through the crystal, and could also help to explain the yellow colour of pyridazino[4,5-*d*]pyridazine.

Table 9. *Shortest intermolecular distances*

Values less than 3·5 Å for contacts involving C and N atoms, and less than 3·0 Å for contacts involving C or N and H atoms.

(I)	x;	y;	z
(II)	$1+x$;	y;	z
(III)	$-x$;	$\frac{1}{2}+y$;	$\frac{1}{2}-z$
(IV)	x;	y;	$\frac{1}{2}+z$
(V)	$1-x$;	$-y$;	$-z$
(VI)	$1-x$;	$\frac{1}{2}+y$;	$\frac{1}{2}-z$
(VII)	$1-x$;	$-\frac{1}{2}+y$;	$\frac{1}{2}-z$
(VIII)	$-x$;	$1-y$;	$-z$

N(1) (I)–C(1) (II)	3·457 Å
–C(1) (VIII)	3·477
–C(2) (III)	3·425
N(2) (I)–C(1) (IV)	3·451
–C(2) (VI)	3·349
C(2) (I)–C(3) (V)	3·473
N(1) (I)–H(1) (VIII)	2·63
–H(2) (VII)	2·79
–H(2) (III)	2·94
N(2) (I)–H(2) (VI)	2·52

References

Adembri, G., De Sio, F., Nesi, R. & Scotton, M. (1967). *Chem. Comm.* p. 1006.

Albano, V., Bellon, P. L., Pompa, F. & Scatturin, V. (1963). *Ric. Sci.* 3A, 1067.

Bertinotti, F., Giacomello, G. & Liquori, A. M. (1956). *Acta Cryst.* **9**, 510.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1957). *Acta Cryst.* **10**, 504.

Cruickshank, D. W. J. (1961*a*). *Acta Cryst.* **14**, 896.

Cruickshank, D. W. J. (1961*b*). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis,* p. 32. Oxford: Pergamon Press.

Hameka, H. F. & Liquori, A. M. (1956). *Proc. K. Ned. Akad. Wetensch.* **B59**, 242.

Higgs, P. W. (1955). *Acta Cryst.* **8**, 99.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Stewart, J. M. (1964). Technical Report TR-64-6, Univ. of Maryland Computer Science Center.

Wheatley, P. J. (1953). *Acta Cryst.* **6**, 369.

Acta Cryst. (1969). B**25**, 2236

The Crystal and Molecular Structure of Guanosine-5′-phosphate Trihydrate

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The crystal structure of guanosine-5′-phosphate trihydrate has been determined by a three-dimensional sharpened Patterson function and a Fourier synthesis, and was refined by the block-diagonal matrix least-squares method to a final R index of 0·086 for non-zero intensity reflexions. The space group is $P2_12_12_1$, and the unit-cell dimensions are $a=10{\cdot}64$, $b=6{\cdot}18$ and $c=25{\cdot}58$ Å with four molecules per unit cell. Of a total of 20 hydrogen atoms in an asymmetric unit, 15 atoms are located by difference Fourier synthesis. The conformation of the guanosine-5′-phosphate molecule in the crystal is similar to that of adenosine-5′-phosphate, and differs significantly from that of the disodium salt of inosine-5′-phosphate. The conformation of purine nucleotides in the solid state is discussed in connexion with that in an aqueous solution.

Introduction

Guanosine-5′-phosphate (9-*β*-5′-phospho-D-ribofuranosylguanine, 5′-GMP) is one of the important ribonucleic acid constituents. To date only the hydrogen-bonded helical structure of dried GMP gel has been reported (Gellert, Lipsett & Davies, 1962). While it is of fundamental importance to determine accurate molecular dimensions for this biochemically important material, the conformation of the molecule in the solid state is also of interest.

The conformation of the ribose or deoxyribose moiety in nucleotides and nucleosides in aqueous solution has been investigated by nuclear magnetic resonance spectra (Jardetzky, 1962, 1960; Lemieux, 1961) but the results do not always coincide with those for the solid state obtained by X-ray diffraction methods. As Jardetzky points out, the conformations of the ribose or deoxyribose moiety should be affected by the crystal field.

The molecular structure of 5′-GMP established by this investigation is compared with those of analogous purine nucleotides, *i.e.* adenosine-5′-phosphate (5′-AMP; Kraut & Jensen, 1963) and the disodium salt of inosine-5′-phosphate (disodium 5′-IMP; Nagashima & Iitaka, 1968), in which the intramolecular interactions between various substituents of the ribose ring are expected to be similar. Comparison of the molecular structures of these compounds may give some information on the factors determining the stable conformation of purine nucleotides in the solid state and in an aqueous solution.

The conventional formula of 5′-GMP and the numbering system used is illustrated in Fig. 1.

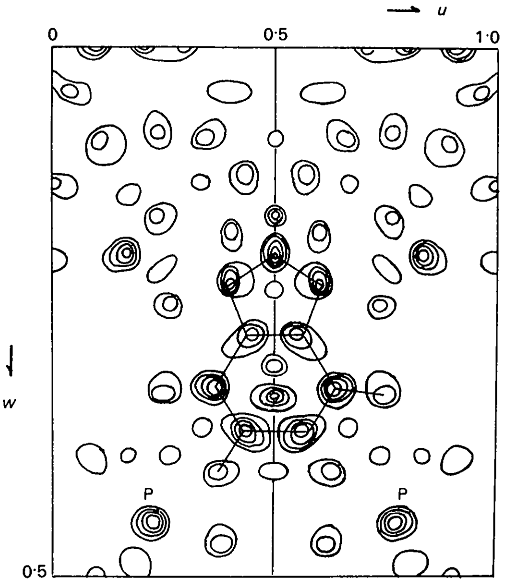


Fig. 1. Patterson map at $v=\frac{1}{2}$, the peak denoted by P corresponds to the vector between two equivalent phosphorus atoms.

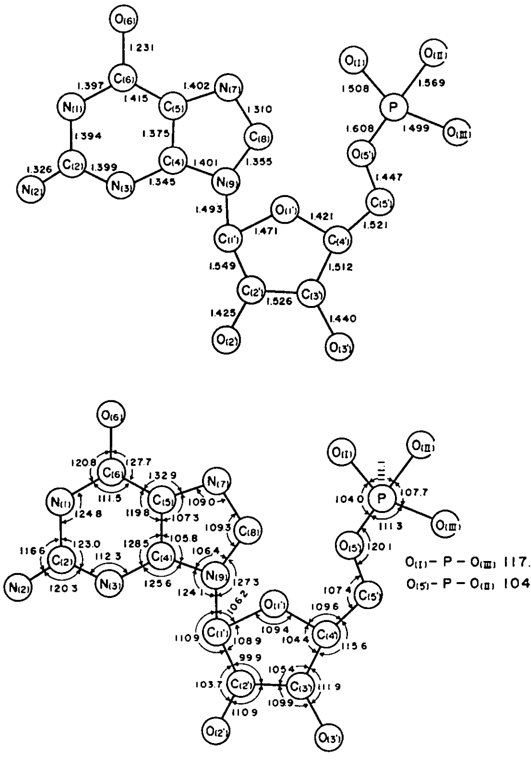


Fig. 2. The bond lengths (Å) and angles (σ) of the 5′-GMP molecule.

Experimental

An aqueous solution of the sodium salt of 5′-GMP was treated with a cation exchange resin (DOWEX-50W), concentrated at 50 °C and slowly cooled to room temperature. Fine needle-shaped crystals were separated from the solution.

The lattice constants and the space group were determined by Weissenberg and precession photographs rotated around the b axis. The crystal belonged to the orthorhombic system, and the systematic absences were h,k and l odd for $h00$, $0k0$ and $00l$ reflexions. The space group was determined as $P2_12_12_1$. Unit-cell parameters were: $a=10{\cdot}64$, $b=6{\cdot}18$, $c=25{\cdot}58$ Å, $V_c=1680$ Å^3. The observed density of the crystals measured by the flotation method was 1·644 g.cm^{-3}, and the calculated value with four molecules per unit cell was 1·650 g.cm^{-3}.

The intensity data were recorded by the multi-film Weissenberg method from the zero to fifth layers around the b axis, and measured visually.

Of the possible 2100 reflexions within the limiting sphere of Cu $K\alpha$ radiation, 1876 reflexions were recorded on the films, 220 of which were too weak to be measured. Lorentz and polarization corrections were applied and the approximate scale and temperature factors for each layer were estimated by Wilson's method. No absorption corrections were applied.

Determination of the structure

A three-dimensional sharpened Patterson function with $F_0^2 \exp [5{\cdot}0(\sin \theta/\lambda)^2]$ as Fourier coefficient was calculated. From packing considerations it was anticipated that the 5′-GMP molecule might be elongated along the c axis with its guanine base plane parallel to (010), since the conformation of the 5′-GMP molecule was expected to be similar to those of 5′-AMP and 5′-IMP.

