

The Crystal and Molecular Structure of a Dinucleoside Phosphate: β -Adenosine-2'- β -uridine-5'-phosphoric Acid*

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The dinucleoside phosphate $A_2P_5'U$, $C_{19}H_{24}N_7O_{12}P$, forms monoclinic crystals from aqueous solution, with $a_0 = 9.783$, $b_0 = 16.013$, $c_0 = 8.718$ Å, $\beta = 90.79^\circ$ and two molecules in the unit cell, together with eight molecules of water. The space group is $P2_1$. The phosphate group was located by a rigid-body search and least-squares fit to the sharpened Patterson distribution, and the remainder of the structure was then determined by Fourier methods, phasing first with the phosphate and then with successively increasing numbers of atoms. After least-squares refinement, all of the hydrogen atoms whose positions are fixed by the molecular framework were found in difference maps; some of the others were also indicated. The final R index was 0.060 for 1781 observed reflections. The molecular topography shows no unexpected features, and is compared with related molecules; a detailed summary of the conformations of phosphate diesters is included. Each $A_2P_5'U$ molecule is hydrogen-bonded to four adjacent nucleotide molecules and nine water molecules; no hydrogen bonds link base moieties directly, but the bases are stacked so that they overlap slightly, with an average interplanar separation of about 3.4 Å. Close contacts of furanose-ring oxygen atoms with nearby bases are also present, as in some other structures of nucleic acid fragments.

Introduction

The enormously varied biochemical role of organic phosphates, particularly in genetic processes and in many enzyme-catalyzed metabolic reactions, has prompted numerous structural studies of nucleosides, nucleotides, and other phosphate esters in recent years. Although the bond distances and angles in these molecules have been predictable with fair precision for a decade or more, the conformations, the intra- and intermolecular hydrogen bonding, and the preferred modes of packing of different molecules or widely separated parts of the same molecule are less well understood. The present study of β -adenosine-2'- β -uridine-5' phosphoric acid ($A_2P_5'U$) was carried out to provide more information about these structural parameters, for although the molecule does not occur naturally, it has many of the structural features of the natural nucleotides. It differs from the natural ribodinucleotides in having but one phosphate group and in having the 2' rather than the 3' linkage of the adenosylribose to the phosphate. A preliminary account of our findings has been reported (Shefter, Barlow, Sparks & Trueblood, 1964).

Experimental

The compound was supplied by Dr A. M. Michelson in the form of prisms grown from aqueous solutions. Weissenberg photographs with Ni-filtered $Cu K\alpha$ radiation showed the crystals to be monoclinic. The only systematic extinctions were $0k0$ with k odd, which indicated space group $P2_1$; $P2_1/m$ is incompatible with the optical activity of the compound. The unit-cell parameters, measured on $h0l$ and $0kl$ Weissenberg photographs calibrated with a quartz crystal ($\lambda = 1.5418$ Å, $a_0 = 4.9131$ Å), are:

$$a_0 = 9.783 \pm 0.006 \text{ \AA}, \quad b_0 = 16.013 \pm 0.007 \text{ \AA}, \\ c_0 = 8.718 \pm 0.007 \text{ \AA}, \quad \text{and } \beta = 90.79 \pm 0.05^\circ.$$

The density of the crystals was found, by flotation in a mixture of bromoform and carbon tetrachloride, to be $1.56 \pm 0.01 \text{ g.cm}^{-3}$; the calculation for two molecules of $C_{19}H_{24}N_7O_{12}P$ and eight molecules of water in the unit cell is 1.569 g.cm^{-3} . Thus the asymmetric unit contains one molecule of dinucleoside phosphate and four molecules of water; if the compound were a trihydrate the calculated density would be 1.526 g.cm^{-3} .

Integrated Weissenberg intensity data were collected with nickel-filtered $Cu K\alpha$ radiation about c ($l=0$ to 7) and b ($k=0$ to 3) from two small crystals with approximately the shape of rectangular parallelepipeds about 0.2 mm in each dimension. The data were estimated in part visually and in part with a densitometer (Baird-Atomic Model CB). No absorption correction was deemed necessary because the crystals were small and relatively uniform in dimensions. Under the experimental conditions used, only about 59% of the Cu sphere

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was accessible, including 2008 independent diffraction maxima; of these, 1786 were intense enough to be estimated. The additional 222 which were below the observable minimum intensity were included in the least-squares refinement with $F_o = 0.71 F_{\min}$ (Hamilton, 1955). After the intensities had been converted to KF^2 in the usual manner, the structure factors obtained for the two crystal settings were put on a common scale by the procedure of Rollett & Sparks (1960).

All calculations were made on an IBM 7090, with programs written in these laboratories. The form factors used for oxygen, nitrogen and carbon are those of Hoerni & Ibers (1954) and the scattering curve for hydrogen is that listed in the *International Tables for X-ray Crystallography* (1962). The phosphorus atomic scattering curve is the same as that given by Tomiie & Stam (1958).

Determination and refinement

Wilson's (1942) method was used to obtain an initial estimate of the approximate scale factor (which differed by approximately 30% from the final scale factor). The F^2 values were then modified by $s^{0.1} \exp(5.66s^2)$, where $s = \sin \theta / \lambda$, and used in the calculation of a sharpened three-dimensional Patterson synthesis with the origin peak removed. Only two peaks in the Harker section $P(u\frac{1}{2}v)$ seemed high enough to correspond to a phosphorus-phosphorus interaction. In order to find which, if either, of these peaks was actually due to the phosphorus-atom interaction and also to find the four oxygen atoms of the phosphate, a rigid-body computer search routine (Sparks, 1961; Nordman & Nakatsu, 1963) was used. The sharpened Patterson function was searched around each of the two Harker peaks for the P-O and O-O vectors; the phosphate group was assumed to have tetrahedral angles, with three P-O bonds of 1.55 Å and one of 1.47 Å. A minimum function was used and it clearly indicated one, and only one, good solution for this model. A least-squares fit to $P(uvw)$ of the five unique parameters for such a rigid group was then made; the parameters chosen were two translational (y being arbitrary in this space group) and three rotational. The positions found for the atoms deviated by an average of less than 0.1 Å from the final positions after refinement. The speed and effectiveness of this search led us to attempt location of a ribose molecule by the same method, but these attempts were abandoned, because the structure was solved by another method. It seems likely that the structure could have been solved by such search techniques, as more complicated groups have been located by similar methods (Nordman & Nakatsu, 1963; Stout, Malofsky & Stout, 1964).

The structure was actually solved by the use of the phosphate group for phasing a three-dimensional Fourier synthesis, even though this group represents only about 24% of the total scattering matter on a Z^2 basis. A model of this Fourier synthesis ($R = 40\%$) was

built and scrutinized for peaks that were compatible with the chemical structure. Of approximately sixty peaks above about $2 \text{ e.}\text{\AA}^{-3}$ in this synthesis, eight in mutually reasonable positions near the phosphate were selected for inclusion in the next stage, each being arbitrarily regarded as carbon in the calculation of phases. The second Fourier synthesis (as well as the first one) was calculated twice, first including all of the observed data, and then omitting all reflections for which $|F_o|/|F_c|$ was less than 0.2. Since this variation in procedure produced no significant changes, all data were included in all further syntheses.

The second Fourier synthesis revealed all of the atoms of the ribose molecule in the uracil residue, and permitted establishing the identity of the eight non-phosphate phasing atoms, all of which were in the two sugar molecules. Three successive difference maps, followed by one further F_o synthesis, delineated the entire nucleotide (except for the hydrogen atoms) and the four water molecules, 43 non-hydrogen atoms in all. R at this point was 0.26.

