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Stereochemistry of Nucleic Acid Constituents.
III. Crystal and Molecular Structure of Adenosine 3′-Phosphate Dihydrate (Adenylic Acid *b*)

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The crystal structure of adenosine 3′-phosphate dihydrate, $H_{14}C_{10}N_5O_7P.2H_2O$, has been solved with three-dimensional integrated Weissenberg intensities. The crystals have space group $P2_1$ and the following lattice constants: $a=9{\cdot}939\pm0{\cdot}005$, $b=6{\cdot}343\pm0{\cdot}002$, $c=11{\cdot}896\pm0{\cdot}005$ Å and $\beta=92^\circ 13'\pm3'$. Approximate x and z coordinates were obtained from the results of Brown and co-workers. The y coordinates were determined from molecular models and successive structure factor and Fourier calculations. Refinement was by the method of full-matrix least squares. P, O, N and C atoms were refined anisotropically and the H atoms were refined isotropically. The final R index is 4·3 %. Average standard deviations in atomic positions are: P, 0·0009 Å; O, 0·003 Å; N, 0·004 Å; C, 0·005 Å and H, 0·06 Å.

One of the water molecules displays a planar, nearly trigonal hydrogen bonding pattern, while the the other is involved in a highly distorted tetrahedral hydrogen bonding scheme. H(O2′) is simultaneously involved in two hydrogen bonds, one of which is an intramolecular hydrogen bond to the ester oxygen O(3′). The structure also exhibits a $C(8)\text{–}H\cdots O_w$ hydrogen bond. The nucleotide exists as a zwitterion with N(1) of the purine protonated by a phosphate proton. The angle between the base and the ribose planes is 55° with the glycosidic torsion angle $\varphi_{CN}=-3{\cdot}9^\circ$. C(3′) of the ribose is displaced by 0·562 Å from the plane of the remaining ring atoms and on the same side as C(5′). The orientation of the C(5′)–O(5′) bond is unusual in that C(5′)–O(5′) is *trans* to C(3′)–C(4′) and *gauche* to O(1′)–C(4′).

Introduction

Brown, Fasman, Magrath, Todd, Cochran & Woolfson (1953) showed that the structure of adenylic acid *b* (Fig. 1) was that of adenosine 3′-phosphate. From elementary chemical analysis Brown & Todd (1952) found that the nucleotide crystallized with 1·5 molecules of water; thus this value was assumed in the initial X-ray work. Since the nucleic acid components exhibit a variety of conformations, it was necessary to carry out the present three-dimensional structural analysis of 3′-AMP* to elucidate its stereochemistry completely. A further point of interest is that to date no detailed study of a 3′ purine nucleotide with the β glycosidic (C–N) linkage has been reported. Moreover, information of the phosphate-3′-sugar conformation would be helpful in postulating probable conformations for polynucleotides. The only other 3′-phosphates that have been so far investigated are the pyrimidine nucleotide 3′-CMP (Alver & Furberg, 1959; Sundaralingam & Jensen, 1965*a*) and vitamin B_{12} (Hodgkin, 1964). The latter differs from 3′-CMP and 3′-AMP in that it possesses an α glycosidic linkage.

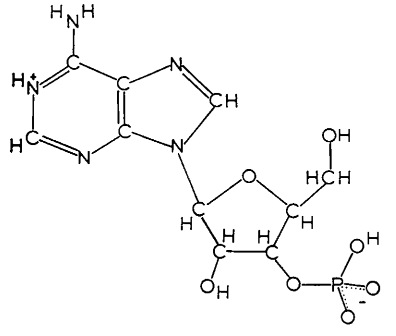

Fig. 1. Chemical formula of adenosine 3′-phosphate.

Experimental

Two suitable crystals for this investigation were crystallized from aqueous solution. The crystals have monoclinic symmetry and the space group is $P2_1$. Unit-cell dimensions were kindly measured by Mr Larry Sieker on a Picker X-ray diffractometer; they are: $a=9{\cdot}939\pm0{\cdot}005$, $b=6{\cdot}343\pm0{\cdot}002$, $c=11{\cdot}896\pm0{\cdot}005$ Å and $\beta=92^\circ 13'\pm3'$ (Cu $K\alpha=1{\cdot}5418$ Å). The calculated density, assuming two molecules of chemical composition $H_{14}C_{10}N_5O_7P\,.\,2H_2O$ per unit cell, is 1·698 g.cm^{-3},

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* Abbreviations used are: adenosine 3′-phosphate, 3′-AMP; adenosine 5′-phosphate, 5′-AMP; cytidine 3′-phosphate, 3′-CMP; β-adenosine-2′-β-uridine 5′-phosphate, AUP,

which may be compared with the observed density of 1·66 g.cm^{-3} for 3′-CMP. Since only two crystals were isolated, the density of 3′-AMP was not measured, but it will be seen later that the structural solution unequivocally demonstrates the presence of two molecules of water of hydration.

Undimensionally integrated (at right angles to the direction of translation by camera) equi-inclination Weissenberg photographs from the two crystals, one mounted about **b** (levels *h*0*l* to *h*5*l*) and the other about **c** (levels *hk*0 to *hk*10) were collected by the multiple-film technique, using Cu $K\alpha$ radiation. Intensities were measured with a recording microdensitometer by tracing the spots on the films at right angles to the direction of integration (Jensen, 1954). Within the linear response range of the film, area (planimetered) under the trace is proportional to the intensity. After subjection of the intensities to Lorentz and polarization corrections, the *b*-axis and *c*-axis reflections were merged together. Altogether 1411 observations were made; this constituted about 85% of the total possible in the reflecting sphere.

Determination of the y coordinate

Approximate *x* and *z* atomic coordinates were measured from the published figure of the (010) projection (Brown *et al.*, 1953). It should be pointed out here that the *a* and *c* axes have been erroneously interchanged in their figure. Trial *y* coordinates of the structure were determined from a molecular model based on the structures of 5′-AMP (Kraut & Jensen, 1963) and 3′-CMP. Initial structure factor and Fourier calculations, using all of the observed structure amplitudes, suggested that the *y* coordinates of some of the atoms were grossly misjudged. It was apparent that large adjustments in the torsion angle φ_{CN} (Donohue & Trueblood, 1960; Sundaralingam & Jensen, 1965*a*) and the conformation about the C(4′)–C(5′) linkage had to be made. Therefore, it was thought expedient to perform the next structure factor calculation with only the atoms in the phosphate group and the '1·5 water molecules'. The half water was taken to be that oxygen atom (ignoring the hydrogen atoms) which had a lower electron density in the (010) projection (Brown *et al.*, 1953). The corresponding Fourier synthesis, computed from the calculated phases and the observed amplitudes, showed a large number of electron density maxima. Care was exercised in assigning atomic positions because the space group symmetry produced several spurious atoms which were mirror-related to the true structure. However, keeping in mind the possible structure variants in this nucleotide, it was possible to assign positions to the rest of the non-hydrogen atoms.

Refinement of the structure

Three cycles of full-matrix least-squares refinement with individual atom isotropic temperature factors gave a discrepancy index R ($R=[\Sigma|F_o|-|F_c|/\Sigma|F_o|]\times 100$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes) of 11%. The least-squares weighting was essentially that of Hughes (1941), where $\sqrt{w}=14/|F_o|$, $F_o>14$; $\sqrt{w}=1{\cdot}0$, $|F_o|\le 14$. The value of $4F_{\min}$ was arbitrarily fixed at 14. The refinement indicated that the temperature factor of the half molecule of water was substantially lower than the average temperature factor of the structure. At this stage a difference Fourier map demonstrated a positive electron density with a shape of a double camel hump at the site of this water molecule, and the position assigned to the water molecule occupied the depression in this hump. This phenomenon was interpreted as primarily due to insufficient scattering matter at the half water site. Therefore, in the ensuing least-squares refinement cycle the full complement of scattering for this water oxygen atom was given and the resulting temperature factor was now comparable to that of other atoms in the structure. Further refinement was carried out with anisotropic temperature factors, and a difference electron density map was then calculated. The map showed the positions of several of the hydrogen atoms in the structure and had no abnormality in the electron density in the region of the water molecules. Subsequent least-squares refinements and difference Fourier maps revealed all of the hydrogen atoms in the structure and their positions were in accord with the stereochemistry of the molecule. The hydrogen atom positional coordinates and individual isotropic temperature factors were also refined, with the use of first the scattering factors of McWeeny (1951) and then those of Stewart, Davidson & Simpson (1965). The scattering factors of C, N, and O were from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and that of P from Freeman & Watson (1961). In the final least-squares cycle the shift in each atomic parameter was less than one-tenth of the error of that parameter. The final *R* value is 4·3%, excluding 12 intense low order reflections which were suspected to be affected by secondary extinction and consequently were given zero weight in the refinement. Observed and calculated structure factors are listed in Table 1.

Results and discussion of the structure

The atomic positional and thermal parameters together with their estimated standard deviations obtained from the least-squares refinement are presented in Tables 2–5. The average estimated standard deviations in positional coordinates are as follows: P 0·0009, O 0·003, N 0·004, C 0·005 and H 0·06 Å, and are generally a few per cent better than those of 3′-CMP (Sundaralingam & Jensen, 1965*a*). The only major difference in the two studies is that in 3′-CMP the refinement was performed with separate level scale factors, while in 3′-AMP a single experimental scale was employed.

There are two molecules of water of crystallization per nucleotide and not 1·5 as previously reported

Table 1. *Observed and calculated structure factors* (× 10) *and phase angles in millicycles*

The extinguished reflections are asterisked, and were given zero weight in the refinement.