On the $(u,\frac{1}{2},w)$ Patterson section the form of the guanine base appeared clearly (Fig. 2). The Patterson peaks were assigned to the vectors from a phosphorus atom to each atom of the guanine base. The map indicates that the y coordinate of the guanine-base plane differs by one half of the b axis period from that of a phosphorus atom, and that the difference between the x coordinates of a phosphorus atom and the C(8) atom of the guanine base is one half of the a axis period.

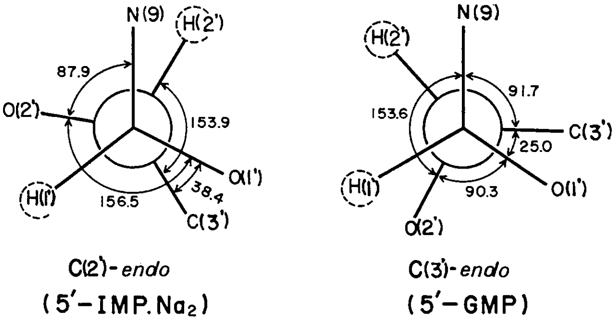
The positional parameters of the phosphorus atom were determined as (0·117, 0·200, 0·029) from $(\frac{1}{2},v,w)$, $(u,\frac{1}{2},w)$ and $(u,v,\frac{1}{2})$ Harker sections. From Fig. 2 the fractional coordinates of each of the atoms belonging to the guanine base could be determined relative to the phosphorus atom. Two sets of positional parameters were possible for the guanine base next to the phosphorus atom, but only one of them could lead to a reasonable result.

Structure factors were calculated by the use of the positional parameters of the phosphorus atom and the atoms belonging to the guanine base (one oxygen, five nitrogen and five carbon atoms) which were determined as described above; the *R* value at this stage was 0·53.

A Fourier synthesis with the weighting system of Sim (1961) revealed the positions of the atoms in the ribose ring. All the remaining atomic coordinates were subsequently obtained. The *R* value for the complete trial structure with isotropic temperature factors was 0·277.

Refinement of the structure

After three cycles of block-diagonal matrix least-squares refinement with isotropic temperature factors, the *R* value was decreased to 0·137. Two cycles of isotropic, and then three cycles of anisotropic, block-diagonal matrix least-squares refinements were carried out, and the *R* value was reduced to 0·095. The weighting scheme at this stage was $W = 30/F_o$ for $F_o > 30$, $W = 1{\cdot}0$ for $30 \geq F_o > 10$ and $W = 0{\cdot}5$ for $F_o \geq 10$.



C(2')-*endo* ($5'$-IMP.Na$_2$)

C(3')-*endo* ($5'$-GMP)

Fig. 3. Internal rotation around the C(1′)–C(2′) bond.

Table 1. *Positional parameters in fractional coordinates and their estimated standard deviations in* Å

	x/a	*y/b*	*z/c*	*S*(*x*)	*S*(*y*)	*S*(*z*)
P	−0·11468	0·70290	0·47390	0·0026	0·0030	0·0022
N(1)	−0·05452	0·31851	0·16132	0·0081	0·0101	0·0076
C(2)	−0·18500	0·31774	0·16167	0·0098	0·0113	0·0085
N(2)	−0·24202	0·30849	0·11549	0·0085	0·0110	0·0076
N(3)	−0·25347	0·31762	0·20572	0·0078	0·0102	0·0075
C(4)	−0·18109	0·32620	0·24877	0·0092	0·0121	0·0088
C(5)	−0·05212	0·32773	0·25214	0·0090	0·0118	0·0092
C(6)	0·02113	0·32290	0·20597	0·0089	0·0115	0·0083
O(6)	0·13647	0·32700	0·20229	0·0068	0·0086	0·0070
N(7)	−0·02097	0·32783	0·30536	0·0076	0·0093	0·0069
C(8)	−0·12448	0·33299	0·33306	0·0091	0·0106	0·0086
N(9)	−0·22493	0·33146	0·30046	0·0076	0·0095	0·0072
C(1′)	−0·36056	0·34063	0·31521	0·0088	0·0116	0·0084
O(1′)	−0·36566	0·30476	0·37003	0·0072	0·0086	0·0061
C(2′)	−0·41698	0·56615	0·30306	0·0086	0·0114	0·0086
O(2′)	−0·54860	0·52274	0·29515	0·0067	0·0087	0·0071
C(3′)	−0·39472	0·67807	0·35543	0·0095	0·0129	0·0096
O(3′)	−0·38155	0·85054	0·36326	0·0075	0·0089	0·0075
C(4′)	−0·40887	0·50299	0·39630	0·0099	0·0133	0·0096
C(5′)	−0·33437	0·53678	0·44637	0·0108	0·0146	0·0104
O(5′)	−0·20871	0·60111	0·43128	0·0071	0·0086	0·0065
O(I)	−0·01391	0·81049	0·44160	0·0076	0·0094	0·0069
O(II)	−0·06075	0·50326	0·50447	0·0086	0·0099	0·0075
O(III)	−0·18384	0·84208	0·51232	0·0081	0·0086	0·0073
O(IV)	0·22353	0·30855	0·33350	0·0071	0·0092	0·0074
O(V)	0·29167	0·29713	0·43776	0·0080	0·0096	0·0075
O(VI)	0·03282	0·23140	0·43793	0·0079	0·0088	0·0078

Table 2. *Positional parameters of hydrogen atoms in fractional coordinates and their estimated standard deviations in* Å

	x/a	*y/b*	*z/c*	*S*(*x*)	*S*(*y*)	*S*(*z*)
H(N1)	−0·010	0·322	0·128	0·13	0·16	0·12
H(N2)	−0·189	0·288	0·092	0·13	0·16	0·12
H′(N2)	−0·330	0·337	0·114	0·13	0·16	0·12
H(C8)	−0·142	0·323	0·372	0·13	0·15	0·12
H(C1′)	−0·407	0·227	0·291	0·12	0·15	0·12
H(C2′)	−0·381	0·642	0·271	0·13	0·14	0·12
H(C4′)	−0·494	0·453	0·408	0·14	0·15	0·12
H(O2′)	−0·567	0·480	0·271	0·13	0·15	0·13
H(C5′)	−0·322	0·347	0·467	0·12	0·15	0·12
H′(C5′)	−0·395	0·650	0·462	0·12	0·15	0·12
H(O IV)	0·242	0·317	0·371	0·13	0·16	0·12
H(O V)	0·326	0·175	0·447	0·12	0·16	0·12
H′(O V)	0·323	0·390	0·463	0·13	0·15	0·12
H(O VI)	0·100	0·185	0·434	0·12	0·15	0·12
H′(O VI)	0·043	0·347	0·471	0·13	0·15	0·12

A difference Fourier synthesis was then calculated. Of a total of 20 hydrogen atoms in the asymmetric unit, 15 were actually located at stereochemically reasonable positions. The peak heights ranged from 0·35 to 0·66 e.Å^{-3}. The positional parameters of the hydrogen atoms were then adjusted by block-diagonal matrix least-squares with their isotropic temperature factors fixed at 3·0 (a slightly higher value than the isotropic temperature factors of non-hydrogen atoms). The R value after this final refinement was 0·086 for 1656 observed reflexions.

Atomic scattering factors used for phosphorus, oxygen, nitrogen, carbon and hydrogen atoms were those of *International Tables for X-ray Crystallography* (1962).

The final parameter shifts of the non-hydrogen atoms, in terms of their standard deviations, were on average 0·30σ and the maximum shift was 0·66σ.

The refined atomic parameters are given in Tables 1, 2 and 3. The observed and calculated structure factors are listed in Table 4.