Block-diagonal least-squares refinement was done with a modified version of ACA Program #317 (Gantzel, Sparks & Trueblood), which minimizes $\sum w(|F_o| - G|F_c|)^2$, where G is a scale factor. Hughes's (1941) weighting scheme was used, with $F_{\min} = 4.1$. After five cycles of refinement of the positions and individual isotropic temperature factors for the 43 atoms, and two additional cycles in which individual anisotropic temperature factors were refined, R had converged to about 0.088 (all observed data); the unobserved data were included in the refinement. A difference Fourier synthesis was then calculated in order to locate as many as possible of the 32 hydrogen atoms present. The estimated standard deviation of the electron density (Cruickshank, 1949) was somewhat greater than 0.13

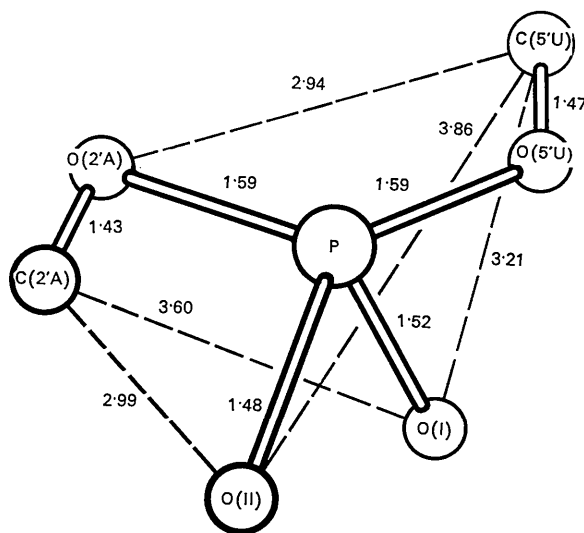


Fig. 1. Distances within the phosphate diester group.

$\text{e.}\text{\AA}^{-3}$ (the uncertainty arising because the data were not complete); among the peaks of height above $0.25 \text{ e.}\text{\AA}^{-3}$ seventeen were in chemically reasonable positions for hydrogen atoms, and these included all sixteen of those on carbons, and also that on N(3U). The positional parameters of these seventeen atoms, together with all parameters of the 43 heavy atoms, were then refined by three cycles of least-squares; the hydrogens were assigned isotropic temperature factors of 4.0 in these calculations.

A final difference synthesis was calculated with all of the observed data except for five reflections which

appeared to suffer from extinction ($R=0.060$; $R=0.065$ including unobserved). One additional hydrogen atom was clearly evident, on N(1A), showing that the phosphate proton had been transferred to N(1) of the adenosine residue. One of the hydrogen atoms of the amino group, N(6A), appeared as a reasonable peak, but the other was rather low and diffuse, and none of the hydrogen atoms of the hydroxyl groups or water molecules appeared distinctly. Although it was possible to surmise the positions of most of these remaining hydrogen atoms from the hydrogen-bonding scheme, the only hydrogen atom position parameters listed in Table 1 are those for the eighteen that were clearly discernible in the difference maps. These are the very ones whose positions are fixed by the geometry of the molecular skeleton; although the e.s.d. of their positions is rather high, about 0.13 \AA , these positions correspond to rea-

Table 1. *Final position parameters* ($\times 10^3$) *for hydrogen atoms**

Attached atom	x	y	z
C(1'U)	407	-34	-32
C(2'U)	525	-45	-300
C(3'U)	765	-67	-165
C(4'U)	647	-173	70
C(5'U)	879	-166	75
	843	-130	232
N(3U)	451	214	-311
C(5U)	764	210	37
C(6U)	716	73	66
C(1'A)	780	0	565
C(2'A)	985	109	409
C(3'A)	1158	63	555
C(4'A)	1017	48	831
C(5'A)	980	186	853
	1166	163	797
C(2A)	412	-108	385
C(8A)	758	223	463
N(1A)	267	-17	267

* The atoms are identified by the number of the attached carbon or nitrogen atom; only those refined by least squares and that on N(1A) are listed. E.s.d.'s are approximately isotropic and equal to 0.13 \AA .

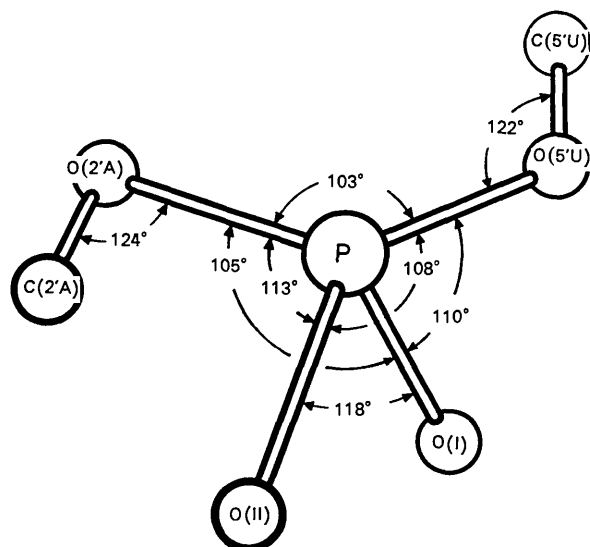


Fig. 2. Bond angles within the phosphate diester group.

Table 2. *Final position parameters* ($\times 10^4$) *of heavy atoms**

	x	y	z
P	10035,2	22	1873,2
O(I)	11255,5	-555,4	1705,7
O(II)	10220,6	911,3	1470,7
C(1'U)	5159,8	-269,5	-542,9
O(1'U)	5916,5	-529,4	755,6
C(2'U)	5466,7	-869,5	-1852,10
O(2'U)	4531,6	-1545,4	-1708,7
C(3'U)	6918,7	-1140,5	-1395,9
O(3'U)	7255,6	-1890,4	-2135,8
C(4'U)	6833,7	-1202,5	341,10
C(5'U)	8129,8	-1130,5	1279,11
O(5'U)	8777,5	-329,3	904,7
N(1U)	5531,6	612,4	-930,8
C(2U)	4729,8	1011,6	-1980,10
O(2U)	3768,7	667,4	-2662,9
N(3U)	5102,8	1824,5	-2300,9
C(4U)	6172,9	2273,6	-1581,12
O(4U)	6418,9	2981,4	-2020,10
C(5U)	6881,10	1816,5	-392,11
C(6U)	6572,8	1022,5	-126,10
C(1'A)	8188,7	552,5	5490,9
O(1'A)	8436,6	1008,4	6853,7
C(2'A)	9554,8	542,5	4731,9
O(2'A)	9557,7	-104,3	3597,7
C(3'A)	10532,8	355,5	6046,10
O(3'A)	10409,7	-516,4	6413,8
C(4'A)	9847,8	874,6	7350,10
C(5'A)	10472,10	1713,7	7660,13
O(5'A)	10728,8	2158,5	6261,9
N(1A)	3613,6	44,4	2969,8
C(2A)	4456,8	-483,5	3734,10
N(3A)	5626,7	-277,4	4366,8
C(4A)	5939,7	535,5	4142,9
C(5A)	5142,8	1126,5	3398,9
C(6A)	3895,8	872,5	2740,10
N(6A)	3044,6	1352,5	1951,9
N(7A)	5771,6	1903,4	3456,8
C(8A)	6932,9	1773,5	4192,11
N(9A)	7069,6	944,4	4663,8
W(1)	10165,8	2592,5	2055,13
W(2)	3317,8	2677,7	5663,11
W(3)	8216,6	3752,4	1167,8
W(4)	8705,8	3262,4	5701,9

* The e.s.d. is shown following each value, set off by a comma.

sonable average bond distances, 1.08 Å for C–H and 1.03 Å for N–H. Table 2 gives the position parameters of the heavier atoms; their thermal parameters are presented in Table 3. The final observed and calculated structure factor amplitudes are listed in Table 4.

The molecular structure and packing

We consider first the individual molecular components – the phosphate, the sugars and the bases – and then the hydrogen-bonding network in the crystal. The atoms are referred to according to the conventional numbering scheme for nucleosides, with the letter U or A appended to designate, respectively, the uridine or adenosine portion of the molecule; the numbering scheme is illustrated in Figs. 3–5. Bond distances and angles are given in these Figures and in Tables 5 and 6.