1,0,L			
0	39	29	000
2,0,L			
0	43	41	500
3,0,L			
*0	566	587	500
4,0,L			
0	154	155	500
5,0,L			
0	26	25	500
6,0,L			
0	153	160	000
7,0,L			
0	245	242	000
8,0,L			
0	267	268	000
9,0,L			
0	56	56	500
11,0,L			
0	69	71	500
12,0,L			
0	23	25	000
0,0,L			
1	156	140	000
*2	896	933	500
3	239	240	500
5	523	532	000
6	120	122	000
7	254	252	500
8	244	251	000
9	261	273	000
10	115	111	500
11	291	289	500
12	38	24	500
13	52	48	000
14	42	33	000
1,0,L			
1	90	101	000
2	239	257	500
3	62	70	000
4	91	85	500
5	34	30	500
6	287	292	500
7	287	276	500
8	26	26	500
10	62	59	000
11	158	164	500
12	40	36	000
13	69	69	000
14	29	23	500
2,0,L			
1	53	53	500
2	170	184	500
3	545	558	000
4	42	23	500
5	55	65	500
6	159	164	500
7	124	123	000
8	64	65	000
9	103	100	500
11	72	76	000
13	61	57	000
14	54	59	500
3,0,L			
*1	590	645	500
2	258	277	000
3	413	420	500
4	131	136	500
5	217	214	500
6	123	118	500
7	286	279	000
8	109	109	000
9	404	434	500
10	115	118	500
11	138	140	000
12	79	79	000
13	72	69	000
14	35	42	500
4,0,L			
1	338	339	000
2	239	246	000
3	246	234	500
4	413	429	500
5	82	77	000
6	313	323	000
7	331	339	000
8	119	117	000
9	174	181	500
11	107	110	000
12	42	40	000
14	39	37	000
5,0,L			
1	148	147	000
2	122	118	500
3	282	282	500
4	145	145	500
5	284	295	000
6	120	114	000
8	279	289	500
10	127	126	000
11	50	46	000
12	28	28	500
13	92	87	500
6,0,L			
1	227	236	000
2	200	200	000
3	51	51	000
4	115	113	500
5	60	53	000
6	199	193	000
10	148	150	000
11	53	47	500
12	55	62	500
7,0,L			
2	300	319	500
3	78	74	000
4	100	92	000
5	42	41	000
6	109	110	500
7	124	121	500
8	93	90	000
9	37	37	500
10	89	85	500
11	114	116	500
8,0,L			
1	43	37	000
2	229	227	500
5	143	144	000
6	24	23	000
7	153	150	500
8	106	102	000
9	117	120	000
10	112	106	500
9,0,L			
1	257	259	500
2	35	31	500
3	69	70	000
4	97	107	000
5	99	96	500
6	95	93	500
7	21	29	500
9	59	53	500
10	75	75	500
10,0,L			
1	122	120	500
3	83	83	000
4	30	29	500
8	55	54	000
11,0,L			
4	111	105	500
5	31	32	000
6	72	72	000
12,0,L			
1	63	67	000
2	36	37	500
-1,0,L			
1	114	113	500
2	49	52	000
3	164	157	500
4	228	215	500
5	116	122	000
6	149	145	000
7	270	271	000
8	259	261	500
9	122	120	000
10	69	63	000
11	145	141	500
12	77	78	500
13	22	13	000
14	71	74	000
-2,0,L			
1	171	171	000
2	361	360	000
3	143	139	500
4	114	113	500
5	349	350	000
6	361	354	000
7	79	78	500
8	37	29	500
9	83	80	000
11	58	67	500
12	22	11	000
14	83	75	000
-3,0,L			
2	60	63	000
3	245	247	500
4	110	104	000
5	159	153	500
6	148	159	000
7	44	42	000
8	155	158	500
9	141	136	500
10	162	157	000
11	204	204	000
12	75	78	000
13	67	72	500
14	59	62	500
-4,0,L			
1	196	210	500
2	351	341	000
3	146	139	000
4	516	516	500
5	153	153	500
6	243	225	500
7	345	350	000
8	220	224	000
9	239	238	500
10	114	114	500
11	71	71	000
13	31	33	000
14	40	40	500
-5,0,L			
1	151	148	500
2	78	76	000
3	37	34	500
4	45	51	500
5	187	179	500
6	247	235	500
7	180	177	000
8	146	143	000
9	48	49	500
10	57	52	500
11	109	103	500
12	120	123	000
13	43	44	000
-6,0,L			
1	280	290	500
2	186	175	000
4	55	55	000
5	98	92	500
6	142	132	500
7	26	35	000
8	90	88	000
9	48	54	500
10	124	123	500
11	38	30	500
13	57	46	500
-7,0,L			
1	120	112	000
2	121	121	500
3	52	51	500
4	80	71	000
5	155	142	000
7	103	98	500
9	145	155	000
10	66	64	500
13	29	20	000
-8,0,L			
1	197	175	000
2	54	51	500
3	200	191	500
4	97	93	500
5	97	91	000
6	145	135	000
8	49	43	500
9	30	30	500
10	50	48	000
11	33	32	500
-9,0,L			
1	207	209	000
2	72	71	000
3	146	147	500
4	45	41	000
5	56	52	000
6	53	47	000
8	36	37	500
9	82	82	000
10	88	92	000
-10,0,L			
1	41	38	000
2	51	45	500
4	30	29	500
5	58	49	500
7	79	76	000
8	79	77	500
-11,0,L			
2	91	90	000
3	31	37	000
4	21	19	500
5	75	75	500
6	43	45	000
7	55	55	000
-12,0,L			
1	58	57	500
2	91	92	000
4	79	83	500
1,1,L			
0	482	483	912
2,1,L			
*0	544	569	835
3,1,L			
*0	472	506	692
4,1,L			
0	155	151	606
5,1,L			
0	240	250	131
6,1,L			
0	91	82	340
7,1,L			
0	75	72	400
9,1,L			
0	199	201	852
10,1,L			
0	103	99	815
11,1,L			
0	30	31	666
0,1,L			
1	405	410	845
*2	375	410	894
3	312	337	409
4	448	425	344
5	44	45	709
6	131	131	031
7	60	71	009
8	61	64	094
9	118	118	814
10	31	40	462
11	53	58	502
12	38	31	183
14	77	77	913
1,1,L			
1	208	218	598
*2	480	503	397
*3	646	683	217
4	238	243	565
5	335	334	432
6	181	181	781
7	215	219	213
8	169	169	281
9	219	218	844
10	133	132	608
11	243	255	331
12	90	83	223
13	51	45	635
14	101	101	772
2,1,L			
1	438	460	235
2	193	198	184
3	99	95	726
4	224	236	543
5	62	70	024
6	192	193	222
7	89	84	420
8	133	130	747
9	246	243	812
10	156	153	965
11	47	40	123
12	43	38	823
14	48	50	595
3,1,L			
1	249	246	074
2	128	129	123
3	279	292	973
4	247	266	750
5	171	175	608
6	272	282	219
7	92	97	481
8	126	123	753
9	211	215	773
10	118	117	205
11	103	97	278
12	45	39	518
13	61	53	738
4,1,L			
1	216	222	345
2	346	345	772
3	148	155	866
4	103	97	876
5	86	81	281
6	129	135	437
7	116	113	923
8	213	211	945
9	60	65	673
10	95	94	576
11	87	85	218
12	82	79	716
13	71	63	993
5,1,L			
1	275	274	954
2	259	258	766
3	288	285	538
4	166	175	227
5	62	64	211
6	82	80	846
7	326	352	792
8	69	75	189
9	287	301	270
10	113	106	487
11	69	64	653
12	41	39	732
13	69	66	224
6,1,L			
1	201	201	604
2	180	188	907
3	119	116	172
4	104	107	335
5	55	59	461
6	128	139	396
7	103	104	775
8	51	49	120
9	117	114	284
10	56	56	881
11	50	48	838
12	58	50	332
7,1,L			
1	202	200	882
2	165	169	757
3	167	168	209
4	146	145	269
5	69	67	367
6	159	159	760
8	93	89	394
9	60	55	213
10	34	28	860
12	36	37	219
8,1,L			
1	193	194	811
2	42	42	896
3	179	174	291
4	185	188	410
5	83	81	539
6	115	113	069
7	66	62	987
8	67	62	322
9	83	79	662
10	86	81	782
9,1,L			
1	91	93	070
2	130	136	446
3	79	78	495
4	88	85	961
5	65	67	781
6	58	58	234
8	64	55	841
9	94	83	862
10,1,L			
1	126	120	231
3	75	61	591
5	106	100	860
6	102	96	291
7	128	122	344
8	100	107	763
11,1,L			
1	69	74	334
2	99	92	121
3	134	127	812
4	45	38	847
6	39	30	401
12,1,L			
1	100	114	375
2	27	27	824
3	75	74	842
-1,1,L			
1	234	234	523
2	39	38	574
3	249	259	916
4	297	300	103
5	196	209	458
6	140	142	478
7	94	92	541
8	180	189	278
9	165	159	348
10	87	90	458
11	59	62	037
12	36	26	660
13	114	111	333
14	30	32	493
-2,1,L			
*1	639	669	103
*2	1085	1288	805
3	149	160	648
4	300	304	804
5	382	364	109
6	190	182	326
7	326	322	729
8	105	109	728
9	166	171	251
10	208	206	951
11	115	115	849
12	117	120	557
13	67	67	226
14	52	44	190
-3,1,L			
1	476	472	978
2	428	431	740
3	142	150	532
4	173	169	427
5	195	199	341
7	205	210	806
8	81	81	037
9	76	81	471
10	184	194	278
11	77	81	707
12	84	82	783
13	25	31	306
14	67	73	349
-4,1,L			
1	353	341	637
2	190	192	961
3	243	244	895
4	205	202	765
5	119	113	315
6	213	206	331
7	163	165	914
8	312	323	850
9	130	128	840
11	51	47	542
13	26	26	046
14	27	20	968
-5,1,L			
1	307	308	358
2	188	189	261
3	169	166	078
4	105	105	593
5	92	92	404
6	30	31	208
7	162	161	317
8	119	122	699
9	61	58	942
10	67	63	447
11	25	28	250
12	44	49	205
13	32	31	652
-6,1,L			
1	226	236	679
2	59	62	267
3	174	174	205
4	131	126	029
5	128	127	775
6	57	57	572
7	74	72	418
8	147	145	226
9	135	135	785
10	109	108	777
11	75	74	194
12	64	66	165
13	36	36	756
-7,1,L			
1	197	193	893
2	239	240	320
3	171	171	350
4	93	95	633
5	51	52	675
6	39	39	016
7	145	149	374
8	128	130	323
9	84	88	880
10	38	36	945
11	68	62	363
12	71	70	489
-8,1,L			
1	210	213	888
2	200	204	773
4	66	64	197
5	128	123	269
6	159	156	698
7	82	82	983
8	114	107	195
10	65	59	761
11	53	50	621
-9,1,L			
1	83	74	449
2	66	61	852
3	110	110	884
5	49	53	381
6	27	29	084
8	93	87	414
9	44	42	513
10	49	52	949
-10,1,L			
1	16	14	915
2	154	147	887
3	85	75	782
5	56	57	261
6	38	37	295
7	34	37	855
8	86	79	707
-11,1,L			
1	115	109	305
2	29	31	195
3	86	80	800
4	66	63	593
5	100	94	306
7	31	44	763
-12,1,L			
1	78	77	359
3	33	35	815
4	10	25	594
1,2,L			
0	272	273	086
2,2,L			
0	266	251	138
3,2,L			
0	204	219	847
4,2,L			
