même chaine, les contacts correspondent à la somme des rayons de van der Waals (1,2 pour H, 1,4 pour O, 1,5 pour N, 1,54 pour C). Entre les groupements méthoxy de chaines voisines les distances sont plus grandes (O...H > 2,75 Å).

Entre les groupements centraux et les $-O-CH_3$ de chaines voisines, on trouve plusieurs distances correspondant aux contacts de van der Waals, N(1)...H(101), N(11)...H(103), N(11)...H(101).

On peut remarquer une différence entre les deux groupements méthoxy, l'un est tourné vers des groupements -CH=N-N=CH- avec trois distances H...N correspondant aux contacts de van der Waals l'autre est dirigé vers des méthoxy de chaines voisines avec trois distances H...O comprises entre 2,75 et 2,9 Å.

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The Crystal Structure of 1,3-Diphosphorylimidazole

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The crystal structure of calcium 1,3-diphosphorylimidazole, $Ca_{1\cdot5}C_3H_3N_2(PO_3)_2.6H_2O$, has been determined by X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with $a = 6\cdot90$, $b = 11\cdot30$, $c = 9\cdot92$ Å, $\alpha = 102\cdot44°$, $\beta = 92\cdot31°$, $\gamma = 106\cdot47°$, $Z = 2$. Refinement of the structure was accomplished by difference-Fourier synthesis, differential synthesis, and least-squares techniques. The final R index is 0·055. One of the calcium ions lies at a center of symmetry, and six octahedrally arranged oxygen atoms are coordinated to it. Seven oxygen atoms are coordinated to the other calcium, and these form a slightly distorted pentagonal bipyramid. The plane of the imidazole ring is normal to the a axis, with distances of 3·40 and 3·50 Å between alternate rings. The average length of the P–N bonds is 1·78 Å. None of the six phosphoryl oxygen atoms is covalently bonded to an atom other than phosphorus; the average P–O bond distance is 1·49 Å. The structure contains infinite chains formed by coordinated calcium and phosphoryl groups, and clathrate-like hydrogen-bonded 'cages'. The crystals were twinned along a plane approximately coincident with the calcium-phosphoryl chain.

Introduction

Many of the steps in either photosynthesis or metabolism – the two chemical processes basic to life – involve phosphated intermediates. Because of this, phosphate transfer agents, such as adenosine triphosphate (ATP), are needed. A number of recent investigations involving such agents have indicated the participation of a phosphorylated imidazole moiety.

Reversible phosphoryl transfer to the imidazole nitrogen can take place quite readily (Rathlev & Rosenberg, 1956); thus the imidazole moiety is well suited to a role as a phosphate carrier in enzymes and transport processes. In addition, DPI (1,3-diphosphorylimidazole or diphosphoimidazole) has been shown to be an effective agent for phosphorylating primary amino groups in aqueous solution (Rathlev & Rosenberg, 1956).

This work was undertaken with the particular goal of providing accurate structural information about the imidazole–phosphate linkage. DPI was regarded as especially well suited to such a study, in view of the expected presence of two symmetric P–N bonds in the molecule (Christensen, 1964).

Only two P–N bonds having nearly 100% single-bond character have been reported in crystal structures, those in *N*-phosphorylcreatine (Herriott & Love, 1967), and sodium phosphoramidate (Hobbs, Corbridge & Raistrick, 1953). The former is a well-known biological 'high-energy' compound (*i.e.* having a high free energy of hydrolysis.) Phosphoimidazole has also been referred to as a 'high-energy' compound by Pullman (1960).

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Experimental

The calcium salt of diphosphorylimidazole (CaDPI) was synthesized by the slow addition of phosphorus oxychloride to an aqueous solution of imidazole at *p*H 11 and 10°C (Rosenberg, 1964; Beard, 1967). The compound was recrystallized as flattened needles, which twin along (001). Single crystals for intensity measurements were obtained by cleaving specimens along the needle axis, *a*. All measurements were made with Mo $K\alpha$ radiation.