No attempt has been made at a rigid-body analysis of the anisotropic thermal parameters because the molecule has many conformational degrees of freedom; consequently corrections to the intramolecular distances for the effects of thermal motion cannot be estimated with confidence. However, it is apparent from inspection of the thermal vibration parameters (Table 3) that significant corrections are needed for many of the bond distances. For example, it has frequently been observed that terminal oxygen atoms are vibrating appreciably relative to the atom to which they are bonded, and such effects are apparent here. Estimates of typical bond-length corrections based on a riding-motion model (Busing & Levy, 1964) are given in Table 7; this Table includes the more extreme cases, but a few other bonds might involve corrections of as much as 0.02 Å. Because of the uncertainty as to the

Table 3. Anisotropic thermal parameters ($\times 10^4$)*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P	41	20	56	1	-32	7
O(I)	36	34	124	31	9	-42
O(II)	65	18	104	-17	-35	10
C(1'U)	63	21	66	-2	-24	-11
O(1'U)	61	26	48	-5	3	-4
C(2'U)	41	19	88	0	-42	-16
O(2'U)	48	32	123	-31	6	-41
C(3'U)	31	24	65	5	14	-6
O(3'U)	64	27	158	9	-27	-48
C(4'U)	50	19	84	-2	-59	4
C(5'U)	69	19	133	-28	-134	35
O(5'U)	61	21	91	-16	-86	25
N(1U)	55	12	98	8	-15	11
C(2U)	50	41	76	18	-7	-6
O(2U)	88	38	199	8	-138	2
N(3U)	98	34	103	2	-60	36
C(4U)	63	35	129	8	23	10
O(4U)	168	27	219	-20	-40	77
C(5U)	113	18	135	8	-17	-5
C(6U)	55	26	98	-5	-22	-15
C(1'A)	29	35	59	14	-31	-3
O(1'A)	59	49	48	18	-2	-42
C(2'A)	75	25	53	4	-36	-22
O(2'A)	116	20	78	-11	43	-10
C(3'A)	63	23	85	17	-54	3
O(3'A)	129	25	146	14	-117	3
C(4'A)	59	37	74	1	-36	-14
C(5'A)	70	42	166	-1	-21	-74
O(5'A)	134	33	175	-18	17	-5
N(1A)	58	19	98	-4	-12	7
C(2A)	63	27	75	2	-34	-5
N(3A)	61	24	63	4	12	-10
C(4A)	36	21	50	6	21	15
C(5A)	38	30	58	-10	1	-5
C(6A)	59	27	82	-6	-2	5
N(6A)	43	30	138	-4	-83	24
N(7A)	48	22	94	-2	-27	9
C(8A)	74	24	122	-15	-14	16
N(9A)	40	24	61	-1	-43	12
W(1)	84	33	422	-5	-97	13
W(2)	106	78	219	6	-42	130
W(3)	65	35	127	-2	-53	10
W(4)	146	28	140	-26	8	-9

* The temperature factor is expressed in the form $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{23}kl - b_{13}hl)$. The e.s.d.'s average about 12% for the b_{ii} , and vary over approximately a twofold range.

Table 4. Observed and calculated structure factor amplitudes

The three columns are, respectively, k , F_o and $|F_c|$. Reflections too weak to be measured are marked with a U; the F_o listed for them is 0.71 F_{min} . Those marked with E are believed to be affected by secondary extinction.

11 10.0 13.5	5 5.2 8.0	3 13.1 12.4	4 4.5 6.4	5 4.5 6.4	6 4.5 6.4	7 4.5 6.4	8 4.5 6.4	9 4.5 6.4	10 4.5 6.4	11 4.5 6.4	12 4.5 6.4	13 4.5 6.4	14 4.5 6.4	15 4.5 6.4	16 4.5 6.4	17 4.5 6.4	18 4.5 6.4	19 4.5 6.4	20 4.5 6.4	21 4.5 6.4	22 4.5 6.4	23 4.5 6.4	24 4.5 6.4	25 4.5 6.4	26 4.5 6.4	27 4.5 6.4	28 4.5 6.4	29 4.5 6.4	30 4.5 6.4	31 4.5 6.4	32 4.5 6.4	33 4.5 6.4	34 4.5 6.4	35 4.5 6.4	36 4.5 6.4	37 4.5 6.4	38 4.5 6.4	39 4.5 6.4	40 4.5 6.4	41 4.5 6.4	42 4.5 6.4	43 4.5 6.4	44 4.5 6.4	45 4.5 6.4	46 4.5 6.4	47 4.5 6.4	48 4.5 6.4	49 4.5 6.4	50 4.5 6.4	51 4.5 6.4	52 4.5 6.4	53 4.5 6.4	54 4.5 6.4	55 4.5 6.4	56 4.5 6.4	57 4.5 6.4	58 4.5 6.4	59 4.5 6.4	60 4.5 6.4	61 4.5 6.4	62 4.5 6.4	63 4.5 6.4	64 4.5 6.4	65 4.5 6.4	66 4.5 6.4	67 4.5 6.4	68 4.5 6.4	69 4.5 6.4	70 4.5 6.4	71 4.5 6.4	72 4.5 6.4	73 4.5 6.4	74 4.5 6.4	75 4.5 6.4	76 4.5 6.4	77 4.5 6.4	78 4.5 6.4	79 4.5 6.4	80 4.5 6.4	81 4.5 6.4	82 4.5 6.4	83 4.5 6.4	84 4.5 6.4	85 4.5 6.4	86 4.5 6.4	87 4.5 6.4	88 4.5 6.4	89 4.5 6.4	90 4.5 6.4	91 4.5 6.4	92 4.5 6.4	93 4.5 6.4	94 4.5 6.4	95 4.5 6.4	96 4.5 6.4	97 4.5 6.4	98 4.5 6.4	99 4.5 6.4	100 4.5 6.4
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Table 4 (cont.)

14 12.2 12.3	15 9.5 9.2	16 7.8 7.6	17 7.1 7.5	18 7.1 7.5	19 7.1 7.5	20 7.1 7.5	21 7.1 7.5	22 7.1 7.5	23 7.1 7.5	24 7.1 7.5	25 7.1 7.5	26 7.1 7.5	27 7.1 7.5	28 7.1 7.5	29 7.1 7.5	30 7.1 7.5	31 7.1 7.5	32 7.1 7.5	33 7.1 7.5	34 7.1 7.5	35 7.1 7.5	36 7.1 7.5	37 7.1 7.5	38 7.1 7.5	39 7.1 7.5	40 7.1 7.5	41 7.1 7.5	42 7.1 7.5	43 7.1 7.5	44 7.1 7.5	45 7.1 7.5	46 7.1 7.5	47 7.1 7.5	48 7.1 7.5	49 7.1 7.5	50 7.1 7.5
14 12.2 12.3	15 9.5 9.2	16 7.8 7.6	17 7.1 7.5	18 7.1 7.5	19 7.1 7.5	20 7.1 7.5	21 7.1 7.5	22 7.1 7.5	23 7.1 7.5	24 7.1 7.5	25 7.1 7.5	26 7.1 7.5	27 7.1 7.5	28 7.1 7.5	29 7.1 7.5	30 7.1 7.5	31 7.1 7.5	32 7.1 7.5	33 7.1 7.5	34 7.1 7.5	35 7.1 7.5	36 7.1 7.5	37 7.1 7.5	38 7.1 7.5	39 7.1 7.5	40 7.1 7.5	41 7.1 7.5	42 7.1 7.5	43 7.1 7.5	44 7.1 7.5	45 7.1 7.5	46 7.1 7.5	47 7.1 7.5	48 7.1 7.5	49 7.1 7.5	50 7.1 7.5

proper model to use for making such corrections and because no such corrections have been applied in the structure analyses of the other nucleosides and nucleotides with which our results will be compared, we have used the uncorrected results in all discussions and illustrations.

The phosphate diester group

The bonded and non-bonded distances and the bond angles of the phosphate diester group are illustrated in Figs. 1 and 2, and the conformation is shown more extensively in Fig. 3. The bond distances and angles are quite in accord with those found in other organic phosphates, which have recently been summarized variously by Li & Caughlan (1965), Karle & Britts (1966), and Sundaralingam & Jensen (1965). The average P-O distance in A2'P5'U is 1.54 Å, with the bonds to esterified oxygen atoms as usual about 0.1 Å longer than those to the other oxygen atoms. The 0.04 Å difference (6σ) in the two shorter P-O bonds seems at

first somewhat surprising; however, as noted later (Table 11), the oxygen atom in the longer of these bonds, O(I), accepts a hydrogen bond from N(1A), the atom to which the phosphate proton has been transferred. Presumably the difference in the P-O(I) and P-O(II) bonds is real and reflects the effect of the positive charge on N(1A). The same situation is found in A5'P (Kraut & Jensen, 1963) and A3'P (Sundaralingam, 1966), although the difference in the P-O bonds concerned is far smaller in each of these structures.