0	209	214	532
5,2,L			
0	364	356	636
6,2,L			
0	161	169	151
7,2,L			
0	174	169	114
8,2,L			
0	290	299	250
9,2,L			
0	97	94	899
10,2,L			
0	40	41	953
11,2,L			
0	43	51	655
12,2,L			
0	51	63	588
0,2,L			
*1	425	493	323
2	113	99	025
3	140	141	199
4	353	345	811
5	78	61	090
6	428	424	284
7	100	93	408
8	75	67	982
10	83	76	769
11	65	62	438
12	84	78	689
13	24	24	782
14	27	29	122
1,2,L			
1	220	235	776
2	239	250	667
3	56	52	596
4	134	142	275
5	321	320	860
6	217	222	685
7	168	159	558
8	102	103	018
9	76	67	241
10	197	208	729
11	102	100	601
12	76	78	229
13	65	63	188
14	32	36	871
2,2,L			
1	268	261	902
2	213	222	330
3	106	99	602
4	236	242	460
5	66	70	412
6	69	57	676
7	141	144	958
8	73	76	391
9	49	44	090
10	34	17	173
11	83	82	498
13	47	54	941
14	47	53	386
3,2,L			
1	381	401	545
2	158	174	819
3	291	304	876
4	107	109	718
5	90	94	570
6	202	216	734
7	159	162	275
8	29	13	925
9	190	205	632
10	67	68	938
11	129	128	966
12	71	64	144
13	92	89	324
14	61	75	488
4,2,L			
1	137	142	086
2	33	28	689
4	96	103	737
5	36	32	204
6	148	150	256
7	212	219	198
8	129	126	254
9	148	152	648
10	73	68	902
11	98	92	217
12	46	45	131
13	51	46	217
5,2,L			
1	106	107	235
2	131	129	903
3	276	288	814
4	238	240	455
6	229	238	141
7	143	143	031
8	168	167	704
9	135	137	637
10	101	98	311
11	80	73	121
12	45	40	722
6,2,L			
1	170	161	197
2	88	86	959
3	193	194	475
4	72	78	373
5	54	51	019
6	64	61	279
7	101	104	132
8	101	102	084
9	125	125	367
10	82	74	878
12	64	68	485
7,2,L			
1	158	156	169
2	102	100	356
3	238	232	778
4	74	87	724
5	205	192	124
6	60	54	374
7	230	214	579
8	151	150	815
9	88	79	112
10	33	33	141
11	55	58	713
8,2,L			
1	86	81	683
2	142	140	756
3	116	106	016
4	31	28	487
5	90	83	175
6	87	78	424
7	146	145	583
8	47	51	117
9	94	88	060
10	54	53	678
9,2,L			
1	170	170	649
2	158	157	553
3	103	98	101
4	130	124	996
5	51	48	460
6	70	64	792
7	41	43	640
9	46	43	775
10,2,L			
1	135	135	669
2	100	101	584
3	83	75	171
4	44	38	251
5	65	65	567
6	35	35	589
7	72	72	056
11,2,L			
1	63	49	857
2	49	37	308
3	23	20	823
5	45	48	804
-1,2,L			
1	258	262	251
2	198	198	694
3	164	165	795
4	126	116	055
5	295	286	981
6	250	242	385
7	61	50	710
8	121	123	458
9	95	94	153
10	149	145	025
11	144	145	722
12	90	87	525
13	90	58	132
14	20	26	221
-2,2,L			
1	157	152	184
2	66	73	389
3	294	295	404
4	131	126	597
5	105	101	125
6	237	221	150
7	117	122	200
8	42	36	609
9	64	69	071
10	60	63	091
11	108	119	572
-3,2,L			
1	273	263	459
2	195	184	761
3	326	317	784
4	33	32	208
5	177	168	323
6	116	111	049
7	56	54	268
8	185	173	796
10	109	110	363
11	78	74	297
12	108	106	115
13	34	33	803
-4,2,L			
1	294	311	520
2	297	317	185
3	243	232	902
4	257	257	660
5	162	158	756
6	96	97	457
7	168	162	129
8	96	95	267
9	176	173	638
10	83	86	684
11	123	121	064
12	41	41	021
13	36	41	577
-5,2,L			
1	167	150	412
2	396	409	082
3	182	178	854
4	207	192	611
5	180	166	703
6	58	55	640
7	96	99	236
8	40	42	269
9	85	89	627
10	58	58	884
11	78	80	143
12	61	62	999
13	60	57	438
-6,2,L			
1	133	134	074
2	85	83	808
3	243	237	487
4	103	101	934
5	103	99	398
6	193	184	623
7	157	155	863
8	160	162	145
10	94	94	638
11	88	87	604
12	68	56	614
-7,2,L			
1	120	117	699
2	147	140	645
3	150	145	198
4	111	109	206
5	89	80	786
6	85	84	610
7	72	71	097
8	120	128	200
10	86	81	637
11	48	47	792
12	52	59	327
-8,2,L			
1	105	98	246
2	106	107	639
3	147	147	683
4	95	97	920
5	149	151	207
6	59	60	155
7	39	37	726
8	82	83	561
9	31	25	200
10	60	61	002
11	70	86	608
-9,2,L			
1	118	112	193
2	41	42	095
3	103	99	458
4	44	42	097
5	139	132	939
6	55	56	139
7	114	115	417
8	99	97	598
9	55	62	157
10	69	83	097
-10,2,L			
1	137	132	121
3	84	81	674
4	84	84	596
6	81	80	119
8	68	78	602
-11,2,L			
1	60	56	341
2	83	81	066
4	61	56	631
5	46	48	641
6	46	46	286
-12,2,L			
1	76	93	618
2	47	65	154
3	46	54	239
1,3,L			
0	113	122	200
2,3,L			
0	266	279	888
3,3,L			
0	303	304	968
4,3,L			
0	175	182	566
5,3,L			
0	95	92	412
6,3,L			
0	155	147	516
7,3,L			
0	88	79	815
8,3,L			
0	203	185	237
9,3,L			
0	105	100	871
10,3,L			
0	48	54	950
11,3,L			
0	62	56	978
0,3,L			
*1	467	519	082
2	213	202	151
3	258	236	457
4	182	188	663
5	183	194	663
6	176	178	088
7	207	217	327
8	162	161	453
9	166	176	836
10	154	161	103
12	46	41	516
13	64	67	448
14	45	59	957
1,3,L			
1	331	338	245
2	350	358	666
3	158	159	404
4	171	175	633
5	108	108	976
6	92	92	402
7	138	136	669
8	120	116	474
9	105	101	072
10	86	79	774
11	73	70	455
12	65	52	635
13	26	21	789
14	44	63	985
2,3,L			
1	164	175	687
2	146	142	377
3	89	97	435
4	115	112	592
5	86	85	886
6	101	104	296
7	82	80	405
8	147	141	035
9	147	142	917
10	58	60	902
11	131	128	335
12	58	58	318
13	61	63	032
3,3,L			
1	120	122	514
2	155	160	459
3	291	294	126
5	203	211	692
7	103	97	599
8	261	277	028
9	98	96	113
10	116	114	553
11	80	80	577
12	31	31	951
13	60	64	855
4,3,L			
1	43	39	774
2	146	143	159
3	318	330	011
4	167	176	804
5	208	210	427
6	114	117	629
7	66	65	113
8	157	156	175
9	78	78	945
10	58	49	591
11	53	47	043
12	72	66	809
13	47	51	213
5,3,L			
1	237	253	264
2	155	151	015
3	121	126	923
4	175	171	898
5	177	173	586
6	139	144	225
7	160	159	027
8	42	42	534
9	123	124	569
10	87	82	583
11	29	27	194
12	37	37	987
6,3,L			
1	30	31	041
2	172	167	913
3	92	84	583
4	101	103	363
5	114	109	411
6	41	38	806
7	203	202	860
9	163	176	429
10	41	36	160
11	53	49	813
7,3,L			
1	249	256	035
2	99	97	694
3	218	216	430
4	210	211	373
5	156	150	841
6	106	98	846
7	74	70	110
8	39	39	561
9	49	44	355
10	31	23	962
8,3,L			
1	150	148	045
2	103	97	806
3	164	159	606
4	92	89	485
5	47	31	343
7	104	101	575
8	77	71	255
9	83	84	109
9,3,L			
1	75	64	104
2	48	47	361
3	71	60	444
4	63	61	893
5	95	92	904
7	110	116	468
8	41	43	906
10,3,L			
1	78	74	541
2	56	59	502
3	68	65	106
4	87	88	828
5	67	55	795
6	70	83	314
7	51	72	346
11,3,L			
1	87	97	385
2	49	53	288
3	35	39	899
4	20	32	105
-1,3,L			
1	264	251	183
2	187	184	061
3	117	113	608
4	158	163	510
5	141	141	490
6	157	150	951
7	140	146	754
8	130	127	608
9	152	153	394
10	102	105	314
11	106	96	855
12	110	115	657
13	47	54	489
14	27	29	518
-2,3,L			
1	183	198	963
2	344	340	889
3	305	303	073
4	210	213	342
5	151	146	246
6	192	183	776
7	114	116	999
8	121	122	190
9	99	92	354
10	35	29	689
11	55	49	926
12	25	20	363
13	42	45	295
14	31	42	554
-3,3,L			
1	149	145	462
2	194	199	016
3	180	186	992
4	160	152	813
5	119	115	684
6	116	113	411
7	45	44	078
8	141	141	052
9	182	180	608
10	52	46	522
11	38	38	132
13	21	21	608
-4,3,L			
1	139	139	625
2	168	165	146
3	156	154	973
4	154	153	977
5	181	178	245
6	234	235	520
7	114	111	747
8	238	238	049
9	134	134	104
10	76	69	283
11	36	36	791
12	82	85	777
13	50	48	234
-5,3,L			
1	85	86	304
2	213	216	593
3	169	160	326
4	45	42	767
5	38	35	698
6	179	173	568
7	110	106	812
8	89	83	007
9	103	107	146
10	30	27	599
11	65	60	624
12	52	51	507
13	34	46	985
-6,3,L			
1	123	118	850
2	168	167	425
3	166	155	413
4	107	101	946
5	28	28	224
6	25	17	237
7	44	45	452
8	38	36	177
9	119	116	869
10	46	41	072
11	110	112	415
12	56	67	348
-7,3,L			
1	120	112	821
2	108	102	516
3	153	155	283
4	71	60	734
5	175	170	751
6	129	121	960
7	116	107	407
8	169	164	471
9	25	12	941
10	68	66	874
11	26	27	021
-8,3,L			
1	161	153	101
2	230	222	178
3	118	111	988
4	127	124	612
5	31	27	632
6	36	38	021
7	139	128	275
8	83	84	532
9	55	49	744
10	53	49	080
-9,3,L			
1	43	43	696
2	219	213	903
3	38	45	102
4	163	160	386
5	24	29	450
6	86	81	825
7	102	97	779
8	59	57	311
9	61	65	366
-10,3,L			
1	42	44	581
2	131	128	998
3	32	32	965
4	50	46	302
5	91	88	402
6	68	54	588
7	88	89	011
-11,3,L			
1	85	78	421
2	61	57	338
3	50	48	813
4	114	114	814
5	43	50	219
0,4,L			
1	207	222	361
2	252	260	764
3	30	20	006
4	200	207	263
5	178	172	457
6	180	184	713
7	92	90	761
8	87	88	209
9	161	166	254
10	56	51	882
11	140	141	774
12	68	73	713
13	68	73	306
1,4,L			
0	246	252	215
2,4,L			
0	167	157	563
3,4,L			
0	297	312	836
4,4,L			
0	172	180	760