Crystal data

$Ca_{1\cdot5}C_3H_3N_2(PO_3)_2.6H_2O$, $M=393\cdot3$.
Triclinic, $P\bar{1}$, $a=6\cdot90\pm0\cdot01$, $b=11\cdot30\pm0\cdot01$, $c=9\cdot92\pm0\cdot01$ Å ($\lambda=0\cdot7107$ Å), $\alpha=102\cdot44\pm0\cdot04°$, $\beta=92\cdot31\pm0\cdot06°$, $\gamma=106\cdot47\pm0\cdot03°$, $V=720\cdot3$ Å^3 at 22°C, $D_m=1\cdot81\pm2$, $D_x=1\cdot813$ g.cm^{-3}, $Z=2$, $\mu=8\cdot6$ cm^{-1} for Mo $K\alpha$.

Centrosymmetry of the structure was suggested by both the statistical test of Howells, Phillips & Rogers (1950), and that of Karle & Hauptman (1953). The results of these tests, in which about 2000 three-dimensional data were used, are shown in Fig. 1 and Table 1. The asymmetric unit consists of one DPI molecule, one calcium ion, and six water molecules. An additional calcium ion lies at a center of symmetry, which was chosen as the origin of the unit cell.

Table 1. *Karle and Hauptman centrosymmetry test*

	Theoretical		Experimental
	$P1$	$P\bar{1}$	hkl
$\langle E\rangle$	0·89	0·80	0·75
$\langle E^2-1\rangle$	0·74	0·97	0·98

Equi-inclination Weissenberg photographs for levels $0kl$ to $6kl$ were taken with integration in the vertical direction.* A binocular microscope at 8 × magnification was used to estimate the intensities by visual comparison with a calibrated scale. The intensities were corrected for Lorentz and polarization factors. Intralevel film ratios and an empirical correction for spot-size were determined by comparing about 40 intensities on each level, measured with a diffractometer, with those obtained photographically. The diffractometer-film ratio was determined from the same intensities.

After partial refinement, about 350 reflections on levels $7\,kl$ to $10\,kl$ were measured with a diffractometer. Those selected for measurement on these levels included (*a*) all with θ less than 30 degrees, (*b*) those with F(calc) greater than 6·0 and $30°<\theta<40°$. In addition, some 300 reflections on the first seven layers were remeasured; these included all reflections for which F(calc) was greater than 25·0, and others which were judged to be of poor quality. The four-circle diffractometer used was equipped with a NaI scintillation detector and pulse height analyzer. The 2θ-scan technique was used and the system was calibrated hourly by measurements of the 200 reflection.

The crystal used for the photographically recorded intensities measured $0\cdot08\times0\cdot14\times0\cdot90$ mm. A second crystal, $0\cdot08\times0\cdot14\times0\cdot28$ mm, was used for all measurements made with the diffractometer. Zr-filtered molybdenum radiation was used throughout. No extinction effects were observed and, since absorption errors were, at most, 4% in F(obs), no absorption correction was made.

There are 4183 unique reflections within the limit of $\sin\theta/\lambda$ less than 0·70 Å^{-1}; of these, 1993 gave a measurable intensity. In addition, 350 non-zero reflections were observed in the range $0\cdot70<\sin\theta/\lambda<0\cdot90$ Å^{-1}.

Determination and refinement of the structure

The sequence of operations performed in the solution and refinement of the structure is given in Table 2. The calcium and phosphorus atoms were located from a sharpened Patterson synthesis, and the heavy-atom method was used to solve the structure. Refinement was accomplished by difference-Fourier synthesis, differential synthesis, and full-matrix least-squares techniques. Computations for the first two methods were performed locally on an IBM 7072 computer using programs written by members of the Crystallography Laboratory at the University of Pittsburgh (Shiono, 1962). The Fourier program was modified to accommodate the triclinic space group $P\bar{1}$. The atomic scattering factors from the *International Tables for X-ray Crystallography* (1962) for Ca^{2+} and neutral P, O, N, C and H were used in all computations.

Final refinement* was performed by minimization of the function $\sum_i w_i[F_i(\text{obs})-GF_i(\text{calc})]^2$. The weighting function, $w=1/(0\cdot025F(\text{obs})+1)$, was derived from a plot of $F(\text{obs})-F(\text{calc})$ *versus* F(obs) to approximate the observational variance. No unobserved reflections were included. Contributions of the hydrogen atoms, which had been positioned from difference syntheses, were included in the calculation of the structure factors, but the hydrogen parameters were not refined.

An arbitrary upper limit of about 120 atomic parameters per cycle was set for the full matrix least-squares calculations in order to reduce computation time. During the last refinement cycle, a few parameters shifted by as much as 0·6 of their estimated standard deviations. These ratios are misleading, perhaps, since the same set of atoms was never refined in successive cycles. For those instances in which a given atom was refined in two successive cycles, the shift/error ratios

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* The direction of integration is along the *x* film coordinate according to Buerger's notation: M. J. Buerger, *X-Ray Crystallography* (1942).