Results and discussion

The bond lengths and angles of the 5′-GMP molecule are shown in Fig. 1. The e.s.d.'s of the bond lengths are: P–O, 0·008; C–O, 0·012; C–N, 0·012 and C–C, 0·015 Å,

Table 3. *Thermal parameters of non-hydrogen atoms and their estimated standard deviations* (*in parentheses*), × 10^5

B_{ij} is defined by

$$T=\exp\,(-B_{11}h^2-B_{22}k^2-B_{33}l^2-2B_{12}hk-2B_{13}hl-2B_{23}kl)\,.$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	431 (18)	1055 (76)	39 (3)	−84 (39)	16 (7)	−34 (13)
N(1)	468 (70)	848 (276)	69 (11)	44 (130)	33 (24)	−70 (50)
C(2)	601 (86)	343 (304)	55 (12)	40 (145)	8 (27)	4 (54)
N(2)	562 (76)	1315 (293)	55 (11)	−44 (147)	−14 (24)	5 (52)
N(3)	409 (66)	1208 (281)	53 (10)	−91 (130)	14 (23)	48 (51)
C(4)	423 (80)	810 (341)	64 (13)	−28 (146)	20 (27)	1 (56)
C(5)	286 (70)	710 (334)	85 (13)	94 (139)	−27 (26)	−52 (56)
C(6)	379 (72)	926 (314)	45 (11)	115 (141)	13 (25)	−15 (54)
O(6)	400 (59)	1531 (254)	99 (11)	46 (114)	35 (22)	7 (47)
N(7)	368 (62)	822 (267)	44 (10)	−42 (117)	9 (21)	−9 (45)
C(8)	275 (70)	741 (315)	70 (12)	144 (139)	−4 (26)	−10 (51)
N(9)	352 (63)	949 (277)	50 (10)	72 (67)	−40 (22)	13 (46)
C(1′)	297 (73)	1226 (350)	53 (12)	−90 (133)	3 (24)	22 (51)
O(1′)	588 (65)	1227 (234)	53 (9)	−56 (122)	13 (20)	46 (41)
C(2′)	246 (72)	1486 (358)	42 (11)	−12 (124)	49 (24)	18 (52)
O(2′)	255 (56)	1966 (268)	89 (11)	−18 (104)	−17 (22)	−71 (46)
C(3′)	340 (76)	1426 (359)	90 (14)	−38 (162)	−41 (29)	15 (61)
O(3′)	491 (64)	1343 (282)	112 (12)	149 (114)	6 (24)	−112 (47)
C(4′)	379 (86)	1885 (392)	62 (13)	44 (147)	45 (28)	−36 (60)
C(5′)	440 (89)	2879 (469)	77 (15)	−309 (171)	97 (32)	−18 (69)
O(5′)	413 (59)	2080 (263)	48 (9)	−87 (108)	30 (20)	−87 (41)
O(I)	648 (70)	1489 (267)	80 (10)	−274 (131)	2 (23)	68 (50)
O(II)	768 (79)	2211 (296)	74 (11)	−138 (134)	24 (26)	110 (49)
O(III)	830 (79)	918 (272)	102 (12)	−124 (123)	81 (25)	−77 (45)
O(IV)	435 (63)	1599 (264)	116 (12)	−20 (123)	−34 (23)	51 (53)
O(V)	686 (72)	1429 (259)	104 (12)	−144 (130)	−56 (25)	−44 (51)
O(VI)	644 (75)	1435 (289)	126 (12)	205 (119)	43 (27)	−4 (48)

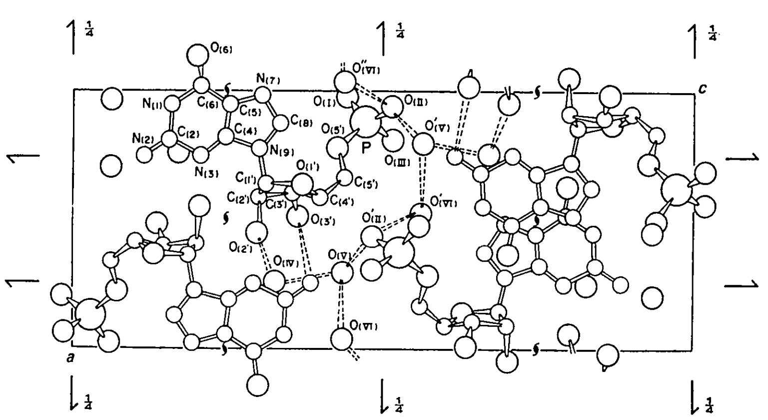


Fig. 4. The crystal structure projected along the b axis.

and that of the bond angles about 1°. Table 5 contains bond lengths and angles of covalent bonds involving hydrogen atoms.

(*a*) *The phosphate group*

The bond lengths and angles in the phosphate group are as expected in an organic monophosphate. Com-