Table 1 (*cont.*)

5,4,L			
0	90	92	569
6,4,L			
0	74	72	379
7,4,L			
0	177	172	260
8,4,L			
0	99	88	386
10,4,L			
0	33	37	842
11,4,L			
0	48	59	745
1,4,L			
1	166	169	018
2	152	147	755
3	76	74	360
4	209	219	083
5	118	121	911
6	95	96	629
7	122	122	674
9	170	163	159
10	125	126	915
11	59	60	757
13	50	49	246
2,4,L			
1	194	203	789
2	64	59	128
3	43	40	205
4	130	133	231
5	317	332	746
6	147	155	748
7	239	233	184
8	199	200	409
9	123	116	744
10	119	116	869
11	57	55	650
12	116	119	228
3,4,L			
1	212	216	668
2	48	45	950
3	253	266	166
5	174	175	932
6	79	73	764
7	97	98	306
8	49	53	926
9	124	127	694
10	52	51	928
11	110	109	218
12	83	85	280
4,4,L			
1	63	52	864
2	115	112	310
3	48	52	914
4	138	140	607
6	85	79	355
7	137	128	384
8	59	53	971
9	61	57	706
11	90	91	302
12	32	24	718
5,4,L			
1	206	207	269
2	194	202	071
3	276	285	905
4	196	203	557
5	100	99	422
6	199	196	213
7	79	71	539
8	56	55	907
9	58	56	986
10	27	26	338
11	32	36	033
6,4,L			
1	273	274	342
2	38	32	245
3	249	251	783
4	129	123	849
5	184	180	330
6	149	145	380
8	115	111	757
9	79	74	370
10	94	89	240
7,4,L			
1	55	57	799
2	73	66	675
3	21	11	917
4	123	118	216
5	128	119	168
6	89	87	751
7	111	105	779
9	62	60	252
8,4,L			
1	24	24	801
4	81	77	254
5	35	21	731
6	147	145	643
7	92	85	802
8	87	85	135
9,4,L			
1	115	111	861
2	64	62	726
3	108	104	200
4	32	33	129
7	34	13	404
10,4,L			
1	75	70	782
2	26	27	340
3	62	58	016
4	38	35	810
5	70	73	708
-1,4,L			
1	147	146	531
2	105	102	540
3	66	68	806
4	18	21	072
5	256	246	138
6	228	226	342
7	203	186	714
8	55	55	868
9	38	43	464
10	90	87	197
12	50	54	649
13	62	61	947
-2,4,L			
1	399	393	355
2	142	136	159
3	309	305	747
4	211	202	715
5	208	200	124
6	308	308	306
7	147	148	422
8	201	187	735
9	27	22	484
10	75	80	186
11	20	17	334
12	34	42	821
13	46	50	682
-3,4,L			
1	93	96	529
2	232	229	172
3	227	218	139
4	271	262	820
6	213	214	411
7	76	74	353
8	76	84	969
9	71	75	833
10	60	62	585
11	128	127	299
12	40	48	120
-4,4,L			
1	88	88	646
2	116	116	215
3	42	31	940
4	45	50	915
5	120	120	741
6	44	42	339
7	74	73	004
8	48	51	546
9	49	49	786
10	50	52	102
11	66	66	123
12	36	33	348
-5,4,L			
1	234	235	698
2	53	47	937
3	181	179	142
4	110	112	253
5	111	115	658
6	227	232	839
7	54	50	069
8	125	129	341
9	31	27	735
10	69	71	802
11	52	52	317
-6,4,L			
1	74	71	131
2	169	176	686
3	55	53	507
4	93	92	049
5	105	101	798
6	90	88	832
7	70	71	250
8	98	92	327
9	28	28	065
10	87	97	773
11	71	75	687
-7,4,L			
1	133	141	423
2	102	96	806
3	115	116	922
4	97	93	323
5	87	88	252
6	56	59	563
7	100	103	749
8	58	59	298
9	60	61	429
10	29	20	189
-8,4,L			
1	19	18	524
2	107	108	893
3	73	70	584
4	61	59	247
5	84	84	210
6	61	59	584
7	20	29	759
9	41	40	153
-9,4,L			
1	87	86	305
2	36	41	045
3	123	130	555
5	126	130	152
6	56	56	333
7	36	41	700
8	73	84	721
-10,4,L			
1	45	51	225
2	75	77	430
4	83	86	918
5	74	79	835
6	63	73	224
-11,4,L			
1	34	40	574
0,5,L			
1	45	41	247
2	132	130	623
3	128	124	374
4	89	86	606
5	137	129	880
6	160	182	029
7	153	157	523
8	75	77	536
9	30	24	763
10	58	41	160
1,5,L			
0	67	54	955
2,5,L			
0	122	120	957
3,5,L			
0	131	124	010
4,5,L			
0	163	169	457
5,5,L			
0	132	137	529
6,5,L			
0	84	85	700
8,5,L			
0	44	47	027
10,5,L			
0	22	35	313
1,5,L			
1	150	147	021
2	73	67	646
3	211	207	476
4	214	216	611
5	211	222	977
6	126	111	055
7	107	115	680
8	84	83	423
9	67	60	040
10	60	64	951
11	27	30	284
2,5,L			
1	136	130	266
2	64	66	591
3	81	84	888
4	149	145	969
5	158	154	584
6	153	147	447
7	50	51	571
8	74	73	098
9	135	153	127
10	35	38	938
11	68	76	561
3,5,L			
1	163	158	535
2	235	240	435
3	105	97	108
4	236	248	935
5	59	57	746
6	123	120	366
7	71	71	314
8	88	82	006
10	43	40	496
11	22	27	414
4,5,L			
1	72	69	877
2	88	79	575
3	174	165	135
4	133	125	152
5	60	54	579
6	130	126	729
7	77	76	108
8	106	111	329
9	31	26	645
10	41	48	581
5,5,L			
1	206	203	462
2	64	68	036
3	153	154	107
4	57	51	175
6	46	47	796
7	109	113	964
8	79	85	195
9	71	82	519
10	25	39	643
6,5,L			
1	100	104	131
2	99	100	011
3	23	7	965
4	102	100	577
5	77	82	681
6	86	83	079
7	17	21	475
9	47	58	591
7,5,L			
1	85	86	180
3	82	80	663
4	93	90	543
5	83	87	892
6	81	88	089
7	46	52	312
8	49	62	540
8,5,L			
1	78	76	140
2	64	71	553
3	105	113	611
4	86	97	991
5	65	70	957
9,5,L			
1	57	57	109
3	93	116	531
5	48	65	087
10,5,L			
1	31	47	249
-1,5,L			
1	105	101	287
2	238	224	086
3	189	179	594
4	235	226	618
5	256	252	067
6	182	163	016
7	60	54	577
8	81	79	589
9	133	148	587
10	22	27	183
11	90	97	979
-2,5,L			
1	170	162	252
2	146	134	159
3	214	216	035
4	99	84	527
5	155	143	490
6	69	67	486
7	100	94	056
9	82	78	474
10	62	64	523
11	84	94	000
-3,5,L			
1	102	99	512
2	56	43	122
3	105	97	998
4	194	193	127
5	123	122	455
6	154	149	676
7	79	73	967
8	96	96	156
10	47	47	092
-4,5,L			
1	56	50	779
2	184	177	468
3	145	137	225
4	58	49	965
5	95	89	598
6	31	21	171
8	85	85	135
9	35	35	117
10	69	77	469
11	32	47	352
-5,5,L			
1	101	101	487
2	251	261	573
4	146	138	989
5	139	138	996
6	129	115	606
7	23	23	868
8	101	103	191
9	21	29	191
10	19	23	649
-6,5,L			
1	70	67	893
2	45	44	830
3	113	116	406
4	51	49	702
5	68	61	961
6	40	39	609
7	84	83	522
8	49	53	181
9	34	36	941
10	29	48	995
-7,5,L			
1	50	57	807
3	86	87	450
5	49	48	997
6	42	33	868
7	29	28	843
8	51	62	670
-8,5,L			
1	80	84	166
2	45	49	204
4	109	111	495
5	21	26	056
6	65	74	012
-9,5,L			
2	79	83	123
3	24	29	239
4	56	63	606
5	34	56	748
-10,5,L			
1	25	42	390
2	44	64	173

Table 2. *Positional coordinates with estimated standard deviations of non-hydrogen atoms*

	x/*a*	*y*/*b*	*z*/*c*
P	0·13420 (9)	0·56500 (0)	0·22303 (8)
O(6)	0·01466 (28)	0·62045 (60)	0·15005 (26)
O(8)	0·13290 (29)	0·63032 (64)	0·34212 (25)
O(7)	0·16576 (34)	0·32103 (63)	0·22155 (26)
O(3′)	0·25693 (27)	0·67564 (62)	0·16087 (23)
O(9)	0·14566 (35)	0·09162 (69)	0·03956 (27)
O(10)	0·33728 (32)	0·45479 (69)	0·47980 (25)
O(5′)	0·48655 (31)	1·16817 (66)	0·36267 (28)
O(1′)	0·59424 (26)	0·83655 (59)	0·23965 (24)
O(2′)	0·47315 (33)	0·62726 (84)	0·02223 (24)
N(1)	0·90013 (34)	−0·01632 (69)	0·21459 (27)
N(3)	0·76062 (35)	0·23997 (70)	0·12471 (27)
N(7)	0·80749 (38)	0·39270 (71)	0·41395 (28)
N(9)	0·69906 (31)	0·51035 (61)	0·25762 (25)
N(6)	0·97434 (37)	−0·01460 (76)	0·40225 (30)
C(2)	0·83257 (36)	0·06762 (96)	0·12481 (32)
C(4)	0·76106 (37)	0·32963 (74)	0·22795 (29)
C(5)	0·82693 (39)	0·25808 (84)	0·32493 (33)
C(6)	0·90301 (37)	0·07268 (93)	0·31890 (32)
C(8)	0·73125 (40)	0·54191 (92)	0·36921 (31)
C(1′)	0·62254 (39)	0·65131 (81)	0·17968 (30)
C(2′)	0·49004 (36)	0·55669 (93)	0·13459 (32)
C(3′)	0·39065 (38)	0·66313 (84)	0·21152 (31)
C(4′)	0·45171 (36)	0·87911 (80)	0·23299 (30)
C(5′)	0·41056 (43)	0·98112 (82)	0·34077 (35)

(Brown & Todd, 1952). The nucleotide exists in the characteristic zwitterion form with N(1) of the base protonated by one of the phosphate protons. A similar finding was made by Kraut & Jensen (1963) in 5′-AMP and by Shefter, Barlow, Sparks & Trueblood (1964) in AUP. In the pyrimidine nucleotide, 3′-CMP, N(3) of the cytosine ring was found to be protonated (Sundaralingam & Jensen, 1965*a*).

The angle formed by the sugar and base planes is 55°. This is lower than other values previously reported for this angle. In current models of deoxyribonucleic acid this angle is about 90°.

Base

The torsion angle φ_{CN}, as defined by Sundaralingam & Jensen (1965*a*) is −3·9°, and the low value is characteristic for the purine nucleosides and nucleotides with the 3′ puckering of the sugar. Larger values for this angle are generally assumed by these compounds when the sugar displays 2′ puckering.

The plane of the amino group is twisted through 17·4° from the purine plane. The atoms comprising the purine ring are planar, but the substituents N(6) and C(1′) are significantly displaced, 0·033 Å and 0·084 Å respectively, on the same side of the purine ring. The ribose carbon atom, C(1′), is out of the adenine plane by nearly 0·1 Å, and the glycosidic C(1′)–N bond makes an angle of about 3·5° with the base plane. Higher values for this angle have been observed in some other purine derivatives, *viz.* 5′-AMP (Kraut & Jensen, 1963) and deoxyadenosine (Watson, Sutor & Tollin, 1965). It may be noted that the phosphorus atom in 3′-AMP is 4·3 Å from the base plane, while in 5′-AMP it is only about 1 Å, and in 3′-CMP it is approximately in the plane of the base.