* These calculations were performed on the IBM 7094 computer at the U.S. Army Missile Support Command, Redstone Arsenal, Alabama, using the *X-ray* 63 *Program System for X-ray Crystallography* (Stewart, 1964).

Table 2. *Steps in the structure refinement*

Method*	Number of atoms refined	R(%)†	Comments
PS	—	45	Ca, P atoms located
DFS	4, 15, 17	20·0	3 cycles performed; trial structure completed
DFS	21	10·3	4 cycles performed; end of isotropic thermal parameter refinement
—	—	8·9	350 reflections on 7*kl*–10*kl* added
DS	21	7·6	Beginning of anisotropic thermal parameter refinement
DFS	—	7·3	12 hydrogen atoms located (only F's having $\sin\theta/\lambda < 0·5$ used)
DS	21	6·7	2 cycles
DFS	—	6·7	3 hydrogen atoms located
DS	21	6·7	End of DS refinement
—	—	6·2	300 reflections measured
LS	4	5·9	Ca, P atoms refined
LS	13	5·7	DPI molecule refined
LS	6	5·6	Water oxygens refined
LS	14	5·5	Ca atoms, all oxygens refined
LS	13	5·5	DPI molecule refined

* PS = sharpened Patterson synthesis, DFS = difference Fourier synthesis, DS = differential synthesis. LS = full matrix least-squares.

† At end of operation described.

were all less than 0·1 in the latter cycle. Convergence is quite fast using the full-matrix technique, and it has generally been observed in this laboratory that the shift/error ratio for a parameter decreases by about a factor of five when it is varied in successive cycles.

The atomic coordinates, the thermal parameters, and their standard deviations are listed in Tables 3 and 4. These parameters give a conventional R index of 0·055 for 2343 independent observed reflections. The observed and calculated structure factors are listed in Table 5. The standard deviations were computed from the least-squares matrix. The standard deviations in the coordinates correspond to positional uncertainties of about 0·002 Å for the calcium and phosphorus

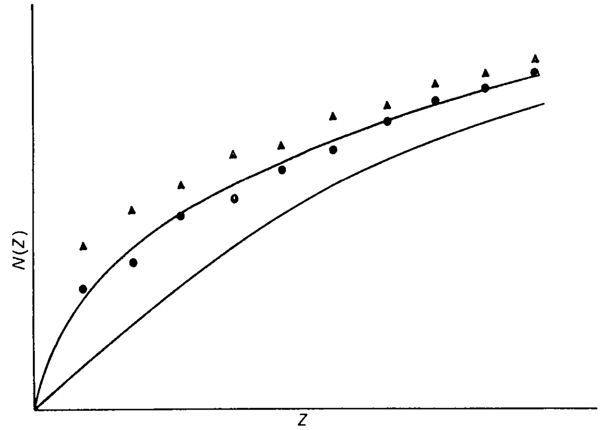

Fig. 1. Howells, Phillips & Rogers (1950) statistical test. Experimental points are shown as: triangles for *hkl* reflections, filled circles for 0*kl* reflections. The upper solid line shows the expected distribution for centric, and the lower for acentric, structures.