The O-P-O angle involving the esterified oxygen atoms is, as always, the smallest (103°), while that involving the two other oxygen atoms of the phosphate group is, again as usual, the largest (118°). The P-O-C angles, 122° and 124°, are in the normal range; for twenty-six phosphate esters which have been studied with at least moderate precision, the value of this angle ranges from 116 to 125°, with an average of 121° and a root mean square deviation of 2.5°. There is no significant difference between mono-esters and (non-cyclic)

Table 5. *Bond distances**

P-O(I)	1·518 Å	C(1'U)-N(1U)	1·496 Å
P-O(II)	1·478	N(1U)-C(2U)	1·357
P-O(5'U)	1·586	C(2U)-O(2U)	1·236
P-O(2'A)	1·593	C(2U)-N(3U)	1·382
		N(3U)-C(4U)	1·409
C(1'U)-C(2'U)	1·526	C(4U)-O(4U)	1·222
C(2'U)-C(3'U)	1·533	C(4U)-C(5U)	1·439
C(3'U)-C(4'U)	1·520	C(5U)-C(6U)	1·327
C(4'U)-C(5'U)	1·504	C(6U)-N(1U)	1·393
C(4'U)-O(1'U)	1·452		
O(1'U)-C(1'U)	1·406	N(1A)-C(2A)	1·350
C(2'U)-O(2'U)	1·424	C(2A)-N(3A)	1·306
C(3'U)-O(3'U)	1·405	N(3A)-C(4A)	1·351
C(5'U)-O(5'U)	1·470	C(4A)-C(5A)	1·382
		C(5A)-C(6A)	1·401
C(1'A)-C(2'A)	1·499	C(6A)-N(1A)	1·370
C(2'A)-C(3'A)	1·512	C(6A)-N(6A)	1·320
C(3'A)-C(4'A)	1·567	C(5A)-N(7A)	1·389
C(4'A)-C(5'A)	1·499	N(7A)-C(8A)	1·313
C(4'A)-O(1'A)	1·457	C(8A)-N(9A)	1·396
O(1'A)-C(1'A)	1·412	N(9A)-C(4A)	1·358
C(2'A)-O(2'A)	1·431	N(9A)-C(1'A)	1·446
C(3'A)-O(3'A)	1·435		
C(5'A)-O(5'A)	1·438		

* Uncorrected for thermal motion; see text and Table 7. The estimated standard deviations are 0·006 Å for the P-O distances, and average 0·010 Å for the other bonds, ranging however up to about 0·013 Å for the bonds to the C(5') atoms. All bond distances involving hydrogen atoms are shown in Figs. 3-5.

 Table 6. *Bond angles**

At atom	Subtended by atoms	Angle	At atom	Subtended by atoms	Angle
P	O(I), O(II)	117·7°	O(2'A)	P, C(2'A)	124·3°
	O(I), O(2'A)	104·8	C(2'A)	O(2'A), C(1'A)	108·9
	O(I), O(5'U)	109·8		O(2'A), C(3'A)	111·9
	O(II), O(2'A)	112·7		C(1'A), C(3'A)	103·1
	O(II), O(5'U)	108·1	C(3'A)	C(2'A), C(4'A)	99·9
	O(2'A), O(5'U)	102·8		C(2'A), O(3'A)	107·9
O(5'U)	P, C(5'U)	121·7		C(4'A), O(3'A)	108·4
C(5'U)	O(5'U), C(4'U)	108·0	C(4'A)	C(3'A), C(5'A)	115·4
C(4'U)	C(5'U), C(3'U)	118·6		C(3'A), O(1'A)	106·0
	C(5'U), O(1'U)	109·1		C(5'A), O(1'A)	107·8
	C(3'U), O(1'U)	104·0	C(5'A)	C(4'A), O(5'A)	111·5
C(3'U)	C(4'U), C(2'U)	102·4	O(1'A)	C(4'A), C(1'A)	109·0
	C(4'U), O(3'U)	114·7	C(1'A)	O(1'A), C(2'A)	103·5
	C(2'U), O(3'U)	110·2		O(1'A), N(9A)	108·4
C(2'U)	C(3'U), C(1'U)	100·1		C(2'A), N(9A)	117·3
	C(3'U), O(2'U)	110·9	N(9A)	C(1'A), C(8A)	129·0
	C(1'U), O(2'U)	106·3		C(1'A), C(4A)	124·4
C(1'U)	C(2'U), O(1'U)	108·0		C(4A), C(8A)	106·6
	C(2'U), N(1U)	112·0	C(8A)	N(7A), N(9A)	111·9
	O(1'U), N(1U)	109·5	N(7A)	C(8A), C(5A)	104·8
O(1'U)	C(1'U), C(4'U)	109·9	C(5A)	N(7A), C(6A)	131·2
N(1U)	C(1'U), C(6U)	120·6		N(7A), C(4A)	110·5
	C(1'U), C(2U)	117·2		C(4A), C(6A)	118·4
	C(2U), C(6U)	121·9	C(6A)	C(5A), N(1A)	113·5
C(2U)	N(1U), N(3U)	115·4		C(5A), N(6A)	125·7
	N(1U), O(2U)	122·9		N(1A), N(6A)	120·8
	N(3U), O(2U)	121·6	N(1A)	C(6A), C(2A)	123·6
N(3U)	C(2U), C(4U)	125·9	C(2A)	N(1A), N(3A)	125·2
C(4U)	N(3U), C(5U)	114·1	N(3A)	C(2A), C(4A)	112·4
	N(3U), O(4U)	118·8	C(4A)	N(3A), C(5A)	126·8
	C(5U), O(4U)	127·0		N(3A), N(9A)	126·9
C(5U)	C(4U), C(6U)	120·3		N(9A), C(5A)	106·2
C(6U)	C(5U), N(1U)	122·1			

* Uncorrected for thermal motion. Estimated standard deviations are about 0·4° for O-P-O angles and 0·5 to 0·8° for the other angles shown. Some angles involving hydrogen atoms are shown in Figs. 4 and 5.

Table 7. Some bond length corrections based on riding model*

Bond	Uncorrected distance	Corrected distance
C(2U)-O(2U)	1.236 Å	1.260 Å
C(4U)-O(4U)	1.222	1.256
C(2'U)-O(2'U)	1.424	1.431
C(3'U)-O(3'U)	1.405	1.424
P-O(I)	1.518	1.533
P-O(II)	1.478	1.488
P-O(5'U)	1.586	1.594
P-O(2'A)	1.593	1.615

* Busing & Levy (1964).

di- and tri-esters, but the angle is somewhat higher for aromatic esters (average 123°) than for aliphatic ones (average 120°). The corresponding angle for mixed aliphatic-aromatic ethers is significantly smaller, 117° (Bryan, 1967; Gramaccioli, Destro & Simonetta, 1968; Romers & Hesper, 1966; van Oijen & Romers, 1966).

There have been many recent discussions of the molecular topography and conformational geometry of phosphate esters, especially in relation to the mechanism of hydrolysis involving cyclic esters (Newton, Cox & Bertrand, 1966; Collin, 1966; Usher, Dennis & Westheimer, 1965; Swank, Caughlan, Ramirez, Madan & Smith, 1967; Kyogoku & Itaka, 1966) and Sundaralingam (1968*b*) has recently made a detailed analysis extending an earlier unpublished survey (Sundaralingam, 1966, p.501). Table 8 lists the torsion angles

around P-O bonds and the dihedral angles between P-O-C planes for all the phosphate diesters and triesters for which we have found parameters in the literature, including three triphosphates. In making these calculations we consider the sequence of atoms C→O→P→O'→C' and calculate the torsion angles, τ , according to the right-hand rule convention of Klyne & Prelog (1960). The dihedral angle δ is defined as the angle between the normals of the C→O→P and P→O'→C' planes; it is not an independent parameter of the structure, being related to the torsion angles and the bond angle O-P-O', θ , by

$$\cos \delta = \cos \tau_1 \cos \tau_2 + \sin \tau_1 \sin \tau_2 \cos \theta$$

(as pointed out to us by Professor J.D. Dunitz). It is nevertheless quite helpful in visualizing the conformations of such esters. In repeating the calculations for some compounds it was occasionally necessary to make corrections to published parameters or angles, as noted.