Bond lengths in the adenine cation (Fig. 2) are generally in very good agreement with those found in the adenosine residue of AUP (Shefter, Barlow, Sparks & Trueblood, 1964; and personal communication). The exceptions are N(9)–C(8) and C(1′)–N(9), which are 1·395 Å and 1·446 Å respectively in AUP (*cf.* Fig. 2). These differences are attributable to the differences in the rotation angles about the bonds C(1′)–N(9) and O(1′)–C(1′) in the system –C(8)–N(9)–C(1′)–O(1′)–C(4′)–. Apparently, rotation about single bonds invol-

Table 3. *Anisotropic thermal parameters* (B_{ij}) *and estimated standard deviations of non-hydrogen atoms*

The expression used for the temperature factor is $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	0·00396 (9)	0·00760 (39)	0·00401 (7)	0·00073 (15)	−0·00049 (6)	−0·00057 (13)
O(6)	0·00558 (29)	0·01210 (129)	0·00578 (23)	0·00127 (43)	−0·00138 (20)	0·00003 (38)
O(8)	0·00635 (30)	0·01675 (125)	0·00456 (21)	0·00157 (47)	−0·00023 (20)	−0·00283 (40)
O(7)	0·00947 (37)	0·00802 (135)	0·00581 (25)	0·00435 (52)	−0·00126 (23)	−0·00040 (41)
O(3′)	0·00481 (28)	0·01351 (110)	0·00462 (21)	0·00113 (45)	−0·00102 (19)	0·00126 (38)
O(9)	0·01160 (42)	0·01322 (135)	0·00570 (24)	0·00324 (63)	−0·00145 (25)	−0·00137 (47)
O(10)	0·00849 (36)	0·01414 (118)	0·00485 (22)	0·00197 (53)	−0·00025 (22)	−0·00033 (44)
O(5′)	0·00700 (33)	0·01093 (116)	0·00691 (27)	−0·00057 (50)	0·00051 (23)	−0·00324 (46)
O(1′)	0·00436 (27)	0·00867 (108)	0·00564 (22)	−0·00016 (41)	−0·00014 (19)	−0·00136 (38)
O(2′)	0·00905 (39)	0·04064 (200)	0·00340 (23)	0·00671 (70)	−0·00076 (22)	−0·00013 (50)
N(1)	0·00572 (33)	0·00859 (131)	0·00397 (24)	0·00076 (49)	−0·00002 (22)	−0·00091 (40)
N(3)	0·00614 (35)	0·01133 (136)	0·00342 (22)	0·00140 (51)	−0·00068 (22)	−0·00108 (42)
N(7)	0·00847 (42)	0·01123 (148)	0·00360 (23)	0·00186 (58)	−0·00122 (24)	−0·00110 (41)
N(9)	0·00481 (31)	0·00780 (140)	0·00318 (22)	0·00145 (43)	−0·00062 (20)	0·00009 (35)
N(6)	0·00705 (39)	0·01322 (150)	0·00483 (26)	0·00294 (56)	−0·00231 (25)	0·00038 (45)
C(2)	0·00560 (37)	0·01249 (155)	0·00439 (28)	0·00046 (72)	−0·00041 (24)	0·00021 (59)
C(4)	0·00548 (37)	0·00299 (137)	0·00358 (25)	0·00012 (51)	−0·00013 (23)	0·00007 (42)
C(5)	0·00460 (36)	0·00900 (140)	0·00444 (27)	0·00153 (55)	−0·00060 (26)	−0·00080 (49)
C(6)	0·00545 (36)	0·01211 (149)	0·00432 (26)	0·00017 (70)	−0·00049 (24)	0·00095 (58)
C(8)	0·00713 (41)	0·01507 (167)	0·00344 (26)	0·00180 (69)	−0·00085 (26)	−0·00134 (55)
C(1′)	0·00603 (39)	0·00871 (144)	0·00309 (25)	0·00120 (57)	0·00044 (24)	0·00075 (45)
C(2′)	0·00536 (35)	0·01048 (149)	0·00453 (27)	0·00097 (68)	−0·00081 (24)	−0·00094 (58)
C(3′)	0·00510 (37)	0·01094 (144)	0·00364 (26)	0·00021 (58)	−0·00075 (24)	0·00014 (49)
C(4′)	0·00444 (36)	0·01070 (157)	0·00367 (26)	−0·00020 (56)	0·00025 (24)	0·00041 (47)
C(5′)	0·00719 (46)	0·00791 (159)	0·00479 (30)	−0·00020 (62)	0·00036 (29)	−0·00113 (52)

Table 4. *Positional coordinates with estimated standard deviations of hydrogen atoms*

	x/a	y/b	z/c
H(N1)	0·956 (6)	−0·156 (14)	0·196 (5)
H(2)	0·839 (9)	−0·015 (10)	0·044 (4)
H(N6)	0·966 (6)	0·022 (12)	0·467 (5)
H(N6′)	1·038 (5)	−0·109 (12)	0·378 (4)
H(8)	0·701 (7)	0·672 (15)	0·415 (6)
H(1′)	0·683 (4)	0·679 (9)	0·115 (4)
H(2′)	0·468 (5)	0·390 (11)	0·139 (4)
H(3′)	0·389 (5)	0·596 (10)	0·281 (4)
H(4′)	0·439 (4)	0·973 (8)	0·172 (3)
H(5′)	0·419 (7)	0·898 (15)	0·407 (6)
H′(5′)	0·312 (5)	1·019 (11)	0·334 (5)
H(O5′)	0·428 (6)	1·250 (11)	0·401 (5)
H(O7)	0·143 (6)	0·256 (15)	0·139 (5)
H(O2′)	0·386 (7)	0·637 (15)	0·012 (5)
H(O10)	0·263 (7)	0·481 (14)	0·446 (6)
H(O10′)	0·364 (6)	0·573 (15)	0·542 (5)
H(O9)	0·089 (4)	0·115 (9)	−0·006 (3)
H(O9′)	0·186 (6)	−0·040 (15)	0·033 (5)

Table 5. *Hydrogen atom temperature factors, using* (*a*) *McWeeny and* (*b*) *Stewart, Davidson & Simpson scattering factors, compared with those of the non-hydrogen atoms* (*c*) *to which they are attached*

	(*a*)	(*b*)	(*b*) − (*a*)	(*c*)	(*b*) − (*c*)
H(N1)	3·2 (1·5)	5·8 (1·7)	2·6	2·4	3·4
H(2)	0·5 (0·9)	2·4 (1·0)	1·9	2·4	0·0
H(N6)	2·1 (1·1)	3·9 (1·3)	1·8	2·8	1·1
H(N6′)	1·4 (1·0)	3·5 (1·2)	2·1	2·8	0·7
H(8)	4·5 (1·7)	6·1 (1·9)	1·6	2·7	3·4
H(1′)	0·2 (0·8)	1·9 (0·9)	1·7	2·3	−0·4
H(2′)	1·1 (1·0)	3·2 (1·1)	2·1	2·5	0·7
H(3′)	0·8 (0·9)	2·5 (1·0)	1·7	2·2	0·3
H(4′)	−0·3 (0·9)	1·5 (0·9)	1·8	2·1	−0·6
H(5′)	3·6 (1·6)	5·9 (1·9)	2·3	3·1	2·8
H′(5′)	1·8 (1·1)	3·7 (1·2)	1·9	3·1	0·6
H(O5′)	1·2 (1·1)	3·4 (1·3)	2·2	3·2	0·2
H(O7)	3·2 (1·4)	5·8 (1·7)	2·6	2·9	2·9
H(O2′)	2·9 (1·4)	5·7 (1·8)	2·8	3·5	2·2
H(O10)	3·0 (1·3)	5·5 (1·6)	2·5	3·5	2·0
H(O10′)	3·4 (1·4)	5·6 (1·6)	2·2	3·5	2·1
H(O9)	−0·1 (0·8)	1·8 (0·9)	1·9	3·8	−2·0
H(O9′)	3·7 (1·5)	5·9 (1·7)	2·2	3·8	2·1

ving hetero-atoms carrying lone pair electrons has an influence on the bond distances and bond angles (Sundaralingam, 1965; Altona & Sundaralingam, 1966). The bond lengths of 5′-AMP (Kraut & Jensen, 1963) are on an average about 0·02 Å greater than that found in 3′-AMP. This discrepancy appears to be indicative of possible errors in the cell dimensions of 5′-AMP, which were measured photographically.

Ribose

The ribose ring is puckered with C(3′) displaced by 0·562 Å from the best four-atom plane of the furanose ring, and on the same side as C(5′). The root-mean-square displacement of the atoms forming the plane is 0·015 Å. The puckering of the ribose when described as a twist of the C(2′)–C(3′) bond relative to the plane C(1′)O(1′)C(4′) is C(3′)-*endo*-C(2′)-*endo*, where C(3′) and C(2′) are displaced by 0·620 and 0·075 Å respectively on the same side as C(5′). Therefore, this precise analysis establishes the fact that the latter conformation is indeed a possible mode of puckering of the furanose ring and lends support to the puckering observed in calcium thymidylate (Trueblood, Horn & Luzzati, 1961; Sundaralingam, 1965). The differences in the ribose conformation are best seen when one considers the conformation angles (as defined in Fig. 3) about the ring bonds. For 3′-AMP these angles are:

$\varphi_{O(1')\rightarrow C(1')} = -3{\cdot}0^\circ$, $\varphi_{C(1')\rightarrow C(2')} = -19{\cdot}7^\circ$, $\varphi_{C(2')\rightarrow C(3')} = 33{\cdot}9^\circ$, $\varphi_{C(3')\rightarrow C(4')} = -36{\cdot}6^\circ$ and $\varphi_{C(4')\rightarrow O(1')} = 24{\cdot}8^\circ$.

The conformation angles of the type H–C–C–H, abbreviated as H–H, in the carbohydrate residue are as follows: H(1′)–H(2′) = 79°, H(2′)–H(3′) = 50°, H(3′)–H(4′) = −167°, H(4′)–H(5′) = 178° and H(4′)–H′(5′) = 59°. In the absence of substitution effects these conformation angles would be correlated with their spin coupling constants obtained from proton magnetic resonance spectra (Karplus, 1959). Jardetzky (1960, 1961, 1962) and Lemieux (1961) have had some success in applying the above correlation to assign specific conformation of the furanosides in solution. The H–H conformation angles obtained in the solid state may prove useful in understanding substitution effects on the Karplus (1959) equation.

The conformation angle O(2′)–C(2′)–C(3′)–O(3′) is 43° while those in 5′-AMP and 3′-CMP are 53° and −48° respectively. It is of interest to compare the conformation angle O(3′)–C(3′)→C(4′)–C(5′) in 3′-AMP (83°), 5′-AMP (76°) and 3′-CMP (151°). The above angles imply that only furanose rings that exhibit C(3′)-*endo** puckering as in 3′-AMP and 5′-AMP, or C(2′)-*exo* puckering as in sucrose (Brown & Levy, 1963; Sundaralingam, 1965), can lend themselves to the formation of the 3′,5′-cyclic phosphates.