Table 4. *Observed and calculated structure factors*

L	FO	FC
H,K=	0	0
2	318	355
4	284	323
6*	878	959
8*	912	925
10	104	91
12*	475	499
14*	432	434
16*	617	630
18	200	198
20	313	332
22*	712	848
24*	0	17
26	296	300
28	179	162
30	353	340
H,K=	1	0
1*	441	417
2	321	285
3	227	194
4*	0	39
5*	874	947
6*	444	457
7*	648	770
8*	94	87
9	154	130
10	229	164
11*	634	579
12	172	174
13	370	334
14	400	385
15	139	113
16	363	359
17	120	109
18*	0	22
19	137	113
20*	443	468
21	241	241
22*	0	17
23	385	460
24	101	115
25*	87	123
26	274	249
27	164	146
28	230	189
29	307	279
30	170	140
31	217	207
H,K=	2	0
0	220	201
1	374	321
2	117	137
3*	076	1288
4	222	219
5*	003	1153
6	116	109
7	399	371
8	112	93
9*	457	469
10*	0	0
11	367	304
12	208	217
13*	65	38
14	206	212
15	130	96
16*	0	35
17	303	319
18	244	218
19	118	104
20	223	242
21	344	384
22	178	168
23	224	230
24*	92	89
25*	0	13
26*	59	66
27*	92	97
28*	0	7
29	161	139
30*	53	65
31*	0	2
32*	61	40
H,K=	3	0
1*	0	50
2*	132	1245
3*	628	579
4	391	393
5*	581	546
6*	0	18
7	212	193
8	338	313
9	178	169
10*	505	519
11	166	177
12*	440	446
13*	444	431
14*	0	26
15*	427	416
16*	0	5
17	138	101
18*	0	5
19	161	143
20*	0	38
21	128	118
22*	0	33
23	479	425
24*	87	123
25*	66	70
26	116	108
27	135	127
28	246	238
29*	66	57
30	102	111
31*	97	88
H,K=	4	0
0	401	314
1	423	300
2	304	293
3*	0	71
4	196	187
5*	531	505
6*	535	500
7	258	234
8*	534	563
9	212	214
10*	69	38
11*	67	86
12	117	66
13	145	134
14*	497	479
15	258	250
16	405	418
17*	0	5
18	361	359
19*	0	23
20	321	330
21*	0	25
22	126	118
23	167	185
24	163	179
25	118	125
26*	79	66
27*	94	70
31*	51	59
H,K=	5	0
1*	712	701
2*	819	756
3	138	136
4	256	236
5	228	234
6	301	279
7	196	195
8	258	230
9*	574	615
10	123	93
11	326	326
12*	67	56
13	290	283
14*	80	62
15	292	296
16*	0	62
17*	0	18
18*	0	7
19	137	128
20	205	237
21	232	269
22	192	180
23*	0	14
24*	0	2
25*	0	7
26*	0	37
27	135	121
28	115	108
29*	54	49
30*	53	63
H,K=	6	0
0*	0	20
1	118	94
2	165	140
3*	53	3
4*	48	35
5*	0	24
6	220	176
7*	539	534
8	188	170
9	349	321
10*	447	389
11*	70	84
12*	0	7
13*	0	1
14	142	129
15*	698	781
16	261	260
17	194	190
18*	0	27
19	126	111
20*	0	6
21	305	354
22	156	164
23*	0	19
24*	0	4
25*	0	0
26	150	136
27	119	98
28*	65	53
29*	74	61
H,K=	7	0
1	118	63
2	273	249
3	131	109
4*	0	48
5	376	381
6	239	224
7	253	213
8	373	398
9	273	260
10	164	137
11	374	408
12	269	246
13	131	94
14	389	424
15	119	111
16	174	167
17*	0	35
18*	0	39
19*	87	87
20*	0	47
21	219	202
22*	0	0
23*	0	8
24	111	117
25*	0	29
26	107	106
27*	0	13
28	130	135
H,K=	8	0
0	291	253
1	222	203
2*	0	42
3	366	360
4	229	251
5	197	187
6	195	218
7*	0	16
8	121	111
9	271	251
10	154	133
11	155	178
12	178	475
13*	539	112
14*	89	104
15*	89	62
16*	87	134
17	150	128
18	119	251
19	237	223
20	263	264
21	126	120
22*	0	21
23*	0	1
24	142	141
25	150	149
26*	75	59
H,K=	9	0
1	124	122
2	176	156
3	124	115
4	203	193
5	239	228
6*	89	86
7*	431	486
8	214	224
9	135	132
10*	0	21
11	373	411
12*	0	16
13*	0	47
14*	0	0
15	119	116
16	101	91
17*	56	60
18*	77	84
19	143	131
20*	70	86
21*	0	41
22*	0	11
23*	91	114
24*	53	63
H,K=	10	0
0*	0	11
1	154	176
2	299	319
3*	0	18
4*	0	43
5	305	307
6*	0	15
7	336	350
8*	0	11
9*	86	68
10	160	152
12*	83	74
11*	0	31
13	229	227
14*	0	0
15*	0	3
16	126	110
17	242	249
18*	65	83
19	126	84
20*	96	107
21	104	99
H,K=	11	0
1	171	147
2	289	285
3*	59	68
4*	59	81
5*	58	37
6	142	123
7*	57	72
8	115	128
9*	0	16
10	247	206
11*	0	11
12	141	149
13*	62	76
14*	0	51
15*	0	18
16	238	215
17*	51	58
H,K=	12	0
0	232	229
1*	65	87
2*	0	29
3*	89	84
4*	71	70
5*	87	87
6	121	102
7*	0	31
8*	81	87
9*	73	73
10	107	99
11*	72	56
12*	97	75
13	110	97
14*	33	25
15*	100	104
H,K=	13	0
1*	68	61
2*	55	53
3*	42	45
4*	0	6
5	142	131
6*	0	18
7	110	101
8*	77	49
9*	99	104
H,K=	0	1
2*	563	834
3	281	283
4*	43	54
5	417	442
6*	729	736
7*	450	402
8*	93	99
9*	639	644
10	184	145
11	363	299
12	311	284
13*	0	9
14	169	143
15	114	96
16	104	98
17*	564	611
18*	87	74
19	128	94
20*	0	34
21	318	325
22	144	117
23	262	290
24	108	117
25*	0	18
26	107	106
27*	65	70
28	137	116
29*	0	58
30*	81	83
31	123	126
32*	49	56
H,K=	1	1
0*	771	1127
1*	596	636
2*	95	122
3*	878	979
4	250	238
5*	684	704
6*	435	416
7*	878	925
8	178	178
9	117	76
10	178	180
11	414	413
12	207	185
13	355	343
14	148	134
15	232	215
16	173	161
17	155	131
18*	71	47
19	237	254
20	145	143
21	119	106
22	221	239
23	141	129
24	133	128
25	257	269
26*	76	73
27	289	276
28	198	180
H,K=	0	1
29	175	58
30	219	83
31*	86	126
32	130	56
H,K=	2	1
0*	452	399
1	188	171
2*	782	833
3*	475	459
4*	762	729
5	238	226
6	273	262
7	213	227
8*	527	482
9*	566	534
10*	614	580
11	353	349
12*	692	655
13	207	196
14*	43	57
15	202	194
16*	47	57
17	111	108
18	365	389
19	106	111
20	402	426
21*	0	23
22	113	94
23	249	248
24	240	242
25	109	107
26	106	120
27	182	168
28*	0	24
29*	61	68
30*	38	41
31*	99	72
32*	74	81
H,K=	3	1
0*	468	419
1	323	305
2*	775	664
3	115	95
4	163	159
5*	474	437
6*	498	458
7*	454	429
8*	435	375
9	178	161
10	154	141
11*	872	915
12*	428	407
13	185	186
14	311	358
15	261	256
16	222	225
17	199	189
18	198	220
19	202	219
20	222	239
21	240	292
22	145	117
23	126	119
24	189	188
25	186	180
26	200	194
27*	97	100
28	128	116
29	130	125
30	149	155
31*	73	72
H,K=	4	1
0*	93	92
1	167	147
2*	535	492
3*	579	562
4	210	221
5*	643	604
6*	561	524
7	196	171
8	410	396
9	210	191
10	259	290
11	182	171
12	211	198
13	175	163
14*	0	20
15	252	254
16*	73	59
17	342	397
18*	59	97
19	189	202
20*	0	27
21	129	136
22	121	128
23	296	350
24	102	93
25*	99	97
26	123	114
27*	0	14
28*	59	65
29*	58	60
30*	38	38
H,K=	5	1
0*	0	16
1	130	82
2	121	104
3*	696	693
4	371	332
5	211	209
6	177	141
7	163	167
8	311	305
9	114	120
10*	552	565
11*	501	498
12*	537	581
13	141	138
14	162	143
15	209	205
16	269	278
17	118	105
18*	55	69
19	251	257
20	187	221
21	178	196
22	110	102
23	234	249
24*	73	57
25	129	136
26	161	158
27*	69	87
28*	94	82
29*	81	67
30	115	138
H,K=	6	1
0*	533	508
1*	512	484
2	266	256
3*	96	68
4	241	218
5*	0	28
6	183	142
7*	46	49
8	230	230
9	255	255
10*	99	83
11*	0	34
12	281	273
13	297	317
14	270	280
15	104	62
16*	55	69
17	207	217
18	414	471
19	159	182
20*	97	80
21	134	150
22	141	157
23	102	97
24	109	111
25*	0	24
26*	53	44
27	143	116
28	146	150
H,K=	7	1
0	263	282
1	153	127
2	121	106
3	250	245
4	290	282
5	113	70
6	266	282
7	242	231
8*	51	42
9	408	434
10	303	322
11*	76	70
12	318	357
13*	521	590
14	144	143
15	223	246
16	179	181
17	147	167
18	132	136
19	134	135
20*	93	94
21*	0	8
22*	70	80
23*	78	105
24*	51	65
25*	98	111
26*	87	81
27*	51	53
H,K=	8	1
0	105	79
1	202	196
2*	71	55
3	279	308
4*	53	54
5	229	221
6	231	214
7	223	204
8	278	315
9	175	167
10	132	129
11	215	259
12	216	235
13	219	217
14	266	300
15*	0	44
16	175	193
17	225	228
18*	85	108
19	161	155
20	171	166
21*	78	94
22*	98	71
23	166	159
24*	46	41
25	107	106
H,K=	9	1
0	137	142
1	137	146
2*	55	73
3	112	112
4*	422	495
5	243	238
6	262	272
7	121	122
8*	0	33
9	179	185
10	223	262
11*	75	80
12	122	131
13*	78	63
14*	77	77
15	106	128
16*	73	89
17	107	121
18	178	159
19*	0	11
20	140	124
21	170	152
22*	89	58
23*	78	66
H,K=	10	1
0	265	295
1	165	175
2	112	101
3	159	164
4	144	162
5*	55	49
6*	0	22
7	144	153
8*	60	76
9*	73	72
10	120	108
11	113	101
12*	65	65
13*	64	50
14	110	105
15*	0	33
16*	86	67
17*	0	31
18*	67	72
19	195	202
20	113	100
21*	65	48
H,K=	11	1
0*	0	41
1	225	205
2*	0	51
3	203	196
4*	0	8
5	169	173
6*	51	60
7	145	117
8*	0	34
9	169	169
10	131	114
11*	69	76
12*	65	76
13*	43	44
14*	97	87
15	121	112
16	109	120
17*	85	91
18	102	93
H,K=	12	1
0*	0	4
1*	0	36
2	215	203
3	191	161
4	181	177
5*	0	40
6*	72	81
7*	82	80
8*	0	16
9*	69	69
10*	0	27
11*	0	7
12*	54	55
13*	44	48
H,K=	13	1
0*	0	34
1*	33	69
2*	47	59
3*	33	43
4*	0	1
5*	86	84
6	103	124
7*	0	16
8*	84	94
9*	91	95
H,K=	0	2
2	219	206
3*	466	507
4	238	235
5*	660	791
6	305	333
7*	90	60
8	304	294
9	228	224
10*	682	646
11	132	120
12	192	194
13	210	227
14	126	123
15*	443	441
16*	53	44
17*	0	36
18	250	241
19	188	192
20	275	278
21	196	197
22	404	467
23	257	240
24*	0	32
25	295	312
26	211	219
27	132	98
28	151	139
29*	79	71
30*	40	58
31*	81	69
H,K=	1	2
0*	737	765
1*	895	1033
2*	816	844
3*	81	50
4*	462	500
5*	701	787
6	150	152
7*	592	617
8*	427	433
9*	491	487
10*	463	465
11	275	293
12	285	298
13	244	227
14*	0	30
15	243	213
16	330	342
17*	0	32
18	142	123
19*	75	64
20*	530	560
21*	453	495
22	248	251
23	260	262
24	208	204
25*	0	31
26	114	97
27	102	91
28	141	138
29	230	215
30*	39	62
31*	32	34
H,K=	2	2
0*	470	410

pared with the values for the phosphate groups in some organic phosphates so far determined by the X-ray diffraction method (Table 6), it can be concluded that the un-ionized OH in the phosphate group corresponds to O(II) and that the phosphate group exists as a monovalent anion.