The conformational nomenclature in Table 8 is that of Klyne & Prelog (1960); although the exact values of the angles are given, the abbreviated descriptions of the conformations are also helpful in comparisons of different systems. A dihedral angle, δ , of 0° can correspond to either the fully-extended conformation, *ap-ap*, approximated in the two phases of $\text{Na}_3\text{P}_3\text{O}_{10}$ and in one of the diester portions of triphenylphosphate, or the *syn-planar* conformation for each of the torsion angles, necessarily approximated in the cyclic esters (methyl pinacol phosphate, methyl ethylene

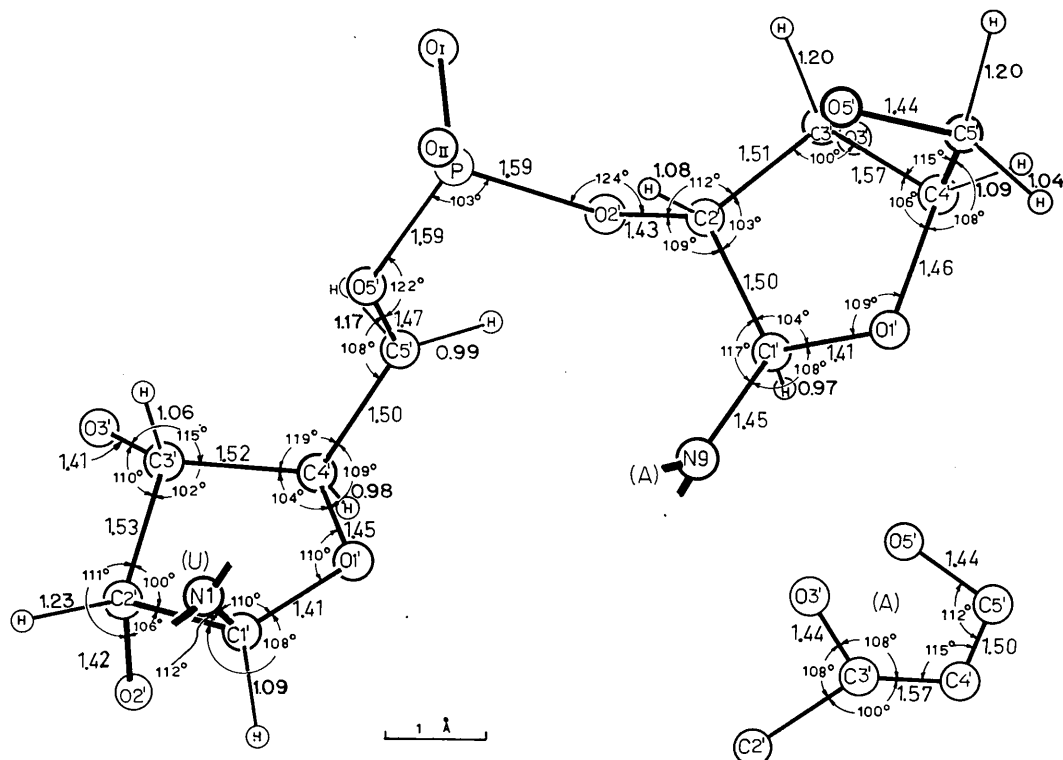


Fig. 3. The diribosyl phosphate portion of the molecule.

phosphate, and acetoinenediol cyclophosphate). A value of $\delta=180^\circ$ corresponds to the planar conformation *sp-ap*, which (not surprisingly) is not observed. Newton, Cox & Bertrand (1966) have pointed out that when there is no constraint (e.g. from cyclization or steric hindrance), the conformation of phosphate esters is such that the C–O–P plane usually passes near to the (or one of the) unesterified oxygen atom(s). This is true for most of the esters in Table 8, and indeed for most of them the carbon atom of at least one C–O–P group is *anti* to the unesterified oxygen which is not far from that C–O–P plane. Since the phosphate group is always approximately tetrahedral, this situation reflects nothing more than the usual tendency to assume a staggered conformation, corresponding to a torsion angle not far from 60° (*syn* clinal, *sc*) or 180° (*anti* periplanar, *ap*). Perusal of Table 8 shows that all but a few of the torsion angles fall in one of these two ranges, the

principal exceptions being in molecules with appreciable steric hindrance (methyl pinacol phosphate and triphenylphosphate). The fact that one of the torsion angles in A2'P5'U is in the less-favored *ac* conformation may reflect a response to packing constraints; as indicated below, the planes of the bases are nearly parallel and only about 3.4 Å apart, and the structure is held together by a strong network of hydrogen bonds.

The data in Table 8 indicate that it is a good generalization that δ will be $105 \pm 20^\circ$ in the absence of steric or bonding constraints. More specifically, for the preferred *sc,sc* and *sc,ap* conformations, δ will be not far from 90° and 120° respectively, these being the values corresponding to τ_1, τ_2 pairs $60^\circ, 60^\circ$ and $60^\circ, 180^\circ$ for a tetrahedral bond angle. The fact that the $P_3O_{10}^{4-}$ ions are in the fully extended conformation may only reflect the high charge on these species; it is, of course, of great interest to know the conformation of diphos-

Table 8. Phosphate diester conformational parameters*

Substance	τ_1	τ_2	δ	Diester conformation†	Reference
A2'P5'U	-128	-47	123	- <i>ac</i> , - <i>sc</i>	This work
Dibenzyl hydrogen phosphate ^a	-67	-172	115	<i>sc</i> , <i>ap</i>	Dunitz & Rollett (1956).
Di- <i>p</i> -chlorophenyl hydrogen phosphate	82	82	106	<i>sc</i> , <i>sc</i>	Calleri & Speakman (1964).
L- α -Glycerylphosphorylcholin, 1	-71	-59	92	- <i>sc</i> , - <i>sc</i>	Abrahamsson & Pascher (1966).
L- α -Glycerylphosphorylcholin, 2	64	66	89	<i>sc</i> , <i>sc</i>	Abrahamsson & Pascher (1966).
Vitamin B ₁₂ , wet	-61	174	118	- <i>sc</i> , <i>ap</i>	Brink-Shoemaker, Cruickshank, Hodgkin, Kamper & Pilling (1964).
Vitamin B ₁₂ , dry ^b	-60	157	113	- <i>sc</i> , <i>ap</i>	Hodgkin, Lindsey, Trueblood & White (1962).
Vitamin B ₁₂ , coenzyme	-70	173	109	- <i>sc</i> , <i>ap</i>	Lenhart (1968).
Diethylphosphate, barium salt	72	68	95	<i>sc</i> , <i>sc</i>	Kyogoku & Iitaka (1966).
Deoxyribonucleic acid-A	-81	-77	96	- <i>sc</i> , - <i>sc</i>	Fuller, Wilkins, Wilson & Hamilton (1965).
Deoxyribonucleic acid-B	-78	-80	98	- <i>sc</i> , - <i>sc</i>	Langridge, Marvin, Seeds, Wilson, Hooper, Wilkins & Hamilton (1960).
Ribonucleic acid-10	-74	-103	107	- <i>sc</i> , - <i>ac</i>	Arnott, Wilkins, Fuller & Langridge (1967).
Ribonucleic acid-11	-83	-78	95	- <i>sc</i> , - <i>sc</i>	Arnott <i>et al.</i> (1967).
Triphenylphosphate ^c	-125	57	99	- <i>ac</i> , <i>sc</i>	Svetich & Caughlan (1965).
	134	-93	78	<i>ac</i> , - <i>ac</i>	
	163	161	26	<i>ap</i> , <i>ap</i>	
Methyl pinacol phosphate ^d	-12	-12	19	<i>sp</i> , <i>sp</i>	Newton <i>et al.</i> (1966).
	-124	-150	67	<i>ac</i> , <i>ac</i>	
	94	107	107	<i>ac</i> , <i>ac</i>	
Methyl ethylene phosphate ^e	11	2	12	<i>sp</i> , <i>sp</i>	Steitz & Lipscomb (1965).
	-108	47	89	- <i>ac</i> , <i>sc</i>	
	124	-58	96	<i>ac</i> , - <i>sc</i>	
Acetoinenediol cyclophosphate ^f	0	-1	1	<i>sp</i> , <i>sp</i>	Swank <i>et al.</i> (1967).
	-113	53	91	- <i>ac</i> , <i>sc</i>	
	110	-51	88	<i>ac</i> , - <i>sc</i>	
Na ₅ P ₃ O ₁₀ , Phase I	165	165	21	<i>ap</i> , <i>ap</i>	Corbridge (1960).
Na ₅ P ₃ O ₁₀ , Phase II	-169	-169	17	<i>ap</i> , <i>ap</i>	Davies & Corbridge (1958).
K ₄ P ₃ O ₉ NH ₂ ·4H ₂ O	-39	160	134	- <i>sc</i> , <i>ap</i>	Hilmer (1965).