An uncommon conformational feature of the ribose moiety is that the orientation of the C(5′)–O(5′) bond with respect to the ring bonds C(4′)–O(1′) and C(4′)–C(3′) is *gauche* and *trans* respectively with conformational angles O(1′)–C(4′)→C(5′)–O(5′) and C(3′)–C(4′)→C(5′)–O(5′) of 56·7° and −171·7° respectively. The only other known compound that displays the above conformation is deoxyadenosine (Watson, Sutor & Tollin, 1965; Sundaralingam, 1965).

The rotation of the C(5′)–O(5′) bond about the C(4′)–C(5′) bond appears to have an influence on the exocyclic angle C(3′)–C(4′)–C(5′), for in the *gauche-gauche* conformation of C(5′)–O(5′) this angle averages about 117°, while significantly smaller values are acquired for the *gauche-trans* conformation, as found in this work (114·3°) and in deoxyadenosine (113·7°), and in the *trans-gauche* conformation as in 5′-fluoro-2′-deoxy-*β*-uridine (114·6°) (Harris & MacIntyre, 1964).

Although the bond lengths in the ribose (Fig. 2) resemble those found in similar compounds, there are, however, a few notable differences in the bond angles, which probably is a consequence of the differences in the ribose conformation. For instance, the angle O(1′)–C(4′)–C(3′) of 103·1° and O(1′)–C(1′)–C(2′) of 108·6° are markedly different from each other, the former being the largest reported value and the latter is the smallest. Likewise, the internal angles involving C(2′)

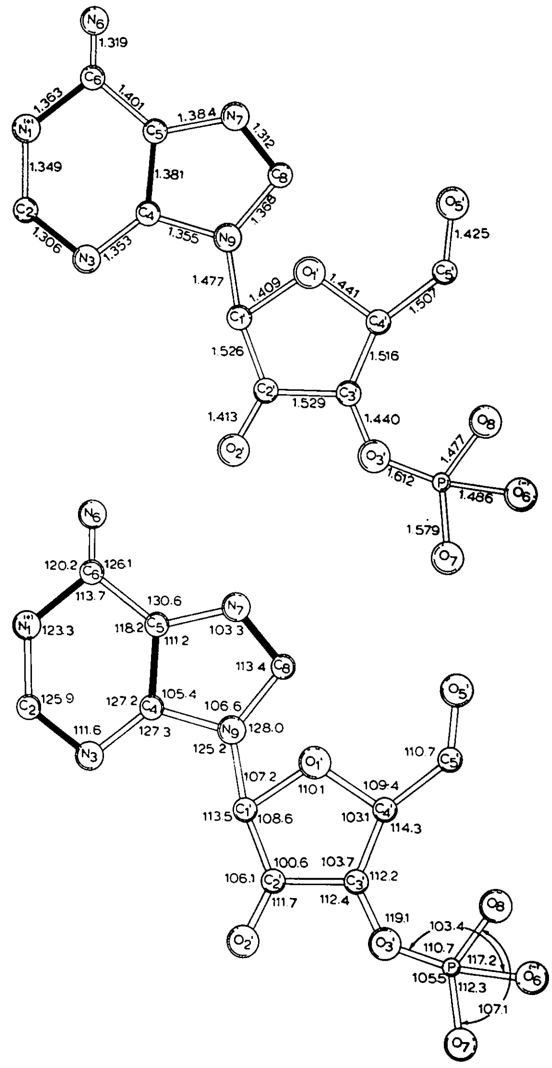

Fig. 2. Bond lengths (Å) and bond angles (°) involving the non-hydrogen atoms. Solid lines indicate the positions of the double bonds in the ground state structure. The average estimated error in the different bonds is: P–O 0·003 Å, C–O 0·005 Å, C–N 0·006 Å and C–C 0·006 Å, and that of the angle is 0·3° (0·1° for the angles involving P). The small errors in the cell constants do not significantly affect the estimated errors in the bond length.

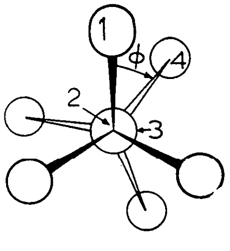

Fig. 3. The conformation angle φ, for example, of the bond 2–3 is here defined as the angle made by the projection of the bond 3–4 relative to the bond 1–2 when viewed in the direction of the bond 2 → 3; positive angles are measured clockwise from the near bond (1–2) to the far bond (3–4).

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* C(3′)-*endo* means C(3′) is displaced on the same side of the best four-atom plane as C(5′), while C(2′)-*exo* means C(2′) is displaced on the opposite side.

and C(3′) are significantly different. Both the exocyclic angles associated with C(3′) are greater than the ideal tetrahedral value, while one of the exocyclic angles involving C(2′), namely C(1′)–C(2′)–O(2′) of 106·1° is not only significantly less than the tetrahedral value but is less than any of the reported values for this angle.

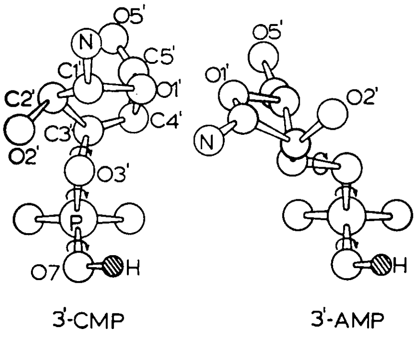
Phosphate

The estimated standard deviation in the P–O bond is about 0·003 Å, and thus from Fig. 2 we can see that all of the four P–O bonds are different from each other. The agreement between the P–O bond lengths as found here and in similar phosphate groups is unsatisfactory (Sundaralingam & Jensen, 1965*b*).

Of interest is the comparison of the phosphate conformation in 3′-AMP and 3′-CMP. In both compounds the proton on the phosphate oxygen has been located and this permits us to compare the conformations of the chain -C(3′)–O(3′)–P–O–H, as shown in Fig. 4. The conformation (*gauche*) angle O(3′)–P→O(7)–H is about the same in both the cases (*ca.* −70°), but the conformation of C(3′)–O(3′)→P–O(7) is distinctly different, about −77° (*gauche*) in 3′-AMP and about 171° (*trans*) in 3′-CMP. The former may be designated as the *folded* (*gauche-gauche*) conformation and the latter the *semi-folded* (*gauche-trans*) conformation. A literature survey of the known phosphates reveals the fact that they fall into one of the two conformations cited above, irrespective of whether the proton is substituted by a carbon, as in the phosphodiester anion, or not (Sundaralingam, to be published). The conformation angles formed by the P–O(3′) bond with respect to the sugar ring bonds C(3′)–C(4′) and C(3′)–C(2′) are −91° and 158° in 3′-CMP, and −123° and 121° in 3′-AMP. The latter values are similar to those found in vitamin B_{12} (Hodgkin, 1964).

Hydrogen atoms

The use of McWeeny scattering factors for hydrogen results in anomalously low temperature factors for the hydrogen atoms, (*cf.* columns (2) and (5), Table 5; see also Jensen & Sundaralingam, 1964; Sundaralingam & Jensen, 1963). But the more recent $f_{\rm H}$ curve of Stewart, Davidson & Simpson (1965) produces hydrogen temperature factors which are generally greater than those of the heavy atoms to which they are attached (Jensen, 1965), and in agreement with expectations (column (3), Table 5). Even now, three of the hydrogen atoms possess temperature factors which are less than their associated heavy atoms. The reason for this behavior is not obvious and may well be due to inaccuracies in the measured intensities. However, the scattering factors from both the above sources produce practically identical values for the covalent bond lengths involving the hydrogen atoms. In fact, the individual differences in the bonds obtained from the two scattering factors are less than 0·1σ of the hydrogen coordinate. Bond lengths and bond angles involving the hydrogen atoms obtained from the $f_{\rm H}$ curve of Stewart *et al.* are shown in Table 6. The composite Fourier map obtained after subtracting the scattering due to the non-hydrogen atoms is illustrated in Fig. 5 which clearly shows all of the hydrogen electron densities.



3'-CMP 3'-AMP

Fig. 4. Comparison of the conformations of the ribophosphate residues in 3′-CMP and 3′-AMP. Note the differences in the rotation angle about the P–O(3′) bond.

Hydrogen bonding

An interesting scheme of three-dimensional hydrogen bonds holds the molecules rather firmly in the crystal lattice (Figs. 6 and 7). Hydrogen bond lengths are presented in Table 7, and hydrogen bond angles are shown in Table 7 and Fig. 8. When symmetry related atoms are involved the specific symmetry operation is shown in square brackets. The ribose 5′ hydroxyl, the water hydroxyl O(10)–H(O10′), and the atoms related to these by the screw axis at $\frac{1}{2}$, 0, $\frac{1}{2}$ form an infinite hydrogen-bonded fourfold helix (Fig. 6). The water oxygen atom O(9), within the error of determination of the hydrogen atoms, forms a trigonal planar system of hydrogen bonds, two O–H···O and one O–H···N. One of the H–O···H angles is close to the tetrahedral value, 111°, while the other, 133°, is considerably larger. The sum of the hydrogen bond angles around O(9) is 358°. Nearly planar trigonally disposed hydrogen bonds for water molecules were first reported by Jeffrey and his associates in barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961) and cytosine monohydrate (Jeffrey & Kinoshita, 1963). The O–H···O hydrogen bonds involving the other water oxygen, O(10), are geometrically similar to the hydrogen bonds involving O(9), except that O(10) is engaged in a fourth hydrogen bond, (C–H···O) (see below).

C–H···O *hydrogen bond*

Sutor (1963) has summarized the evidence for the existence of C–H···O hydrogen bonds in the solid state. In 3′-AMP the presence of the electronegative nitrogen atoms N(7) and N(9) on either side of C(8) enhances the electronegativity of this carbon atom, thereby making it suitable for hydrogen bonding, which is evidenced by the short H(8)···O(10) distance of 2·24 ± 0·06 Å. A value considerably less than the sum of the van der Waals radii for oxygen and hydrogen (2·60 Å). It may be noted, however, that the C(8)··· O(10) distance of 3·262 Å is greater than the van der

Waals contact distance (3·10 Å). Therefore, it is important to locate hydrogen atoms to help decide whether one is confronted with a van der Waals contact or a hydrogen bond.