Table 4 (*cont.*)

L	FO	FC
1	245	230
2	270	299
3*	562	527
4	280	291
5	251	247
6	393	391
7	375	360
8*	493	518
9	225	203
10*	660	626
11	246	232
12	205	185
13	416	390
14	316	343
15	281	270
16*	60	62
17	297	314
18	263	277
19	137	115
20*	87	94
21	139	141
22	186	178
23	305	338
24	160	173
25	141	133
26	137	156
27	103	95
28*	0	32
29*	0	32
30	132	121
H,K=	3	2
0*	0	14
1	341	308
2*	584	575
3*	542	526
4	176	185
5	292	304
6*	466	463
7	356	351
8*	490	493
9	316	318
10	379	376
11	111	95
12	250	230
13*	433	427
14*	58	54
15	264	235
16	276	268
17	324	350
18	165	142
19	171	166
20	186	172
21	162	167
22	152	153
23	189	183
24	164	158
25*	81	70
26*	54	27
27*	50	49
28	184	148
29	143	111
H,K=	4	2
0	232	217
1*	518	510
2	213	221
3	348	313
4	212	204
5	295	263
6	382	371
7	263	251
8	405	398
9	214	194
10	166	136
11	303	288
12*	0	37
13	229	208
14	143	132
15	337	359
16	299	302
17	120	109
18	367	401
19	237	242
20	299	327
21	182	197
22*	82	93
23*	84	96
24*	0	47
25*	78	79
26*	51	52
27*	52	54
28*	74	65
29	133	125
30*	53	42
H,K=	5	2
0	230	232
1	230	223
2	383	374
3	383	351
4	397	397
5	244	242
6	292	287
7	168	135
8	234	220
9	189	132
10	215	185
11	336	354
12*	0	45
13	273	257
14	267	274
15	175	172
16	130	121
17	170	139
18*	100	91
19*	83	76
20*	0	33
21	125	132
22	203	198
23*	81	72
24	117	116
25	198	184
26	143	120
27	144	138
28	162	153
29*	81	94
H,K=	6	2
0	210	196
1*	430	416
2	199	175
3	101	78
4	215	178
5	316	293
6	283	271
7	144	125
8	117	116
9*	74	50
10	272	265
11	129	111
12	256	253
13*	76	103
14	225	243
15	267	250
16	196	189
17	186	191
18*	68	58
19	160	178
20	199	220
21	253	263
22*	79	67
23*	76	99
24*	0	19
25*	80	64
26	109	88
27*	89	90
28*	49	58
H,K=	7	2
0	175	141
1	352	346
2	212	193
3	177	162
4	320	328
5*	441	407
6	301	293
7	156	146
8*	510	546
9	257	241
10*	0	29
11	134	123
12*	99	89
13	215	201
14	288	283
15	124	142
16*	0	35
17	179	191
18	161	183
19	101	103
20*	0	23
21*	0	22
22*	73	84
23	133	125
24*	44	51
25	120	112
26	101	119
H,K=	8	2
0*	496	538
1	255	270
2	128	86
3*	65	62
4	209	201
5	156	155
6	265	279
7	123	118
8*	67	77
9	319	348
10	236	256
11	243	238
12	352	348
13	308	307
14*	67	72
15*	0	72
16*	0	49
17	116	115
18	121	131
19*	72	76
20	128	133
21*	48	50
22*	56	90
23	116	108
24*	92	72
25*	90	89
H,K=	9	2
0	152	170
1	192	200
2	274	276
3	305	323
4	193	211
5	125	109
6	147	163
7	186	206
8	141	130
9	159	153
10	157	136
11	228	240
12	120	111
13	196	224
14*	63	72
15	200	218
16*	59	76
17*	0	20
18*	86	105
19*	47	57
20*	89	89
21	118	121
22	123	125
23*	88	89
H,K=	10	2
0*	86	72
1	157	176
2	147	151
3*	86	95
4	192	206
5	209	224
6	186	172
7*	59	55
8	102	98
9*	0	48
10	123	118
11*	97	98
12*	0	27
13*	58	81
14	102	110
15*	49	57
16*	46	59
17	194	189
18	148	125
19*	0	30
20	111	122
H,K=	11	2
0*	0	6
1*	56	73
2	181	165
3	221	220
4*	42	45
5*	54	62
6	115	112
7	106	108
8*	92	109
9*	50	45
10	182	169
11*	0	20
12	126	131
13*	75	79
14*	0	8
15	174	154
16	132	116
H,K=	12	2
0	181	179
1	161	165
2	114	109
3	112	86
4*	86	71
5	134	139
6*	55	60
7*	53	61
8*	0	40
9*	65	61
10	132	145
11*	95	82
12*	30	35
13*	68	79
H,K=	13	2
0*	0	28
1*	0	26
2	105	109
3*	72	85
4*	28	50
5*	90	112
H,K=	0	3
2*	81	140
3	139	156
4	112	148
5	158	158
6	131	138
7	367	379
8*	698	710
9	238	254
10*	97	61
11*	46	58
12	387	397
13	191	185
14*	443	433
15*	461	476
16	200	185
17	262	262
18*	506	532
19*	88	106
20	290	271
21	126	130
22*	0	37
23*	0	18
24*	0	16
25*	0	2
26	207	194
27*	0	30
28*	0	38
29*	67	46
30	105	149
H,K=	1	3
0*	520	562
1	193	227
2*	550	581
3	120	124
4	206	227
5	111	99
6	182	167
7	247	250
8	194	173
9	189	205
10	272	284
11*	51	59
12	257	257
13	383	388
14	236	221
15	283	281
16	160	164
17	279	291
18	327	330
19	268	269
20	135	113
21*	88	79
22	224	257
23	149	145
24	118	101
25*	66	69
26*	0	23
27	120	95
28	133	108
29*	66	53
30*	95	73
H,K=	2	3
0	308	272
1	175	144
2*	531	506
3	331	326
4	139	115
5*	434	426
6	223	243
7	200	182
8	136	123
9*	466	466
10	223	201
11	131	131
12	398	367
13*	587	616
14	163	164
15	108	109
16	144	145
17	138	108
18	172	191
19	153	161
20	176	170
21	217	221
22*	62	63
23	145	133
24	107	111
25*	78	78
26*	73	55
27	116	88
28	165	176
29	133	132
H,K=	3	3
0	226	245
1*	0	9
2	113	87
3*	527	473
4	202	201
5	353	308
6	327	326
7	187	185
8*	97	116
9	285	293
10*	577	586
11	144	133
12	254	240
13*	89	85
14	214	186
15	301	299
16	177	175
17*	77	72
18	148	146
19	176	185
20	279	297
21	187	196
22*	0	45
23*	83	98
24*	79	99
25	107	117
26	142	135
27	156	138
28*	96	77
H,K=	4	3
0	346	297
1	218	218
2*	464	467
3	207	194
4	126	116
5	278	317
6	203	188
7*	43	50
8*	427	413
9	212	195
10*	462	433
11*	54	37
12*	56	40
13	257	237
14	127	122
15	130	129
16	175	177
17	148	127
18	137	119
19	137	147
20*	0	30
21	157	191
22	214	222
23	114	113
24	118	123
25	123	125
26	138	117
27*	0	28
28	152	151
H,K=	5	3
0*	0	28
1	258	262
2	404	370
3*	501	506
4	185	176
5*	91	55
6	286	285
7*	58	55
8	266	252
9*	55	40
10	277	270
11	198	182
12	281	277
13	160	148
14	132	108
15	294	313
16	119	117
17*	68	59
18	101	91
19*	78	85
20	219	248
21	243	269
22	250	235
23	180	183
24	174	163
25	183	164
26	101	110
27*	85	105
H,K=	6	3
0	296	292
1	328	347
2	164	170
3	110	88
4	172	154
5	157	149
6	127	110
7	205	193
8	257	250
9*	59	25
10*	0	33
11	208	206
12	267	273
13	176	175
14*	0	41
15	161	170
16*	62	57
17	268	288
18	122	119
19	119	114
20	129	130
21	144	136
22	144	154
23	120	107
24*	69	62
25*	68	71
H,K=	7	3
0	275	283
1*	59	42
2	363	420
3	297	289
4	149	145
5	114	103
6	261	231
7	323	353
8	151	144
9	230	237
10*	62	60
11*	0	24
12	273	285
13	268	282
14	167	151
15	154	166
16*	86	70
17*	83	82
18*	81	87
19*	0	28
20	183	186
21*	66	93
22*	62	63
23*	42	47
24	127	112
25*	50	59
H,K=	8	3
0*	62	74
1	216	218
2	216	215
3	148	141
4	161	192
5	204	218
6	195	188
7	157	144
8	286	309
9	204	220
10	156	160
11	277	321
12*	67	95
13	118	125
14	220	235
15*	0	37
16	185	173
17*	60	73
18	101	112
19*	0	29
20*	79	88
21	103	101
22	128	107
23	130	145
H,K=	9	3
0	198	196
1	198	207
2*	0	44
3*	0	10
4	124	116
5	238	259
6*	100	101
7	227	245
8*	61	88
9*	85	93
10	220	245
11	196	179
12*	81	95
13*	0	29
14*	77	117
15	202	200
16*	74	84
17	116	99
18*	0	36
19*	67	79
20*	61	55
21	165	163
H,K=	10	3
0*	92	108
1	118	107
2	118	128
3*	94	99
4*	58	50
5*	58	43
6	174	179
7*	80	77
8*	79	79
9*	0	24
10*	95	112
11	118	118
12*	0	16
13*	0	34
14*	0	28
15*	69	65
16	178	168
17*	69	76
18*	83	87
H,K=	11	3
0*	0	46
1*	73	73
2	167	155
3*	0	48
4*	88	84
5	150	144
6	135	141
7	117	111
8*	0	5
9*	86	83
10*	96	88
11*	92	85
12*	0	38
13	116	102
14*	54	65
H,K=	12	3
0*	40	64
1*	97	96
2	146	178
3*	0	31
4*	61	69
5*	90	99
6*	0	33
7*	92	119
8*	53	72
9*	27	36
H,K=	0	4
2	256	395
3	226	233
4*	92	92
5	282	309
6	149	138
7	128	121
8*	0	4
9*	546	570
10*	0	57
11	270	240
12*	85	91
13*	463	470
14*	0	44
15*	455	455
16*	79	79
17*	57	46
18	195	172
19*	72	91
20*	0	23
21	342	408
22*	0	0
23	316	291
24	105	62
25	323	289
26*	0	42
27	133	149
H,K=	1	4
0	214	222
1	199	198
2	357	424
3	220	220
4	112	122
5*	84	83
6	132	111
7	219	204
8	218	203
9	252	242
10	237	257
11	168	129
12	309	310
13*	100	93
14	164	171
15	340	363
16*	70	64
17	127	117
18	211	193
19*	72	75
20	279	310
21	274	308
22	105	106
23*	98	117
24	191	174
25	107	100
26*	0	28
27*	62	76
H,K=	2	4
0	243	244
1*	98	109
2	226	226
3	214	196
4	246	257
5	212	181
6*	42	36
7	178	139
8*	429	455
9*	45	43
10	345	361
11*	96	87
12	323	325
13*	0	37
14	266	275
15*	55	57
16*	72	68
17	114	121
18	187	183
19	197	193
20*	71	61
21*	0	19
22	133	139
23	108	111
24*	0	41
25*	43	49
26*	55	55
27*	81	77
H,K=	3	4
0*	71	70
1*	92	80
2	212	213
3*	467	495
4	220	225
5	107	71
6	148	131
7	252	245
8	162	145
9*	0	30
10*	0	29
11	292	299
12	265	253
13	263	253
14	114	120
15	237	227
16	102	101
17	261	280
18*	92	101
19	149	177
20*	74	87
21*	53	63
22*	45	56
23*	78	84
24	188	177
25	143	141
26	125	128
27*	82	100
H,K=	4	4
0	123	100
1	333	334
2	100	103
3	168	171
4	102	92
5	333	318
6*	0	33
7	313	286
8	164	152
9	206	199
10*	41	19
11	272	247
12	123	107
13*	90	82
14*	25	32
15	227	227
16	136	119
17*	57	79
18	151	150
19*	24	26
20*	0	20
21	173	156
22*	49	43
23	164	151
24	109	96
25	154	146
26*	80	83
H,K=	5	4
0*	461	499
1	108	98
2	164	159
3	317	314
4	313	284
5	185	168
6	237	234
7	155	153
8*	41	65
9*	0	43
10	168	169
11*	0	30
12*	62	65
13*	0	24
14	187	196
15*	0	20
16	139	142
17	146	146
18	164	189
19	155	147
20*	88	74
21*	96	89
22	253	266
23	197	176
24*	0	29
25	103	104
H,K=	6	4
0	201	183
1	120	115
2*	68	66