* Only the *relative* signs of the torsion angles are important for those molecules which occur in crystals with symmetry elements of the second kind.

† Nomenclature of Klyne & Prelog (1960). Abbreviations: *a*, *anti*; *s*, *syn*; *c*, *clinal*; *p*, *peri-planar*.

^a δ incorrect in original (J. D. Dunitz & J. S. Rollett, private communication, 1968).

^b γ of P4O corrected to +0.0144; sign error in reference cited.

^c First δ listed here given as 84° in reference cited.

^d γ of C(8) corrected to 0.224 (J. A. Bertrand, private communication, 1968).

^e γ of O(5) corrected to -0.2137; sign error in reference cited (W. N. Lipscomb, private communication, 1968).

^f Positions and cell dimensions correct in reference cited, but some distances and angles incorrect (C. Caughlan, private communication, 1968).

phate esters and triphosphate esters because of their biological importance, and it seems likely to us that their conformation may be pH-dependent, being more like that of $P_3O_{10}^{5-}$ at high pH and more like that of the other compounds in Table 8 at physiological and low pH. However, their conformations may also be strongly influenced by the ions present.

Bases

The bond lengths and angles in the two bases are shown in Figs. 4 and 5. The values for the uracil moiety are in fairly good agreement with those observed in a variety of 5-substituted uracil nucleosides and nucleotides and in uracil itself (Stewart & Jensen, 1967). Even though the 5-substituted uracil compounds have groups of varying electronegativity attached, such as fluorine (Harris & MacIntyre, 1964), bromine (Iball, Morgan & Wilson, 1966), iodine (Camerman & Trotter, 1964) and methyl (Trueblood, Horn & Luzzati, 1961), no significant trend in their ring bond distances and angles appears evident. The least-squares plane through the pyrimidine ring (Table 9) shows that the ring is slightly, but significantly, distorted from planarity; the exo-

cyclic oxygen atoms are displaced by 0.10 and 0.06 Å on opposite sides of the plane. Such distortions are commonly observed in the structures of nucleic acid

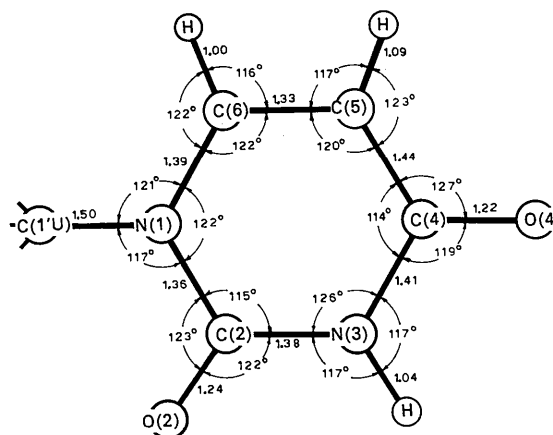


Fig. 4. The uracil residue.

Table 9. Some least-squares planes*

	Adenosine		Uridine		Phosphate diester	
	I	II	III	IV	V	VI
l_1	-0.4705	-0.2396	-0.6514	-0.7141	-0.6388	0.9313
l_2	0.2175	-0.8282	0.3060	-0.6377	0.4731	-0.2441
l_3	0.8552	0.5066	0.6943	0.2889	0.6067	0.2703
D (Å)	-0.581	0.233	3.764	3.434	5.250	-9.555

Deviations of atoms, Å × 10³

N(1)	2		-31	-1296		
C(2)	5		32			
N(3)	12		-4			
C(4)	-17		-25			
C(5)	-3		28			
C(6)	-12		-1			
N(7)	22					
C(8)	-5					
N(9)	-3	-604				
O(2)			57			
O(4)			-104			
N(6)	-46					
C(1')	-34	22	12	-36		-1078
O(1')	1035	-35	198	38		0
C(2')	-1236	-622	-1281	21		0
O(2')		-270		1402	1129	0
C(3')		-19		-597		1259
O(3')		1327		-260		
C(4')		32		-23	252	
C(5')		-1089		-757	0	
O(5')					0	-1226
P					0	0
O(I)					-1290	1299
O(II)					342	-270

* The equation of each plane is $l_1X + l_2Y + l_3Z + D = 0$, with X , Y and Z orthogonalized coordinates (in Å) parallel to \mathbf{a} , \mathbf{b} and \mathbf{c}^* . Deviations in boldface signify atoms used to define the plane.

fragments, and presumably result primarily from non-bonded intra- and intermolecular contacts. The potential function for such distortions is a relatively flat one.

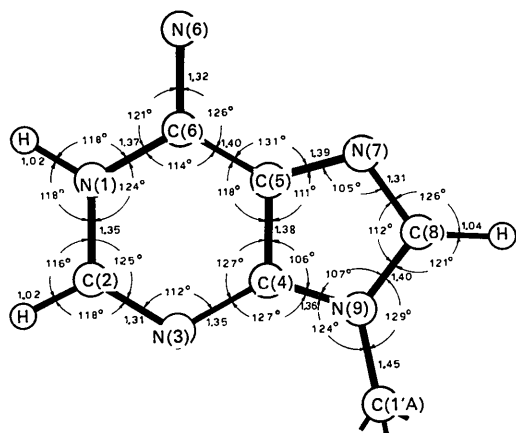


Fig. 5. The adenine residue.

The adenine portion of the molecule exists as a zwitterion, protonated in the N(1) position by O(1) of the phosphate group. A similar arrangement has been found in the structures of adenosine-5'-phosphate (Kraut & Jensen, 1963) and adenosine-3'-phosphate (Sundaralingam, 1966). Most of the bond distances in the adenine portion of the present molecule are in excellent agreement (within 1 e.s.d.) with those found in the base of the latter structure. The exceptions are the N(9)-C(8) and N(9)-C(1') bond lengths, which are correspondingly 0.03 Å smaller and 0.03 Å greater in the A3'P structure. The marked differences in the rotational angles about the glycosidic bond and about the adjacent furanose bonds in the two structures may, as noted by Sundaralingam (1966), be responsible for the observed variations in the geometry around N(9). The atoms comprising the purine framework are essentially coplanar in this compound (Table 9). Both N(6A) and C(1'A) are significantly displaced on the same side of the ring, as was also found in A3'P, but the C(1') atom is displaced 0.05 Å further from the base plane in the latter compound.

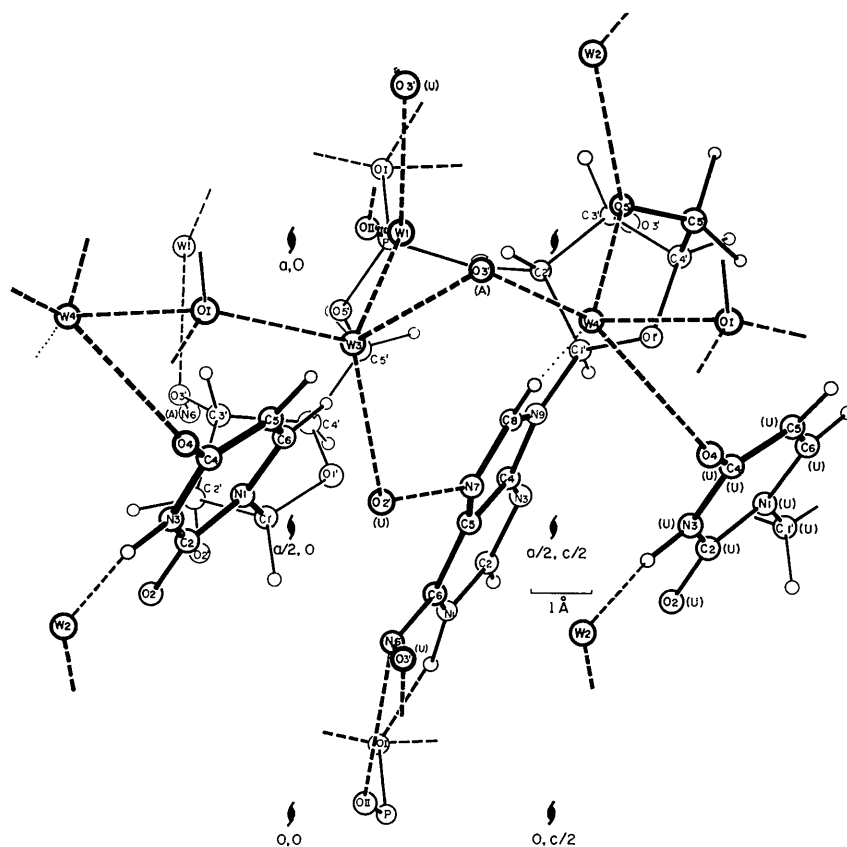


Fig. 6. A portion of the structure viewed in the $-b$ direction. Possible hydrogen bonds are indicated by dashed lines for N-H...O and O-H...O, and dotted lines for C-H...O. The interaction between W(4) and O(4U) is probably only a van der Waals contact (see text).