The phosphate oxygen atoms O(6), O(8) and ribose oxygen atoms O(2′) and O(5′) form a pattern of hydrogen bonds similar to that described for 3′-CMP (Sundaralingam & Jensen, 1965*a*). However, in 3′-AMP, O(7) of the phosphate is involved in only a donor hydrogen bond, *viz.* P–O–H···O–H (Fig. 6) which is the shortest in the structure, 2·619 Å. The monovalent anionic phosphate monoester group always forms a very short hydrogen bond that involves the hydroxyl group, suggesting that the O–H is highly polarized; other examples are 3′-CMP, P–O–H···$^-$O–P 2·532 Å and 5′-AMP, P–O–H···O=P 2·525 Å. The latter hydrogen bonds are even shorter than that found in 3′-AMP probably because of the phosphorus atoms at both

Table 6. *Bond lengths and bond angles involving covalently bonded hydrogen atoms**

O(7)—H(O7)	1·09 Å	N(6)-H(N6′)	0·92 Å
O(9)—H(O9)	0·78	C(2)-H(2)	1·10
O(9)—H(O9′)	0·94	C(8)-H(8)	1·03
O(10)-H(O10)	0·85	C(1′)-H(1′)	1·01
O(10)-H(O10′)	1·10	C(2′)-H(2′)	1·09
O(5′)-H(O5′)	0·89	C(3′)-H(3′)	0·95
O(2′)-H(O2′)	0·87	C(4′)-H(4′)	0·95
N(1)-H(N1)	1·10	C(5′)-H(5′)	0·98
N(6)-H(N6)	0·81	C(5′)-H′(5′)	1·02
P——O(7)—H(O7)	111°	N(9)-C(1′)-H(1′)	106°
H(O9)—O(O9)-H(O9′)	114	C(2′)-C(1′)-H(1′)	110
H(O10)-O(10)-H(O10′)	112	O(2′)-C(2′)-H(2′)	110
C(5′)—O(5′)—H(O5′)	102	C(1′)-C(2′)-H(2′)	124
C(2′)—O(2′)—H(O2′)	103	C(3′)-C(2′)-H(2′)	105
C(2)—N(1)—H(N1)	115	O(3′)-C(3′)-H(3′)	111
C(6)—N(1)—H(N1)	122	C(2′)-C(3′)-H(3′)	112
C(6)—N(6)—H(N6)	120	C(4′)-C(3′)-H(3′)	106
C(6)—N(6)—H(N6′)	113	O(1′)-C(4′)-H(4′)	104
H(N6)-N(6)—H(N6′)	126	C(3′)-C(4′)-H(4′)	114
N(1)—C(2)—H(2)	117	C(5′)-C(4′)-H(4′)	111
N(3)—C(2)—H(2)	117	O(5′)-C(5′)-H(5′)	106
N(7)—C(8)—H(8)	122	O(5′)-C(5′)-H′(5′)	107
N(9)—C(8)—H(8)	125	C(4′)-C(5′)-H(5′)	116
O(1′)—C(1′)—H(1′)	113	C(4′)-C(5′)-H′(5′)	110
		H(5′)-C(5′)-H′(5′)	107

* Average estimated standard deviation in the bonds is 0·06 Å and in the angles is 4°.

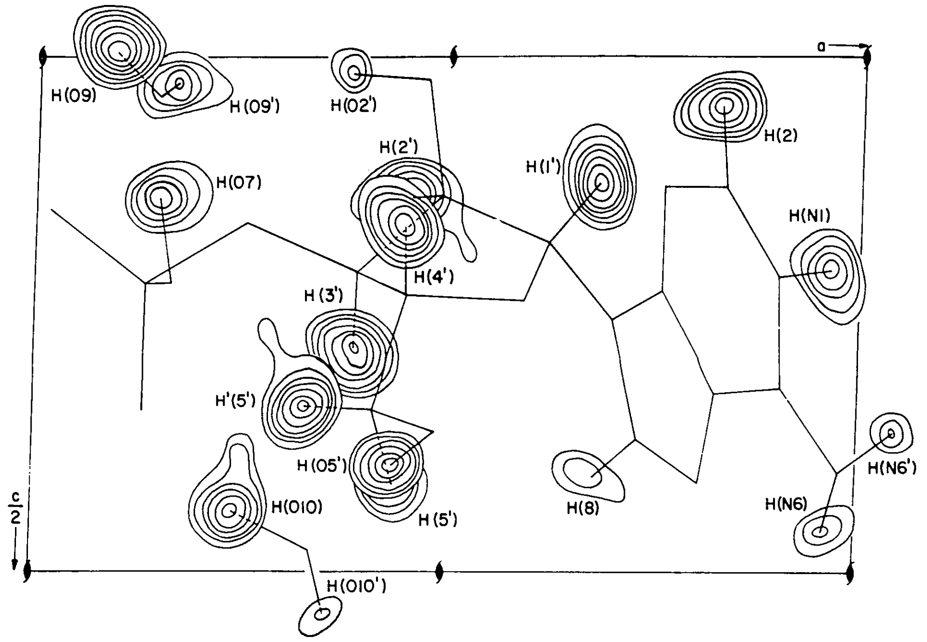


Fig. 5. A composite difference Fourier synthesis showing the hydrogen atoms. Contours plotted at intervals of 0·05 e.Å^{-3}, beginning at 0·1 e.Å^{-3}.

ends of the hydrogen bond. There is another short hydrogen bond (2·695 Å) in the structure, involving N(1) of the base and the phosphate oxygen O(6). Note the proton transfer from O(6) to N(1). This type of hydrogen bond is so characteristic of the nucleotides that it can be employed as a constraint in proposing packing models for these compounds.

The amino hydrogen H(N6′) participates in a nearly linear hydrogen bond with O(8) of the phosphate in an adjacent unit-cell, N–H···O 2·856 Å. It is not clear whether the other amino proton is hydrogen bonded to N(7) of a neighboring molecule, since the N–H···N distance is 3·016 Å and the N–H···N angle is 105°.

H(O2′) probably is simultaneously involved in an intramolecular hydrogen bond to the ester oxygen O(3′), H(O2′)···O(3′) = 2·22 ± 0·06 Å and O(2′)···O(3′) = 2·776 Å, and a hydrogen bond to N(3) at $1-x$, $\frac{1}{2}+y$, $-z$, O(2′)···N(3) = 2·941 Å.

Intramolecular distances

The closest C···O intramolecular distance in the structure is 3·143 Å, involving the base atom C(2) at x, $1+y$, z, and the ribose ring oxygen O(1′) (Table 8). The latter atom appears to show a tendency to form close contacts with neighboring base atoms, rather than participate in hydrogen bonding. On the other hand, pyranose ring oxygens are noted for displaying intramolecular hydrogen bonding. Shefter & Trueblood (1965) recently reported a very short contact (2·74 Å) between the ribose ring atom O(1′) and an adjacent base atom C(4), in the crystal structure of barium uridine-5′-phosphate. Although such interactions are

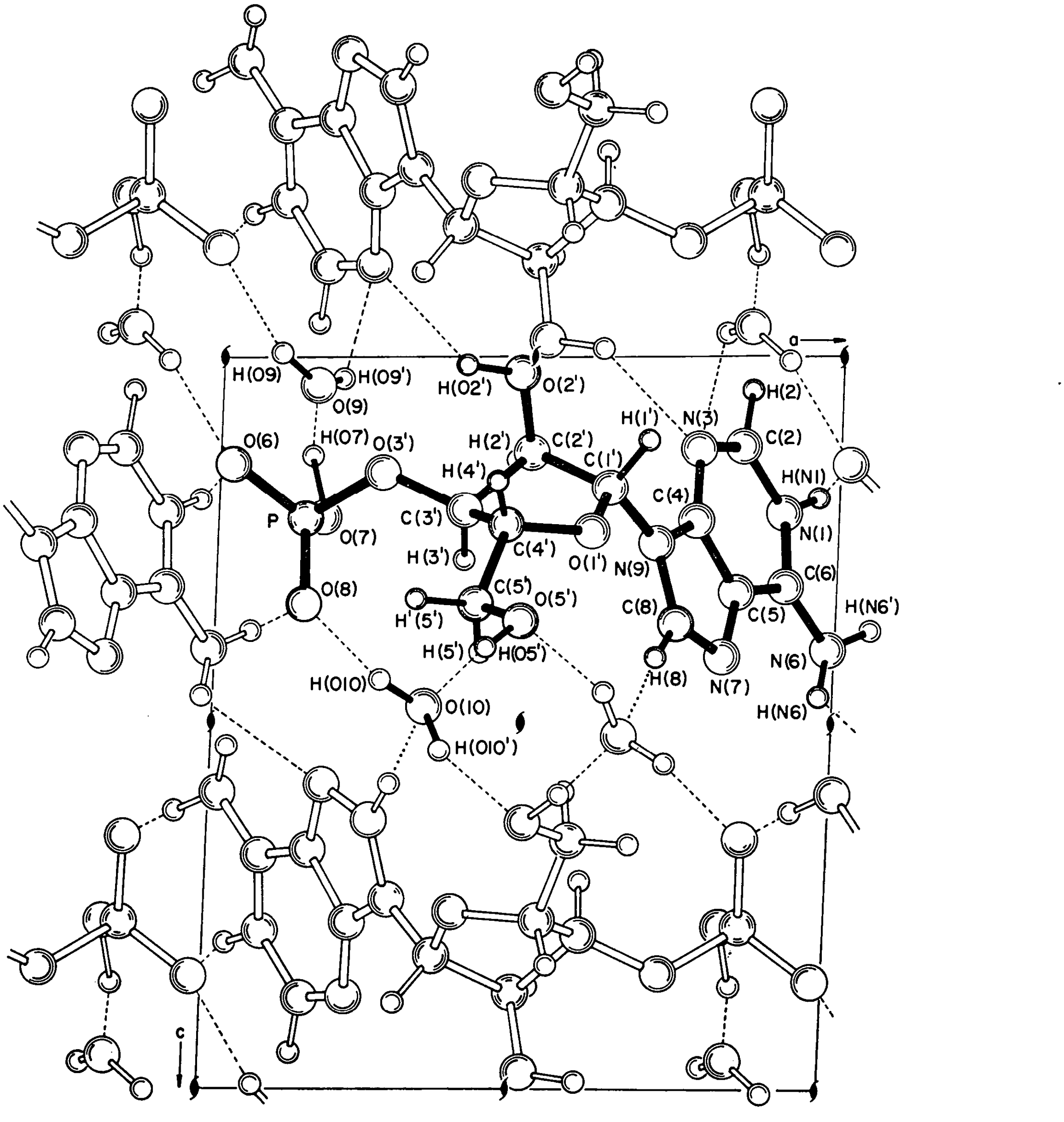


Fig. 6. The (010) projection of the structure, illustrating the hydrogen bonding scheme; the reference molecule is indicated by solid lines.

