group are normal, with the exception of the angle O(7)–P–O(3′), 100·6 (0·2)°. This is significantly smaller than the tetrahedral value, and is perhaps due to the fact that both O(3′) and O(7) atoms are coordinated to the Na(2) ion (see below). It is, however, in agreement with the value of 101·4° for this bond angle quoted by Arnott (1970) and Sundaralingam & Jensen (1965).

Sodium ion coordination

There are two non-equivalent sodium ions associated with each molecule of UMP(3′). The ion Na(1) is surrounded by six oxygen atoms (all from water molecules) at distances 2·365 to 2·620 Å, and directed towards the corners of a distorted octahedron. The second sodium ion Na(2) is also surrounded by six oxygen atoms at distances 2·336 to 2·710 Å; of these, three are water oxygen atoms [*W*(1), *W*(2), *W*(3)], two hydroxyl oxygen atoms [O(2′) and O(5′)], and one phosphate oxygen atom [O(3′)]. In addition to these coordinating atoms, the phosphate oxygen O(7) is 2·867 Å from Na(2). Considering this oxygen atom also as a coordinating atom, the Na(2) coordination polyhedron can be described as a capped octahedron, with O(7) capping the face defined by *W*(2), *W*(3) and O(3′). Table 7 gives the details of the sodium coordination polyhedra, and Fig. 3 illustrates them as seen down the *c* axis.

The two adjacent octahedra surrounding Na(1) and Na(2) share a face described by the atoms *W*(1), *W*(2), and *W*(3). The two equivalent octahedra Na(1) and Na(1) $(-X, -Y, Z)$ share the face *W*(2) $(-X, -Y, Z)$, *W*(4), and *W*(2). The Na(1) octahedron further shares two of its corners, one with that of Na(1) $(-X+1, -Y, Z)$ and another with that of Na(2) $(-X, -Y, Z)$. The sharing of metal coordination polyhedra has given rise to a tightly packed crystal structure with sodium–sodium distances of 3·263 Å [(Na(1)–Na(1) $(-X, -Y, Z)$] and 3·328 Å [Na(1)–Na(2)]. A literature survey shows that only the present structure and that of hydrated NaIMP(5′) (Rao & Sundaralingam, 1969) have an extended polyhedra network as described above. A stereoscopic view of the sharing of polyhedra is shown in Fig. 3.

Molecular packing and hydrogen bonding

Figs. 4 and 5 give the molecular packing and hydrogen bonding viewed down the *c* axis and the *a* axis,

Table 8. *Hydrogen bonds and angles*

X–H·········Y		$X\cdots Y$	X–H	H$\cdots Y$	∠X–H$\cdots Y$
O(5′)–H(05′)$(x, y, z+1)$	–O(2)	2·939 Å	0·732 Å	2·221 Å	166·8°
O(2′)–H(2′)	–O(8)	2·574	0·854	1·726	171·7
N(3)–H(3)	–O(4)$(x-\frac{1}{2}, \frac{1}{2}-y, -z)$	2·871	0·763	2·127	165·2
W(1)–H(*W*1)	–O(8)	2·828	0·899	1·935	171·8
W(1)–H′(*W*1)	–O(7)$(x+1, y, z)$	2·705	0·861	1·884	159·1
W(2)–H(*W*2)	–O(8)	2·937	0·735	2·256	154·4
W(2)–H′(*W*2)	–O(9)	2·725	0·772	1·977	162·9
W(3)–H(*W*3)	–O(7)$(x+1, y, z)$	2·785	0·970	1·849	161·1
W(3)–H′(*W*3)	–O(9)	2·687	0·793	1·918	163·4
W(4)–H(*W*4)	–O(7)	2·766	0·781	2·044	153·6
W(5)–H(*W*5)	–O(9)	3·026	0·786	2·254	167·9