The torsion angles about the glycosidic bonds (φ_{CN}) as defined by Donohue & Trueblood (1960), are -5° and -54° for the uridine and adenosine portions of the molecule respectively. Recently Haschemeyer & Rich (1967) have demonstrated that steric barriers to free rotation about this bond in nucleosides are dependent on the mode of puckering of the sugar and the nature of the base. The presence of the phosphate group and the other base impose additional constraints on the possible values of this torsion angle in the oligonucleotide. There is an intramolecular contact of 2.33 \AA , between the hydrogen atom on C(6U) and atom O(5'U), which might be considered part of a weak hydrogen bond (Sutor, 1963), although as Donohue (1968) points out, this H...O distance is considerably longer than those found in O-H...O and N-H...O hydrogen bonds. A similar C-H...O contact is also present in crystalline barium uridine phosphate (Shefter & Trueblood, 1965) and calcium thymidine phosphate (Trueblood, Horn & Luzatti, 1961). We agree with Donohue (1968) that contacts such as these probably do not represent hydrogen bonds in the usual sense of the term; those cited here may merely be incidental consequences of the other factors primarily responsible for the conformation about the glycosidic bond.

The two bases are stacked nearly parallel to one another, as shown in Fig. 6; the angle between the normals to the purine and pyrimidine planes is 14.8° . The closest approach of any two atoms in the different bases is 3.40 \AA , between C(6U) and C(5A); this is also the approximate average spacing between the planes of successive bases measured along their average normal. As Fig. 6 shows, any given base (e.g. the adenine ring in the center of Fig. 6) overlaps slightly with its neighbors on each side along *c*; the two interplanar spacings are 3.33 and 3.50 \AA when measured along the average normal to the rings. The stacked arrangement of the bases in the crystal is consistent with circular dichroism studies of the same compound in solution (Brahms, Maurizot & Michelson, 1967), which suggests that the molecular conformation found in this crystal is characteristic of the molecule and not simply of this particular crystal. The parallel stacking of planar molecules is, of course, a characteristic of a great variety of organic structures and presumably reflects a tendency to maximize attractive van der Waals interactions, with perhaps some dipolar or π - π interactions playing a role as well. The overall molecular conformation of A2'P5'U is a complex function of the base stacking, the glycosidic torsional angles, the conformation of the sugars, and the conformation of the phosphate diester linkage, and each of these factors may be influenced by the hydrogen bonding scheme. However, as discussed below, the fact that the majority of the hydrogen bonds formed by a given molecule are with surrounding water molecules is consistent with the view that the molecular conformation may be a rather stable and persistent one, which does not adjust

in a major way to the packing. Rather, perhaps water molecules move into the interstices, at once minimizing the voids and forming hydrogen bonds with most potential donors and acceptors which are not already involved in such bonds.

Sugars

The furanose rings are significantly puckered (Table 9). In the uridine ribose, C(3') is displaced from the plane of the other four atoms by 0.60 \AA , whereas in the adenosine ribose C(2') is out of the plane of the other ring atoms by 0.62 \AA . In each ring the displacement is *endo* (Sundaralingam, 1965), *i.e.* the respective atom is out of the plane on the same side as C(5'). The configuration of the ribose moieties can best be described in terms of torsional angles about the various ring bonds (Brown & Levy, 1963; Sundaralingam, 1965); these angles are given in Table 10. The angles between the normals to the sugar and base planes are 62 and 69° in the uridine and adenosine residues, respectively. These values are comparable to those in other nucleosides and nucleotides.

Table 10. *Some torsion angles**

	Uridine	Adenosine
O(1')→C(1')	+6.9°	-30.5°
C(1')→C(2')	-28.5	43.5
C(2')→C(3')	38.2	-37.8
C(3')→C(4')	-35.5	20.2
C(4')→O(1')	18.2	6.1
φ_{CN}	-5	-54
$ \varphi_{OO} $	62	73
$ \varphi_{OC} $	57	45

* The first five angles are the twist angles in the furanose rings (Brown & Levy, 1963). φ_{CN} is the torsion angle about the glycosidic C-N bond (Donohue & Trueblood, 1960). The last two angles give the conformation about the C(5')-C(4') bond (Shefter & Trueblood, 1965).

The average C-C distance in the two ribose residues is 1.520 \AA , in excellent agreement with the average values of 1.523 and 1.522 \AA in various furanose and pyranose derivatives reported, respectively, by Sundaralingam (1965) and by Berman, Chu & Jeffrey (1967). Since no allowance for possible thermal motion has been made in any of these studies it is doubtful whether these values should be considered significantly shorter than the average value of 1.537 \AA for the bond length between two tetrahedral carbon atoms (Sutton, 1965). The C-O bond lengths in the present ribose residues average 1.433 \AA , with both C(1')-O(1') bonds substantially shorter than the adjacent O(1')-C(4') bonds. These results are again in accordance with earlier findings. Sundaralingam (1965, 1968a) has pointed out that a difference in the lengths of the two C-O bonds involving O(1'), comparable to that found here, is common in nucleosides and nucleotides, as well as in other furanose derivatives, and has attributed it to the presence of the additional electronega-

tive atom (nitrogen or oxygen) on C(1'). Berman *et al.* (1967) have noted a similar effect in pyranose sugars.

It is commonly found in crystal structures of nucleosides and nucleotides that the ether oxygen of the furanose ring does not participate to any significant extent in hydrogen bonding (Sundaralingam, 1968*a*). However, in a number of structures, there does appear to be a relatively short intermolecular contact between O(1') and a neighboring pyrimidine or purine base (Shefter & Trueblood, 1965; Sundaralingam, 1966; Shefter, 1968). In the present structure the following short contacts of this kind were observed: O(1'U) to C(2A), 2.98 Å; O(1'U) to N(1A), 3.13 Å; O(1'A) to C(5U) of the molecule at $(x, y, 1+z)$, 3.14 Å. Although these distances are not appreciably shorter than the sum of the appropriate van der Waals radii, unlike the shortest corresponding contact in crystalline barium uridine phosphate, 2.74 Å (Shefter & Trueblood, 1965), the fact that similar arrangements have now been found involving four sugar-base combinations in three different structures suggests that some sort of weak interaction may be involved. However, perhaps it is no more than the 'dimple effect', the tendency of one atom to

nestle in the hollow of a nearby ring, manifested for example in crystals of biphenylene (Waser & Lu, 1944), octaphenylcyclooctatetraene (Pawley, Lipscomb & Freedman, 1964) and 4-nitroaniline (Trueblood, Goldish & Donohue, 1961).

Hydrogen bonding

Each molecule is hydrogen-bonded directly to four neighbouring A2'P5'U molecules and to nine water molecules. This network of bonds is illustrated in Fig. 6, and pertinent data are given in Table 11. Because not all of the potential hydrogen-bonding hydrogen atoms were located, the identification of donor and acceptor atoms in Table 11 is not unambiguous; however, the first six pairs listed are reasonably definite, since there was good evidence for those hydrogen atoms.