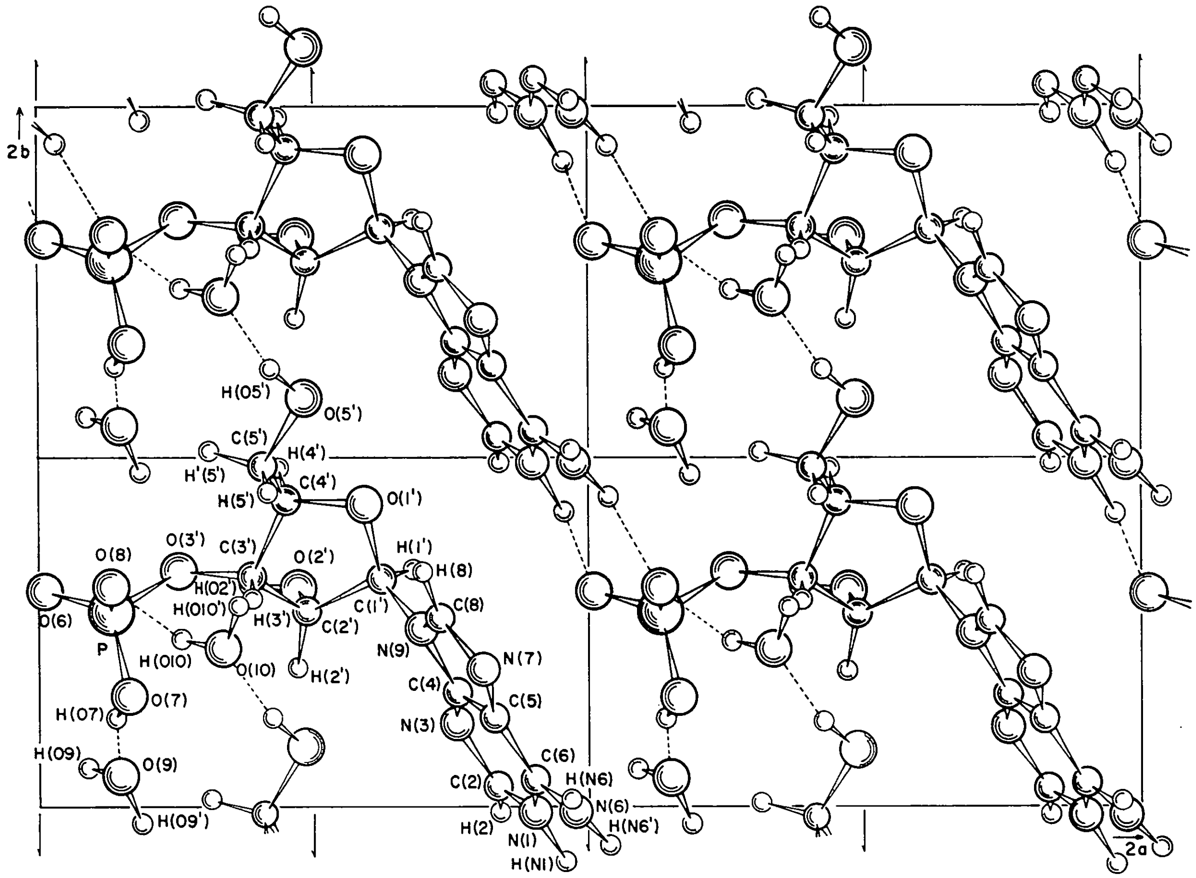


Fig. 7. A view of the structure along one half of the *c* axis. Note the ribose ring oxygen pointing towards the adjacent base.

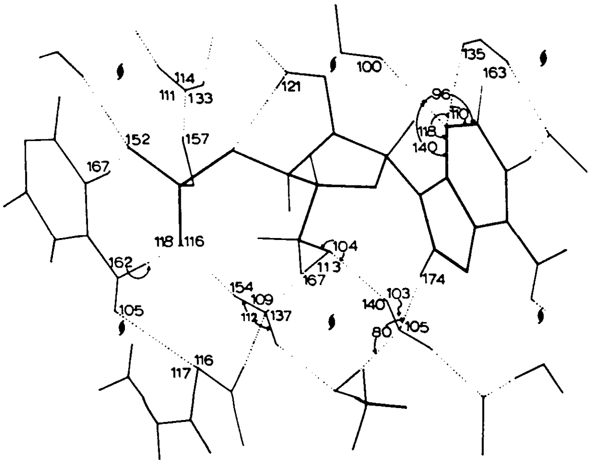


Fig. 8. Some of the bond angles involving the hydrogen bonds.

unlikely to occur in the Watson–Crick double helices of DNA (Crick & Watson, 1954; Langridge, Marvin, Seeds, Wilson, Hooper, Wilkins & Hamilton, 1960) and ribonucleic acid (Spencer, Fuller, Wilkins & Brown, 1962; Langridge & Gomatos, 1963; Tomita & Rich, 1964), nonetheless they may play a role in stabilizing certain conformations of the non-double helical regions of transfer ribonucleic acid.

All of the crystallographic computations were carried out on an IBM 7094 computer with the X-ray 63 System of Programs, Technical Report TR-64-6 (NSG-398), Computer Science Center, University of Maryland, and Research Computer Laboratory, University of Washington. Dr David B. Dekker, Director, Research Computer Laboratory, University of Washington, Seattle, is hereby thanked for his kind cooperation and the award of large grants of computer time which made possible the rapid completion of the structure solution and refinement.

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Table 7. *Distances and angles involving hydrogen bonds*

The numbers in square brackets indicate the symmetry related atoms, and those without square brackets belong to the reference molecule (Table 2).

[1]	x,	y,	z	[7]	x,	$-1+y$,	z
[2]	$1-x$,	$\frac{1}{2}+y$,	$-z$	[8]	$-1+x$,	y,	z
[3]	$1-x$,	$-\frac{1}{2}+y$,	$-z$	[9]	$-1+x$,	$1+y$,	z
[4]	$1-x$,	$\frac{1}{2}+y$,	$1-z$	[10]	$-x$,	$\frac{1}{2}+y$,	$-z$
[5]	x,	$1+y$,	z	[11]	$2-x$,	$\frac{1}{2}+y$,	$1-z$
[6]	$1+x$,	y,	z	[12]	$1-x$,	$-\frac{1}{2}+y$,	$1-z$

O(6)	O(9)[10]	2·717 Å	N(6)	O(8)[7]	2·856 Å
O(6)	H(O9)[10]	1·97	H(N6′)	O(8)[7]	1·97
O(9)	O(7)[1]	2·610	O(2′)	N(3)[2]	2·941
O(9)	H(O7)[1]	1·56	H(O2′)	N(3)[2]	2·25
O(5′)	O(10)[4]	2·856	N(6)	N(7)[11]	3·076
O(5′)	H(O10′)[4]	1·93	H(N6)	N(7)[11]	2·76
O(5′)	O(10)[5]	2·758	N(3)	O(9)[2]	3·131
H(O5′)	O(10)[5]	1·88	N(3)	H(O9′)[2]	2·40
O(10)	O(8)	2·791	C(8)	O(10)[4]	3·262
H(O10)	O(8)	2·01	H(8)	O(10)[4]	2·24
N(1)	O(6)[7]	2·695	O(2′)	O(3′)	2·776
H(N1)	O(6)[7]	1·61	H(O2′)	O(3′)	2·23

P————O(6)———H(O9)[10]	152°	O(10)—H(O10)—O(8)	154°
O(6)———H(O9)[10]-O(9)[10]	163	N(1)——H(N1)——O(6)[7]	168
O(7)———H(O7)——O(9)	157	N(6)——H(N6′)——O(8)[7]	162
H(O7)——O(9)———H(O9)	111	H(N6′)-O(8)[7]——P[7]	118
H(O7)——O(9)———H(O9′)	133	O(2′)—H(O2′)——N(3)[2]	100
O(5′)———H(O5′)———O(10)[5]	167	H(O2′)-N(3)[2]——C(4)[2]	140
H(O5′)——O(10)[5]——H(O10)[5]	109	H(O2′)-N(3)[2]——C(2)[2]	96
H(O5′)——O(10)[5]——H(O10′)[5]	137	O(2′)—H(O2′)——O(3′)	121
C(5′)———O(5′)———H(O10′)[4]	104	N(3)——H(O9′)[2]-O(9)[2]	135
H(O5′)——O(5′)———H(O10′)[4]	113	C(2)——N(3)———H(O9′)[2]	110
O(5′)———H(O10′)[4]-O(10)[4]	141	C(4)——N(3)———H(O9′)[2]	118
H(O10′)[4]-O(10)[4]——H(8)	103	N(6)——H(N6)——N(7)[11]	106
H(O10)[4]-O(10)[4]——H(8)	105	H(N6)-N(7)[11]—C(5)[11]	117
H(8)———O(10)[4]——H(O5′)[12]	80	H(N6)-N(7)[11]—C(8)[6]	116
C(8)———H(8)———O(10)[4]	174		

Table 8. *The shortest intermolecular distances**

O(1′)	C(2)[5]	3·143 Å	O(8)	N(6)[4]	3·388 Å
C(5′)	O(10)[4]	3·233	O(10)	N(7)[4]	3·395
O(6)	C(4)[8]	3·286	C(5′)	H(O10′)[4]	2·660
O(7)	C(6)[8]	3·298	H(O2′)	C(2)[2]	2·710
C(2)	O(9)[6]	3·313	H(O10′)	C(5)[4]	2·762
O(6)	C(2)[9]	3·372	H(1′)	O(9)[2]	2·612
O(3′)	O(9)[5]	3·185	O(2′)	H(4′)[3]	2·675
O(2′)	O(2′)[2]	3·263	O(9)	H(2)[2]	2·693
O(5′)	N(9)[5]	3·307	H(O10′)	N(7)[4]	2·697
O(9)	N(1)[8]	3·340	H(O5′)	H(O10)[5]	2·304
O(8)	N(7)[4]	3·378			

* See Table 7 for designation of numbers in square brackets.

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The Crystal Structure of 1-Phenyl-2-(2-pyridyl)ethanedione-1,2

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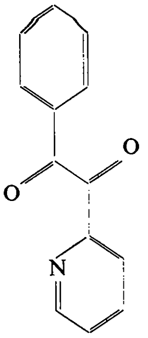
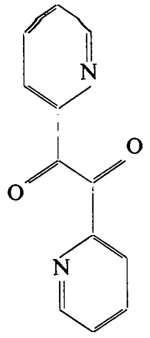
The crystal structure of 1-phenyl-2-(2-pyridyl)ethanedione-1,2 has been determined from three-dimensional intensity data and refined by the least-squares method with anisotropic thermal parameters. The positions of all the hydrogen atoms were found by a three-dimensional difference Fourier synthesis and included in the refinements. The crystal is monoclinic, space group $P2_1/c$, $a=11\cdot45$, $b=6\cdot55$, $c=14\cdot60$ Å and $\beta=90\cdot4°$. The molecular configuration is quite close to that of 2,2′-pyridil, 1,2-di-(2-pyridyl)ethanedione-1,2. The molecule consists of two planar parts, one of which contains a pyridine ring, a carbonyl group and its adjacent carbon atom, and the other contains a phenyl group, a carbonyl group and its nearest carbon atom; the angle between the two planes is 88·1°. The carbonyl oxygen of the phenyl part of the molecule is shifted from the plane by 0·1 Å. The characteristic feature of the crystal structure is plane-to-plane parallel stackings formed by pairs of pyridine rings and phenyl planes. The difference between the melting points of the present crystal and 2,2′-pyridil is discussed in terms of the difference in their crystal structures.

Introduction

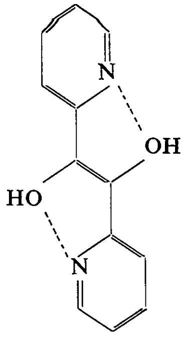
The crystal structure of 1,2-di-(2-pyridyl)ethanedione-1,2 (pyridil) (II) has been reported by two of the present authors (Hirokawa & Ashida, 1961). The mode of packing of the molecules in the crystal is unique; in short, it shows a plane-to-plane stacking made by four almost parallel pyridine rings, with interplanar distances corresponding to the normal van der Waals contact. The molecular conformation of 1-phenyl-2-(2-pyridyl)ethanedione-1,2 (hereafter called PPED) (I) is supposed to be similar to that of pyridil; however,



(I) PPED



(II) Pyridil



(III) Pyridoin