Table 3. *Atomic coordinates and standard deviations*

	x	y	z
Ca(1)	0·0000 (0)	0·0000 (0)	0·0000 (0)
Ca(2)	0·7219 (1)	0·4332 (1)	0·0339 (1)
P(1)	0·1938 (2)	0·3486 (1)	0·1183 (1)
P(3)	0·1220 (2)	0·2907 (1)	0·6585 (1)
N(1)	0·2091 (7)	0·3860 (4)	0·3018 (4)
N(3)	0·1840 (7)	0·3625 (4)	0·5151 (5)
C(2)	0·1671 (8)	0·3012 (5)	0·3810 (6)
C(4)	0·2421 (10)	0·4904 (6)	0·5218 (7)
C(5)	0·2567 (10)	0·5058 (6)	0·3898 (7)
O(11)	0·1616 (6)	0·2089 (4)	0·0887 (4)
O(12)	0·0284 (5)	0·3967 (4)	0·0737 (4)
O(13)	0·3934 (5)	0·4264 (3)	0·0880 (4)
O(31)	0·1710 (7)	0·4037 (4)	0·7747 (4)
O(32)	−0·1001 (6)	0·2202 (4)	0·6208 (4)
O(33)	0·2536 (6)	0·2039 (4)	0·6547 (5)
W(1)	0·1690 (8)	0·0127 (5)	0·7996 (5)
W(2)	0·7241 (9)	0·0406 (6)	0·8943 (7)
W(3)	0·6345 (6)	0·2772 (4)	0·8147 (4)
W(4)	0·6069 (7)	0·2382 (5)	0·1206 (6)
W(5)	0·2849 (8)	0·0385 (4)	0·4123 (5)
W(6)	0·6707 (7)	0·1621 (5)	0·3664 (5)
H(2)*	0·124	0·200	0·345
H(4)	0·270	0·567	0·615
H(5)	0·291	0·594	0·358
H(11)	0·185	0·060	0·750
H(12)	0·785	0·045	0·235
H(21)	0·680	0·040	0·800
H(22)	0·660	0·080	0·940
H(31)	0·745	0·270	0·775
H(32)	0·525	0·220	0·760
H(41)	0·625	0·220	0·195
H(42)	0·480	0·210	0·095
H(51)	0·770	0·050	0·580
H(52)	0·215	0·085	0·480
H(61)	0·740	0·210	0·440
H(62)	0·550	0·140	0·390

* Hydrogen atoms in water molecules are numbered with two digits, the first corresponds to the parent oxygen; H(2), H(4), and H(5) are attached to C(2), C(4), and C(5). Isotropic temperature factors of 3·5 Å^2 were assumed for all hydrogen atoms.

atoms, about 0·005 Å for the nitrogen and oxygen atoms, and about 0·007 Å for the carbon atoms.

A final difference synthesis was computed after the least-squares refinement, with the hydrogen atom contributions omitted from the calculated structure factors. All observed structure factors were included. All fifteen hydrogen positions (as shown in Table 3) were within one-half grid point of $\varrho(\text{obs})-\varrho(\text{calc})$ peaks in the 0·32–0·59 e.Å^{-3} range. The map showed about twelve spurious peaks with heights of 0·30–0·36 e.Å^{-3} and approximately the same number of depressions with similar magnitudes. In addition to these, the region near Ca(2) and P(1) contained a fair amount of noise; none of these $\Delta\varrho$ values exceeded 0·5 e.Å^{-3}, however.

Discussion

The imidazole ring

The bond distances and angles involving the imidazole ring and its attached phosphoryl groups are shown in Fig. 2. The chemically equivalent bonds and angles in the imidazole ring of DPI differ by no more than 1·6 standard deviations.

The crystal structure of imidazole, $C_3H_4N_2$, has been determined by Martinez-Carrera (1966) using −150 °C data; these results are given for comparison in Table 6. The imidazole bonds show some significant differences from DPI. In particular, the N(3)–C(2) distance is shorter in imidazole where an increase in π bonding is expected because N(3) carries no hydrogen atom.

The plane of the imidazole ring

Least-squares plane calculations show that the imidazole ring of DPI is planar, within experimental error. Displacements of the five ring atoms are given in Table 7; the root mean square deviation is 0·004 Å. The displacements of the phosphorus and oxygen atoms from the plane of the ring are given in the same Table. O(11) and O(31) lie much nearer the plane than the other four oxygen atoms; it will be noted that these two atoms are the only ones which coordinate to single calcium ions (Figs. 3 and 6).

P(1) and P(3) are displaced from the plane by 0·08 and 0·15 Å, respectively. These deviations are surprisingly large, since, in view of the high degree of π bonding in the imidazole ring, all substituents should lie in the plane of the ring. The environment of each