Table 4 (*cont.*)

L	FO	FC
3	171	176
4	305	306
5*	70	87
6	342	401
7	127	136
8	171	167
9	185	193
10	235	223
11	109	94
12	115	115
13*	62	70
14	234	248
15*	0	10
16	212	213
17*	53	65
18	134	136
19	129	126
20	103	95
21*	73	83
22*	0	41
23	135	128
24*	81	77
H,K=	7	4
0	150	144
1	301	331
2	146	124
3	248	244
4	127	131
5	127	125
6	147	139
7*	0	21
8	228	233
9	109	107
10	194	187
11	134	135
12	138	125
13	136	144
14	119	124
15*	23	41
16*	97	91
17	136	141
18*	0	41
19	115	105
20	141	141
21*	63	80
H,K=	8	4
0*	80	55
1*	57	53
2*	98	108
3	127	123
4*	80	95
5	180	203
6	188	188
7*	0	37
8*	96	100
9	293	265
10	150	108
11	228	190
12	188	187
13	276	233
14	106	84
15*	77	94
16*	73	64
17*	0	38
18*	68	86
19*	61	65
20*	96	101
H,K=	9	4
0*	54	48
1*	77	95
2	211	194
3	216	184
4	215	202
5*	0	41
6*	0	23
7*	0	40
8	241	234
9	206	188
10	155	119
11*	43	64
12*	92	101
13*	34	28
14	173	154
15*	63	88
16	100	86
17*	41	40
18	131	148
H,K=	10	4
0*	0	55
1	167	153
2	119	102
3*	83	70
4	176	152
5*	36	37
6	212	200
7*	76	103
8	158	135
9	118	118
10	171	170
11	173	165
12*	61	62
13*	59	70
14	169	195
15*	89	90
H,K=	11	4
0*	0	28
1*	63	61
2	116	129
3	182	202
4*	0	17
5*	0	23
6*	0	39
7	117	111
8*	71	69
9*	28	27
10*	87	98
H,K=	0	5
2*	67	90
3*	93	98
4*	55	39
5	147	139
6*	31	38
7	160	168
8	284	295
9*	83	63
10	252	275
11	172	172
12	257	263
13	243	248
14	171	159
15*	81	77
16	115	83
17*	45	21
18*	67	71
19	110	108
20	237	239
21*	72	60
22*	0	33
23*	0	26
24*	0	10
25*	55	57
H,K=	1	5
0	259	340
1	213	238
2*	48	48
3	263	320
4*	0	10
5	246	240
6	278	278
7	231	241
8	305	333
9	163	145
10	121	112
11	151	137
12	123	114
13	126	141
14	239	227
15	227	210
16	124	115
17	123	119
18	145	148
19	234	239
20	152	133
21	159	120
22	116	106
23*	27	47
24*	66	62
25*	69	51
H,K=	2	5
0*	49	47
1*	84	89
2*	87	104
3*	84	79
4	118	115
5	258	280
6	110	105
7	259	278
8	190	178
9	253	261
10	239	287
11	142	155
12	201	196
13	298	311
14*	36	41
15	115	103
16	129	113
17*	0	22
18*	61	43
19*	0	14
20*	96	81
21*	0	49
22	112	90
23	184	206
24	133	156
25	103	114
H,K=	3	5
0	304	374
1*	0	23
2	289	362
3	135	121
4	110	114
5	131	121
6	176	187
7*	64	49
8	148	128
9*	68	62
10	244	262
11	187	188
12	232	233
13	187	165
14	151	139
15	197	199
16*	99	84
17	133	128
18*	48	37
19*	47	47
20	254	262
21	169	139
22*	33	29
23*	38	38
24	136	140
H,K=	4	5
0	166	211
1	145	167
2	246	285
3*	51	52
4	232	265
5*	57	62
6*	67	75
7	131	131
8	189	183
9	107	96
10	273	287
11*	51	59
12*	86	76
13*	0	7
14*	93	92
15*	0	18
16*	75	77
17	103	111
18*	78	86
19*	0	19
20*	41	68
21	107	78
22	115	101
23	121	106
H,K=	5	5
0*	42	48
1	275	311
2*	95	81
3	288	334
4*	99	114
5	132	112
6*	50	57
7	117	114
8*	93	84
9	165	171
10	169	165
11*	63	74
12	138	146
13*	76	71
14	115	110
15*	0	34
16	156	166
17*	0	19
18*	85	89
19	138	116
20	173	166
21	237	234
22	103	103
H,K=	6	5
0	172	185
1	178	193
2	182	202
3	115	116
4*	100	78
5	152	165
6*	93	92
7	163	180
8	110	110
9	131	137
10*	0	26
11	116	96
12*	55	65
13	195	183
14*	75	94
15	178	159
16	165	146
17*	78	53
18	151	124
19	129	113
20	110	97
21	102	114
H,K=	7	5
0	191	208
1*	0	45
2	182	181
3*	72	75
4*	0	41
5	140	140
6	114	103
7*	0	21
8*	83	81
9	133	136
10	142	140
11	200	171
12	280	253
13	131	109
14*	83	81
15	156	135
16	166	133
17*	68	49
18	135	120
H,K=	8	5
0*	0	36
1*	34	63
2*	88	92
3*	0	28
4*	0	22
5	122	104
6*	0	27
7	155	130
8	282	293
9	123	117
10*	53	56
11	200	196
12*	78	94
13	102	81
14	214	219
15	127	118
H,K=	9	5
0*	85	95
1*	85	81
2	174	154
3*	0	36
4	117	109
5	204	215
6*	74	57
7*	88	90
8*	70	75
9*	75	63
10*	0	35
11*	37	48
12*	83	72
13*	96	104
H,K=	10	5
0	116	93
1*	94	76
2	105	69
3	113	88
4*	23	44
5	123	96
6*	76	65
7*	94	80
8*	85	72