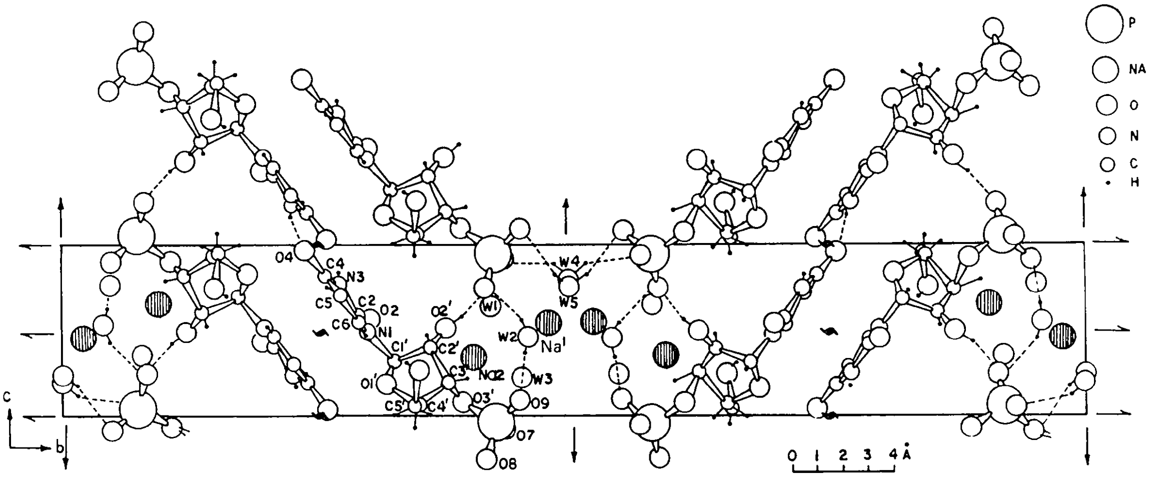

Fig. 5. Molecular packing diagram viewed down the *a* axis. Dotted lines indicate hydrogen bonds (supplement to those shown in Fig. 4).

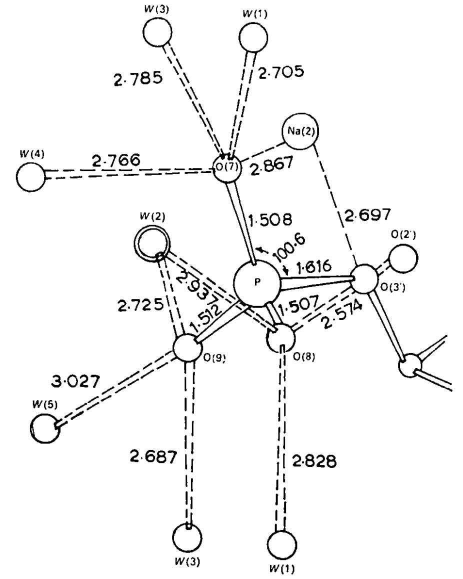

Fig. 6. The environment of phosphate group oxygen atoms. ----indicates coordination to the Na ions. ====indicates hydrogen bonds. Each phosphate oxygen atom, except O(3′) in the ester linkage, participates in three hydrogen bonds·

respectively. All available hydrogen atoms participate in hydrogen bonding. No intramolecular hydrogen bonding is seen in this structure. Table 8 gives the details regarding the hydrogen bonding and other short contacts.

The shortest hydrogen bond is between the hydroxyl oxygen O(2′) and the phosphate oxygen O(8) [2·574 Å, O(2)–H···O(8) = 172°]. The other hydroxyl oxygen atom [O(5′)] is hydrogen bonded to the base carbonyl oxygen O(2). The environments of these two hydroxyl oxygen atoms show that both have one covalently linked carbon atom, one hydrogen bonded atom, and one sodium ion attached. All four atoms are approximately coplanar, the angles subtended at the hydroxyl oxygen atoms being close to 120°.

No water–water or water–hydroxyl hydrogen bonds are observed in this structure. All of the water molecules participate in hydrogen bonding with the phosphate oxygen atoms. Each water molecule participates in two hydrogen bonds and is coordinated to at least two metal ions, thus having a minimum of four nearest neighbours. The environment of the water oxygen atoms is shown in Fig. 7. The contacts between $W(1)$ and O(3′) (3·06 Å) and $W(2)$ and $W(4)$ (2·983 Å) are appar-