There are no hydrogen bonds linking sugars directly; those which do not involve intervening water molecules involve the amino nitrogen or ring nitrogen atoms and either phosphate oxygens or ribose hydroxyl groups. The angles listed in Table 11 indicate that the geometry of each of these bonds accords well with normal expectations (Pimentel & McClellan, 1960;

Table 11. Possible hydrogen bonds*

Donor atom	Acceptor atom	Position of acceptor atom†	Distance	Relevant angles	
O(3'U)	W(1)	$2-x, y-\frac{1}{2}, -z$	2.66 Å	C(3'U)-O(3'U)···W(1)	119°
N(3U)	W(2)	$x, y, z-1$	2.83	C(4U)-N(3U)···W(2)	119
				C(2U)-N(3U)···W(2)	114
				N(3U)-H·····W(2)	173
N(1A)	O(I)	$x-1, y, z$	2.72	C(6A)-N(1A)···O(I)	117
				C(2A)-N(1A)···O(I)	119
				N(1A)-H·····O(I)	165
O(5'A)	W(4)	x, y, z	2.69	C(5'A)-O(5'A)···W(4)	110
N(6A)	O(3'U)	$1-x, \frac{1}{2}+y, -z$	2.83	C(6A)-N(6A)···O(3'U)	128
	O(II)	$x-1, y, z$	2.88	C(6A)-N(6A)···O(II)	122
				O(3'U)-N(6A)···O(II)	99
O(3'A)	W(3)	$2-x, y-\frac{1}{2}, 1-z$	2.75	C(3'A)-O(3'A)···W(3)	123
O(2'U)	N(7A)	$1-x, y-\frac{1}{2}, -z$	2.93	C(2'U)-O(2'U)···N(7A)	131
				N(7A)···O(2'U)···W(3)	98
				O(2'U)···N(7A)-C(5A)	134
				O(2'U)···N(7A)-C(8A)	118
W(1)	W(3)	x, y, z	2.77	W(3)·····W(1)···O(II)	129
	O(II)	x, y, z	2.75	W(3)·····W(1)···O(3'U)	117
				O(3'U)·····W(1)···O(II)	107
W(2)	O(5'A)	$x-1, y, z$	2.72	W(2)·····O(5'A)-C(5'A)	119
				N(3U)·····W(2)···O(5'A)	108
W(3)	O(2'U)	$1-x, \frac{1}{2}+y, -z$	2.78	O(I)·····W(3)···O(2'U)	114
	O(I)	$2-x, \frac{1}{2}+y, -z$	2.79	O(I)·····W(3)···W(1)	112
				O(I)·····W(3)···O(3'A)	115
				W(1)·····W(3)···O(2'U)	120
				W(1)·····W(3)···O(3'A)	75
				O(2'U)·····W(3)···O(3'A)	114
W(4)	O(3'A)	$2-x, \frac{1}{2}+y, 1-z$	2.83	W(4)·····O(3'A)-C(3'A)	120
	O(I)	$2-x, \frac{1}{2}+y, 1-z$	2.95	O(3'A)·····W(4)···O(I)	93
	O(4U)	$x, y, 1+z$	3.05	O(4U)·····W(4)···O(I)	66
				O(3'A)·····W(4)···O(4U)	140
				O(5'A)·····W(4)···O(3'A)	110
				O(5'A)·····W(4)···O(I)	106
				O(5'A)·····W(4)···O(4U)	109

* Only the hydrogen atoms on N(3U) and N(1A) were located unambiguously, but there were peaks on the final difference map in reasonable positions for some of the others, including those on O(5'A), O(3'U), and the amino nitrogen, N(6A).

† Relative to parameters of Table 2.

Hamilton & Ibers, 1968). The phosphate oxygen atom O(I) apparently accepts three hydrogen bonds, from N(1A) and water molecules *W*(3) and *W*(4), which are arranged nearly tetrahedrally around O(I); the angles subtended at O(I) by these atoms, together with the bonded phosphorus atom, range from 85 to 119°. Although the amino hydrogen atoms were located only imprecisely, the arrangement of their hydrogen-bonded neighbors, O(3'U) and O(II) of two different molecules, suggests that the amino group is twisted about 25° from the adenine plane, just as in adenosine-5'-phosphate (Kraut & Jensen, 1963). A similar twist is also present in A3'P (Sundaralingam, 1966).

Apparently only one hydrogen atom of water molecule *W*(2) is involved in a hydrogen bond, to O(5'A); *W*(2) also accepts a hydrogen bond from N(3U). This water molecule has three additional non-bonded neighbors in the range 3.19 to 3.44 Å, and ten more below 4.0 Å. The b_{22} and b_{33} values of *W*(2) (Table 3) indicate high thermal motion for this molecule, corresponding to root mean square displacements of about 0.29 Å in directions parallel to **b** and **c**, consistent with the hydrogen-bonding scheme of Fig. 6. Water molecule *W*(1) is involved in only three hydrogen bonds, as indicated in Fig. 6 and Table 11; three non-bonded atoms at distances of about 3.4 to 4.0 Å are grouped together around the fourth tetrahedral position. The unusually high value of b_{33} for *W*(1), corresponding to an r.m.s. displacement of about 0.40 Å, suggests that there may be slight disorder in the *z*-parameter of *W*(1), which is consistent with the hydrogen-bonding environment of this molecule. Water molecule *W*(3) has four hydrogen-bonded neighbors, arranged approximately tetrahedrally. *W*(4) appears to be engaged in three O-H...O bonds, and one fairly close van der Waals contact, with O(4U); both the assignment of hydrogen atoms to hydrogen bonds and the considerable deviation of the angles involving O(4U) suggest that no hydrogen bond is involved in this contact. However, there is a short C-H...O contact involving C(8A), which is just 3.22 Å from *W*(4); furthermore the alignment of the three atoms is nearly linear, the angle C(8A)-H...*W*(4) being 172°. An almost identical arrangement of C(8A) and a water molecule is found in hydrated crystals of A3'P (Sundaralingam, 1966). These contacts suggest that weak C-H...O bonds may be present (Sutor, 1963), but Donohue's (1968) reservations about such systems should again be noted.

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The Crystal and Molecular Structure of Bis(dimethyldithiophosphato)nickel(II), Ni[(CH₃O)₂PS₂]₂

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Crystals of bis(dimethyldithiophosphato)nickel(II) are orthorhombic, space group *Pbca*, with $Z=4$. Unit-cell dimensions are $a=10.290\pm 0.002$, $b=8.640\pm 0.002$, $c=16.356\pm 0.004$ Å. The structure has been determined from a three-dimensional Patterson synthesis and a series of three-dimensional ρ and $A\rho$ syntheses, and refined by the method of full-matrix least squares. The molecular structure has been found to be similar to the ethyl compound, Ni[(C₂H₅O)₂PS₂]₂, but has been more accurately determined by use of scaled two-axis Weissenberg data and refined to a value of $R=0.075$. The molecule is centrosymmetric about the nickel atom, and the nickel and four sulphur atoms are in square-planar configuration. The Ni-S bond lengths of 2.22 and 2.23 Å agree very well with those found in the ethyl compound and other square-planar nickel(II) complexes.

Introduction

The structure of bis(diethyldithiophosphato)nickel(II) has been reported (McConnell & Kastalsky, 1967). The present structure of the corresponding methyl compound has been determined with a much greater accuracy ($R=0.075$ against 0.115), by means of three-dimensional data obtained about two axes. In the report on the ethyl compound, reservations were expressed with regard to the significance of the thermal ellipsoids obtained, in view of the fact that data had been obtained about one axis only, and were also considered less accurate than in the present case for other reasons. It is interesting to report that the molecular structure of the methyl compound is very similar, with thermal ellipsoids of the same general shape and orientation, thus tending to confirm the original tentative conclusions.

Both compounds are diamagnetic, deep purple in colour and highly soluble in both polar and non-polar solvents. This combination of properties was considered sufficiently unusual to warrant the structure determination of these two compounds in order to verify the theoretical predictions of a square-planar configuration of nickel and sulphur, with Ni-S distances of 2.1–2.3 Å (Lopez-Castro & Truter, 1963).

Experimental

Crystal data

Bis(dimethyldithiophosphato)nickel(II), Ni[(CH₃O)₂PS₂]₂.

Colour: deep purple, almost opaque.

Solubility: highly soluble in most organic solvents, both polar and non-polar; soluble also in water and very slightly in paraffin oil.