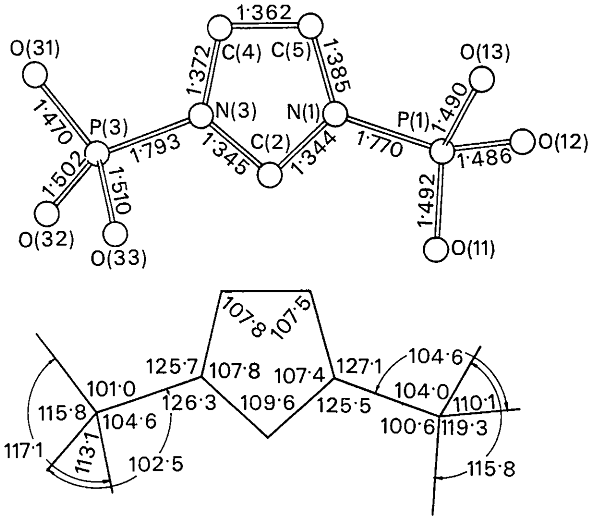

Fig. 2. Bond distances and angles in the diphosphoimidazole molecule. Distances are in Å and angles in degrees. Standard deviations, in Å for the bonds are: P–N, 0·006; P–O, 0·005; N–C, 0·008; and C–C, 0·009. Standard deviations for the angles are: O–P–O and N–P–O, 0·3°; P–N–C, 0·4°; N–C–N C–N–C and N–C–C, 0·5°.

Table 4. *Anisotropic thermal parameters and standard deviations*

The temperature factor expression is:

$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+B_{12}2hka^*b^*+B_{13}2hla^*c^*+B_{23}2klb^*c^*)\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca(1)	1·83 (5)	1·34 (5)	1·82 (6)	0·29 (4)	0·26 (4)	0·34 (4)
Ca(2)	0·61 (2)	1·17 (3)	1·23 (3)	0·32 (2)	0·11 (2)	0·32 (2)
P(1)	0·82 (4)	1·33 (4)	1·36 (4)	0·37 (3)	0·22 (3)	0·43 (3)
P(3)	1·43 (4)	1·65 (4)	1·23 (5)	0·41 (3)	0·21 (3)	0·33 (3)
N(1)	1·96 (16)	1·73 (15)	1·46 (17)	0·61 (12)	0·31 (13)	0·54 (12)
N(3)	2·14 (18)	1·64 (15)	1·81 (18)	0·36 (13)	0·42 (14)	0·74 (13)
C(2)	2·13 (20)	2·34 (21)	1·64 (21)	0·71 (16)	0·64 (16)	0·95 (16)
C(4)	4·82 (34)	1·73 (20)	2·58 (28)	0·81 (20)	0·64 (23)	0·61 (18)
C(5)	4·66 (33)	2·12 (22)	1·98 (24)	0·75 (21)	0·63 (22)	0·53 (18)
O(11)	2·69 (16)	1·46 (13)	2·13 (17)	0·46 (11)	0·22 (13)	0·27 (11)
O(12)	1·27 (13)	2·84 (16)	1·98 (16)	1·14 (12)	0·24 (11)	0·83 (12)
O(13)	0·87 (12)	2·21 (14)	1·83 (15)	0·54 (10)	0·58 (10)	0·87 (11)
O(31)	2·79 (17)	2·46 (17)	1·74 (16)	0·49 (13)	0·14 (13)	−0·08 (12)
O(32)	1·82 (14)	2·23 (16)	2·41 (18)	0·43 (12)	0·12 (12)	0·43 (12)
O(33)	2·70 (17)	2·40 (16)	2·51 (18)	1·14 (14)	0·25 (14)	0·79 (13)
W(1)	4·70 (25)	3·24 (21)	3·35 (24)	1·92 (18)	2·16 (19)	1·80 (17)
W(2)	4·43 (27)	4·55 (28)	5·32 (32)	1·87 (22)	−1·11 (24)	1·21 (23)
W(3)	1·65 (15)	2·89 (17)	1·99 (17)	0·53 (12)	0·14 (12)	0·04 (13)
W(4)	2·22 (18)	3·87 (22)	5·67 (30)	0·81 (16)	0·61 (18)	3·03 (21)
W(5)	4·17 (24)	2·86 (20)	3·26 (23)	0·64 (17)	1·23 (18)	0·77 (16)
W(6)	3·07 (21)	4·53 (25)	2·45 (21)	0·61 (18)	0·10 (16)	0·72 (17)

phosphoryl group, as shown in Fig. 3, is symmetric across the plane of the imidazole ring, except for $W(4)$. In view of this, the displacements of the phosphorus atoms are even more surprising.

The P–N *bonds*

This structure analysis is one of the first to report a P–N bond where nitrogen is a member of an aromatic group. Goldstein & Ladell (1967) have reported several triazole phosphate structures with similar bonding. In such cases the P–N bond is expected to have a high degree of single-bond character. The P–N single-bond length predicted by the Schomaker–Stevenson formula is 1·786 Å, using the expression given by Pauling (1960). The average length of these two bonds, 1·782 Å, seems compatible with this prediction.