Table 5. *Bond lengths and angles involving hydrogen atoms*

Bond lengths

N(1)–H(N1)	0·97 Å	C(5′)—H(C5′)	1·30 Å
C(8) –H(C8)	1·01	C(5′)—H′(C5′)	1·03
N(2)–H(N2)	0·83	O(IV)–H(O IV)	0·99
N(2)–H′(N2)	0·95	O(V)–H(O V)	0·87
C(1′)–H(C1′)	1·06	O(V)–H′(O V)	0·92
C(2′)–H(C2′)	1·03	O(VI)–H(O VI)	0·78
C(4′)–H(C4′)	1·01	O(VI)–H′(O VI)	1·10
		O(2′) –H(O2′)	0·70

Bond angles

H(N1) –N(1)–C(6)	116°	H(C2′)—C(2′)—C(3′)	116°
H(N1) –N(1)–C(2)	119	H(C4′)—C(4′)—C(3′)	121
H(C8)—C(8) –N(7)	133	H(C4′)—C(4′)—O(1′)	102
H(C8)—C(8) –N(9)	128	H(C4′)—C(4′)—C(5′)	105
H′(N2)–N(2)–H(N2)	131	H(C5′)—C(5′)—H′(C5′)	121
H′(N2)–N(2)–C(2)	119	H(C5′)—C(5′)—C(4′)	106
H(N2) –N(2)–C(2)	110	H(C5′)—C(5′)—O(5′)	106
H(C1′)–C(1′)–N(9)	106	H′(C5′)—C(5′)—C(4′)	95
H(C1′)–C(1′)–C(2′)	107	H′(C5′)—C(5′)—O(5′)	120
H(C1′)–C(1′)–O(1′)	113	H(O V)—O(V)—H′(O V)	101
H(C2′)–C(2′)–C(1′)	115	H(O VI)–O(VI)–H′(O VI)	105
H(C2′)–C(2′)–O(2′)	111	H(O2′)—O(2′) –C(2′)	118

Hydrogen bonding at the phosphate group will be discussed later.

(*b*) *The guanine ring*

The bond lengths and angles in the guanine group of 5′-GMP are very close to the corresponding values of guanine bases and their derivatives determined so far by X-ray crystal structure analysis.

The C(6)–O(6) bond length of 1·231 Å corresponds to a C–O double bond. It shows that the guanine base is in a lactam form. The C(2)–N(2) bond (1·326 Å) has a considerable amount of double bond character. Simi-

Table 6. *Bond lengths* (Å) *and angles* (°) *in some organic phosphates*

		P=O	P–O$^-$	P–OH	P–OR
2-Aminoethyl phosphate	(1)	1·493	1·503	1·557	1·591
L-Serine phosphate	(2)	1·497	1·517	1·560	1·608
3′-CMP(monoclinic form)	(3)	1·480	1·498	1·588	1·610
3′-CMP(orthorhombic form)	(4)	1·483	1·504	1·551	1·611
3′-AMP	(5)	1·477	1·486	1·579	1·612
5′-AMP	(6)	1·495	1·514	1·566	1·610
5′-GMP	(7)	1·499	1·508	1·569	1·608

	O=P–O$^-$	O=P–OH	O=P–OR	HO–P–O$^-$	RO–P–O$^-$	RO–P–OH
2-Aminoethyl phosphate	117·4	109·8	103·9	109·3	109·6	106·2
3′-CMP(monoclinic form)	117·5	112·5	105·5	105·5	110·9	104·3
3′-CMP(orthorhombic form)	116·0	113·6	110·1	106·1	108·5	101·5
3′-AMP	117·2	107·1	110·7	112·3	103·4	105·5
5′-AMP	118·2	106·4	105·7	110·2	108·7	106·5
5′-GMP	117·0	107·7	111·3	111·1	104·0	104·9

(1) Kraut (1961)
(2) McCallum, Robertson & Sim (1959)
(3) Bugg & Marsh (1967)
(4) Sundaralingam & Jensen (1965)
(5) Sundaralingam (1966)
(6) Kraut & Jensen (1963)
(7) This investigation.

lar values have been reported for the length of the C–N bond between an amino group and a purine or pyrimidine base, *i.e.* 1·331 Å in deoxyguanosine (Haschemeyer & Sobell, 1965), 1·312 Å in 5′-AMP (Kraut & Jensen, 1963), 1·332 Å in cytosine (Jeffrey & Kinoshita, 1963) and 1·331 Å in cytidine-3′-phosphate (3′-CMP; Bugg & Marsh, 1967).

The deviation of the glycosidic bond N(9)–C(1′) from the guanine-base plane is 0·067 Å at the C(1′) atom position (see Table 7). A similar small deviation from the plane has also been encountered in calcium thymidylate (0·050 Å; Horn & Luzatti, 1961). In contrast, this deviation is large in 5′-AMP (0·211 Å; Kraut & Jensen, 1963).

Table 7. *Deviations from the least-squares plane of the guanine ring*

The equation of the least-squares plane, with coefficients equal to the direction cosines with respect to the crystallographic axes is:

$$-0{\cdot}0034X+0{\cdot}9998Y-0{\cdot}0213Z=1{\cdot}880\ \text{Å}\ .$$

	Deviation		Deviation
N(1)	0·003 Å	N(7)	0·020 Å
C(2)	0·002	C(8)	0·001
N(3)	0·020	N(9)	0·013
C(4)	0·007	O(6)*	0·026
C(5)	0·010	N(2)*	0·028
C(6)	0·003	C(1′)*	0·067

* Atoms excluded from the calculation of the least-squares plane.

(*c*) *Conformation of the molecule*

The ribose ring puckering in 5′-GMP is described as C(3′)-*endo*, in which the C(3′) atom is displaced by 0·515 Å from the plane formed by the remaining four ring atoms (see Table 8). This deviation from the plane is rather small compared with the values of 0·66 Å in 5′-AMP (Kraut & Jensen, 1963) and 0·62 Å in disodium 5′-IMP (Nagashima & Iitaka, 1968).

Table 8. *Deviations from the least-squares plane of the ribose ring of* 5′-GMP

The equation of the least-squares plane, with coefficients equal to the direction cosines with respect to the crystallographic axes is:

$$0{\cdot}9279X+0{\cdot}3703Y+0{\cdot}0443Z=-2{\cdot}457\ \text{Å}\ .$$

	Deviation		Deviation
C(1′)	0·035 Å	N(9)*	1·336 Å
C(2′)	−0·020	O(2′)*	−1·428
C(3′)*	0·515	O(3′)*	0·062
C(4′)	0·021	C(5′)*	0·891
O(1′)	−0·036		

* Atoms excluded from the calculation of the least-squares plane.

Conformational aspects of the 5′-GMP molecule in the solid state are summarized in Table 9 together with those of the other two purine nucleotides, disodium 5′-IMP and 5′-AMP. As is seen in the Table, the whole molecular structure of 5′-GMP resembles 5′-AMP and differs significantly from 5′-IMP.

Internal rotation of the ribose ring around the C(1′)–C(2′) bond is illustrated in Fig. 3. In the C(2′)-*endo* conformation (disodium 5′-IMP) H(1′) and H(2) are *trans*, and in the C(3′)-*endo* conformation they are *gauche* with respect to their central bond, C(1′)–C(2′).

Proton spin-spin coupling constants between H(1′) and H(2′) of 5′-GMP and 5′-IMP in aqueous solution (*p*H 7) have been obtained in our laboratory, and the corresponding value in 5′-AMP was reported by Jardetzky (1962). These values are listed in Table 10. The dihedral angle H(1′)-C(1′)–C(2′)-H(2′) was estimated as shown in the Table. These results suggest that both these purine nucleotides have the same ribose conformation as each other, *i.e.* C(2′)-*endo*, in aqueous solution. In the C(3′)-*endo* conformation the dihedral angle H(1′)–C(1′)–C(2′)–H(2′) is expected to be about 90° as is seen in Fig. 3. If this were also the case in aqueous solution the spin-spin coupling constant between them would be much smaller.

Table 9. *Conformation of crystalline purine 5′- nucleotides*

	Ribose conformation	φ_{CN}*	φ_{OO}†	φ_{OC}‡
5′-GMP	C(3′)-*endo*	−12·4	71·9	45·9
5′-AMP	C(3′)-*endo*	−18	78	40
5′-IMP.Na$_2$	C(2′)-*endo*	−43	60·5	56

* The dihedral angle O(1′)–C(1′)–N(9)–C(8); the sign of the angle is as defined by Donohue & Trueblood (1960), Sundaralingam & Jensen (1965).