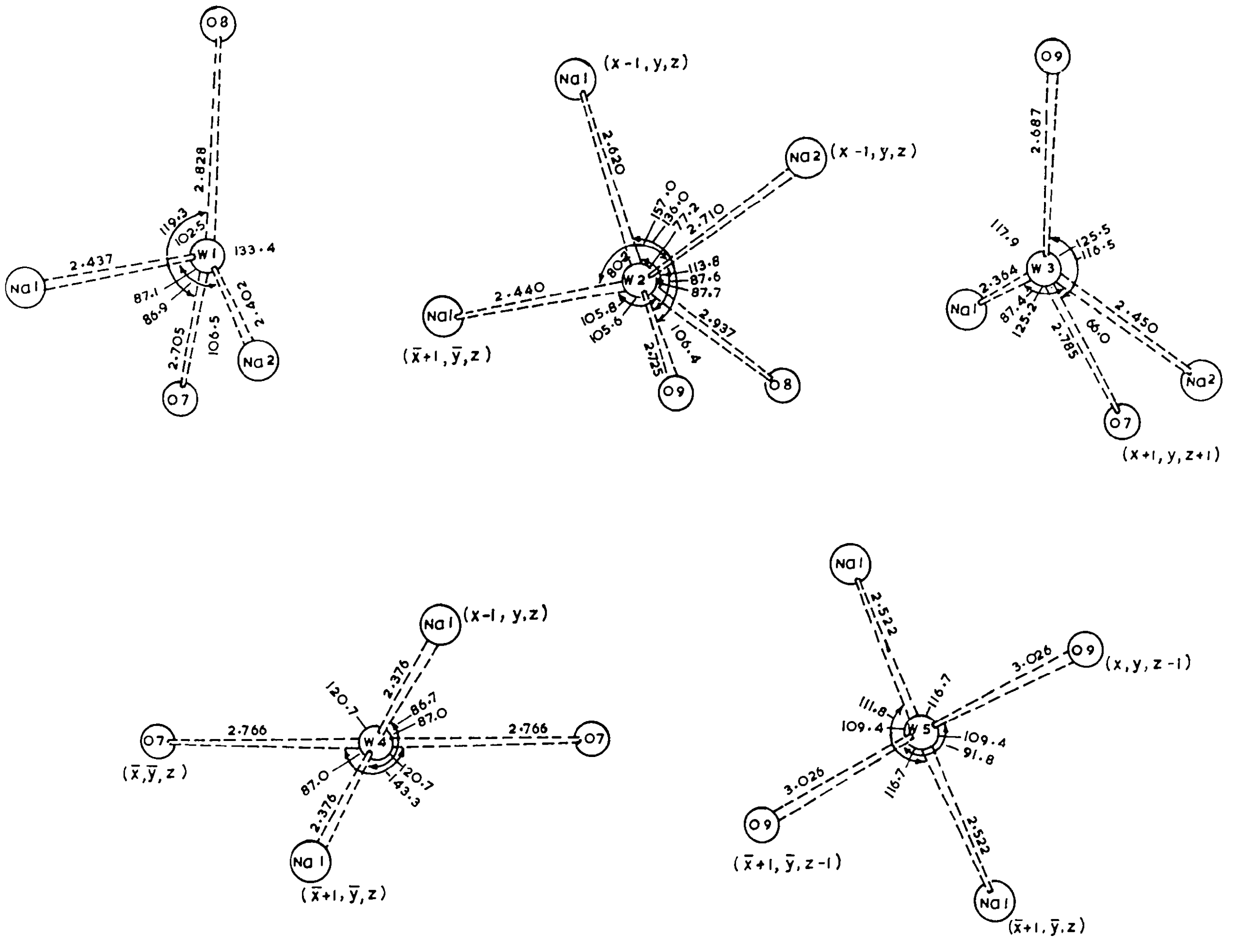

Fig. 7. Bond lengths and bond angles in the environment of the water oxygen atoms.

ently short, because they form the edges of the sodium coordination polyhedra.

Adjacent molecules related by a 2_1 screw parallel to the *a* axis are linked by a hydrogen bond between N(3) and O(4) ($\frac{1}{2}+X$, $\frac{1}{2}-Y$, $-Z$) (2·854 Å), and the molecules related by a translation along the *a* axis have a hydrogen bond between O(5′) and O(2) ($X+1$, Y, Z). These hydrogen bonds give rise to an infinite chain of nucleotide molecules parallel to the *a* axis. The nucleotide chains are stacked against the sodium coordination polyhedra (Fig. 3) as alternate channels in the structure.

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The Crystal and Molecular Structure of 5-Methylbenzfurazan-1-oxide

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The crystal and molecular structure of 5-methylbenzfurazan-1-oxide, $C_7H_6N_2O_2$, has been determined. The compound crystallizes in monoclinic crystals with $a=4{\cdot}031$ (3), $b=15{\cdot}042$ (7), $c=11{\cdot}425$ (9) Å, $\beta=92{\cdot}82$ (7)°, in space group $P2_1/c\,(C_{2h}^5)$ with four molecules in the unit cell. Least-squares refinement of counter data gave a final conventional R factor of 0·059. Bond lengths were determined to an e.s.d. of 0·005 Å for the uncorrected values. Analysis was made of the rigid body motion, and libration corrections ranging from 0·003 to 0·009 Å were made.

Introduction

Earlier the structure of 5-chlorobenzfuroxan (=5-chlorobenzfurazan-1-oxide) was determined in this laboratory (Britton & Noland, 1962*a*, *b*). The question of interest at the time was whether this compound contained two *ortho*-nitroso groups or whether it was indeed the benzfuroxan. The structure was shown to be the benzfuroxan, but the bond lengths and angles were poorly determined, primarily because of the low melting point and high volatility of the compound. Shortly after the structure of the chlorobenzfuroxan was determined, a preliminary study (unpublished) of 5-methylbenzfuroxan was undertaken to see whether the methyl