† The dihedral angle O(5′)–C(5′)–C(4′)–O(1′).

‡ The dihedral angle O(5′)–C(5′)–C(4′)–C(3′). The notations φ_{OO}, φ_{OC} are those of Shefter & Trueblood (1965).

Table 10. H(1′)–H(2′) *proton spin-spin coupling constants in an aqueous solution and the estimated dihedral angle between them*

	*p*H	$J_{H(1')-H(2')}$	Dihedral angle	Ribose conformation
5′-GMP	7	5·1 c.p.s.	140	C(2′)-*endo*
5′-IMP	7	5·1	140	C(2′)-*endo*
5′-AMP	1∼2	4·6	135	C(2′)-*endo*
	7∼8	5·0	140	C(2′)-*endo*

The C(3′)-*endo* ribose conformation in 5′-GMP is probably the result of packing and hydrogen bonding requirements. In fact, the OH group attached to the C(3′) atom is hydrogen-bonded to the amino nitrogen atom of the guanine base, and the C(3′)-*endo* conformation may be favourable for the formation of the hydrogen bond. On the other hand, in crystalline disodium 5′-IMP the ribose conformation is C(2′)-*endo*, which is the same as would be expected in aqueous solution. The alkali-metal salt crystals of the nucleotides contain a comparatively large number of water molecules of crystallization, and it might be supposed that in these crystals the environments around the nucleotide molecules are somewhat similar to those in aqueous solution.

In purine nucleotides or nucleosides which have the C(3′)-*endo* ribose conformation, only the *anti* region is allowed with respect to the internal rotation around the glycosidic bond ($-150° < \varphi_{CN} < +20°$; Haschemeyer & Rich, 1967). In fact the φ_{CN} values are small when the ribose puckering is C(3′)-*endo*; for instance −20° in 5′-AMP (Kraut & Jensen, 1963), −4° in 3′-AMP (Sundaralingam, 1966) and −11° in adenosine (Haschemeyer & Sobell, 1965). The C(3′)–H(3′) bond is approximately in the axial position with respect to the ribose ring when the ribose conformation is C(3′)-*endo*. The non-bonded repulsion between an axial hydrogen atom H(3′) of the ribose ring and the H(8) atom of the purine base will cause a rotation around the glycosidic bond to reduce the φ_{CN} value.

(*d*) *Description of the structure and the hydrogen bonding*

The crystal structure viewed along the *b* axis is shown in Fig. 4. The guanine bases are stacked with their planes parallel to (010). The perpendicular distance between two parallel guanine bases is 3·09 Å corresponding half of the *b* axis period. The closest intermolecular distance is 3·18 Å, which is found between N(7) of one guanine base and C(6) of another guanine base, separated by one half of the *b* axis period by the twofold screw axis symmetry operation along this direction.

Three oxygen atoms of water molecules are linked with each other by hydrogen bonds. The O(V) atom of one water molecule makes a hydrogen bond with O(II) of one phosphate group, and the O(VI) atom of the same water molecule is hydrogen bonded to O(II) of the other phosphate group; thus an infinite hydrogen bond chain is formed along the *a* axis (Fig. 4). O(VI) is also hydrogen bonded along the *b* axis to O(I) of the phosphate group in the adjacent unit cell, and two phosphate groups are linked with each other along the *b* axis by the bonding sequence P–O(I)–O(VI)–O(II)–P (not shown in Fig. 4).

The O(2′) atom of the ribose OH group is hydrogen bonded to O(IV) of the water molecule. The distance between O(3′) of the ribose OH group, which is attached to the out-of-plane carbon atom in the ribose ring, and N(2) of the guanine amino group of the adjacent molecule is 3·00 Å, indicating a hydrogen bond between these two atoms. Hydrogen bonds between the ribose OH group and nitrogen atoms of the purine bases have been reported also in 3′-AMP (Sundaralingam, 1966) and 5′-AMP (Kraut & Jensen, 1963).

Hydrogen bond lengths and angles are given in Table 11.

Table 11. *Hydrogen bond lengths and angles*

The suffices i and ii denote atoms which belong to the adjacent unit cell along the *b* axis.

Bond length

O(2′) –O(IV)	2·931 Å	O′(II)—O′(VI)	2·591 Å
O(IV)–O(V)	2·766	O″(VI)^{i}–O(I)^{ii}	2·649
O(V)—O(VI)	2·784	O(3′)——N(2)	3·002
O(V)—O′(II)	2·845		

Bond angles

C(2′) –O(2′)—O(IV)	148·9°
O(2′) –O(IV)—O(V)	96·8

Table 11 (*cont.*)

Bond angles

O(IV)–O(V) —O(VI)	75·3
O(IV)–O(V) —O′(II)	131·5
O(VI)–O(V) —O′(II)	116·8
O(V) –O′(II)—O′(VI)	97·5
O′(II)–O′(VI) –O′(V)	106·6
O(II)^{i}–O″(VI)–O(I)^{ii}	122·8
P——O(II)—O′(V)	124·8
P——O(II)—O″(VI)	108·8
P^{i}——O(I) —O″(VI)^{ii}	125·9
C(3′) –O(3′)—N′(2)	125·8
O(3′) –N′(2) —C′(2)	106·3

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References

Bugg, E. & Marsh, R. E. (1967). *J. Mol. Biol.* **25**, 67.

Donohue, J. & Trueblood, K. N. (1960). *J. Mol. Biol.* **2**, 363.

Gellert, M., Lipsett, M. N. & Davis, D. R. (1962). *Proc. Nat. Acad. Sci. Wash.* **48**, 2013.

Haschemeyer, A. E. V. & Rich, A. (1967). *J. Mol. Biol.* **27**, 369.

Haschemeyer, A. E. V. & Sobell, H. M. (1965). *Acta Cryst.* **19**, 125.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Jardetzky, C. D. (1960). *J. Amer. Chem. Soc.* **82**, 229.

Jardetzky, C. D. (1962). *J. Amer. Chem. Soc.* **84**, 62.

Jeffrey, G. A. & Kinoshita, Y. (1963). *Acta Cryst.* **16**, 20.

Kraut, J. (1961). *Acta Cryst.* **14**, 1146.

Kraut, J. & Jensen, L. H. (1963). *Acta Cryst.* **16**, 79.

Lemieux, R. U. (1961). *Canad. J. Chem.* **39**, 116.

McCallum, G. H., Robertson, J. M. & Sim, G. A. (1959). *Nature, Lond.* **184**, 1863.

Nagashima, N. & Iitaka, Y. (1968). *Acta Cryst.* B**24**, 1136.

Sakurai, T. (1967). *UNICS Program System*. Japan Crystallographic Association.

Shefter, E. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 1067.

Sim, G. A. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 227. Oxford: Pergamon Press.

Sundaralingam, M. (1966). *Acta Cryst.* **21**, 495.

Sundaralingam, M. & Jensen, L. H. (1965). *J. Mol. Biol.* **13**, 914.

Trueblood, K. N., Horn, P. & Luzzati, V. (1961). *Acta Cryst.* **14**, 965.

Acta Cryst. (1969). B**25**, 2245

Five-Coordinate Adducts of Cupric β-Diketone Complexes: the Structure of 4-Methylpyridine bis-(*o*-hydroxyacetophenonato)copper (II)

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4-Methylpyridine bis-(*o*-hydroxyacetophenonato)copper(II) is the first 'stable' 1:1 adduct of a cupric β-diketone to have its structure determined by X-rays. The copper atom is five-coordinated and has a tetragonal pyramidal environment. Four oxygen atoms form an approximate square-planar arrangement about the copper atom, which is raised slightly out of this plane towards the apical nitrogen atom. The discrete molecule has a twofold axis of symmetry. Copper–oxygen and carbon–oxygen bond distances indicate that the π-electron system of the coordinated β-diketone framework has been largely destroyed by the presence of a benzene ring in the *o*-hydroxyacetophenone residue. The crystals, which decompose during irradiation, crystallize in the orthorhombic system, space group *Pbcn*, with lattice constants $a = 9{\cdot}23 \pm 0{\cdot}05$, $b = 13{\cdot}99 \pm 0{\cdot}07$, $c = 15{\cdot}59 \pm 0{\cdot}08$ Å. The intensities of three-dimensional equi-inclination Weissenberg data were estimated visually and the structure was solved by Patterson and Fourier techniques. Refinement of atomic parameters was carried out by the method of least-squares.

Introduction

Cupric complexes with β-diketones have been extensively investigated in recent years, and X-ray crystallographic studies have shown that their structures are essentially square-planar, although in some cases there is evidence of weak axial interactions (Boyko, 1963; Barclay & Cooper, 1965; Hall, McKinnon & Waters, 1965). Graddon (1959) observed changes in the visible spectra of these compounds in chloroform, produced by increasing the concentrations of various heterocyclic bases, and he proposed the formation of