Table 5. *Observed and calculated structure factors*

The structure factors are shown in groups of constant *h*. The figures in each column give *k*, *l*, *F*(obs) × 10, and *F*(calc) × 10.

••• H=0 •••			
0	1	415	393
0	2	405	398
0	3	402	389
0	4	508	-507
0	6	110	112
0	7	298	-287
0	8	177	188
0	9	154	166
1	-14	191	176
1	-12	142	119
1	-11	319	312
1	-10	116	109
1	-8	208	188
1	-6	156	-172
1	-5	520	539
1	-4	198	190
1	-3	572	573
1	-2	481	436
1	-1	173	-155
1	1	164	-148
1	2	893	-877
1	3	621	-606
1	4	384	-369
1	5	72	77
1	6	233	237
1	7	351	369
1	8	122	-123
1	9	93	94
1	12	103	112
1	13	109	108
2	-12	84	-85
2	-11	224	-216
2	-9	82	-89
2	-8	182	-199
2	-7	247	240
2	-6	64	-63
2	-5	165	167
2	-4	202	218
2	-3	489	-477
2	-2	33	23
2	-1	260	251
2	1	599	565
2	2	992	1021
2	3	384	364
2	4	1025	1019
2	5	369	341
2	6	173	-180
2	7	187	160
2	10	179	188
3	-12	130	146
3	-10	215	205
3	-9	289	294
3	-8	184	170
3	-7	401	410
3	-6	385	398
3	-4	518	496
3	-3	117	100
3	-2	387	-386
3	-1	664	649
3	0	519	487
3	1	33	-47
3	2	110	109
3	3	476	-475
3	6	111	-97
3	7	121	-115
3	9	151	126
4	-11	159	159
4	-7	291	-321
4	-5	191	214
4	-4	634	-584
4	-3	185	-169
4	-2	443	-403
4	-1	305	-296
4	0	364	365
4	1	137	153
4	2	414	370
4	3	359	346
4	4	296	320
4	5	458	430
4	6	324	324
4	7	253	257
4	12	182	174
5	-13	139	143
5	-10	165	143
5	-9	71	74
5	-8	205	194
5	-7	177	187
5	-5	420	425
5	-4	244	256
5	-3	299	277
5	-2	268	273
5	-1	289	265
5	0	629	628
5	1	746	734
5	2	153	153
5	3	51	60
5	4	70	81
5	5	275	-271
5	6	227	-238
5	7	116	-125
5	8	128	-130
6	-10	166	174
6	-8	93	100
6	-5	95	-102
6	-3	53	-49
6	-2	86	70
6	-1	123	-124
6	1	363	-354
6	3	130	-110
6	4	144	-150
6	5	133	137
6	6	238	248
6	7	89	109
6	8	260	284
6	9	169	181
6	11	153	129
7	-9	121	104
7	-8	70	-83
7	-7	123	-143
7	-6	316	342
7	-5	449	437
7	-4	129	142
7	-3	420	419
7	-1	276	269
7	0	176	174
7	1	256	251
7	2	94	80
7	3	322	309
7	4	340	326
7	5	254	241
7	6	97	115
7	8	153	-121
7	10	100	-116
8	-14	150	177
8	-13	93	109
8	-8	266	270
8	-7	151	169
8	-6	181	207
8	-5	130	138
8	-4	115	117
8	-3	181	-178
8	-2	358	-372
8	-1	234	-239
8	1	69	77
8	2	179	193
8	3	230	-224
8	4	71	73
8	5	140	-131
8	6	64	-63
8	10	217	198
9	-14	116	-132
9	-13	94	-105
9	-10	188	185
9	-9	79	97
9	-6	140	-115
9	-5	176	-190
9	-2	131	127
9	-1	425	457
9	0	112	97
9	1	229	236
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6	3	179	-174
7	-10	121	113
7	-8	254	-242
7	-6	151	-142
7	5	195	179
7	8	133	115
8	-10	105	-96
8	-7	161	146
8	-6	275	279
8	-5	155	135
8	-4	200	203
8	-3	167	158
8	0	203	205
8	3	166	148
9	-11	145	146
9	-10	128	120
9	-9	149	148
9	-8	159	150
9	-4	152	-177
9	2	143	-116
10	-9	108	-108
10	-8	126	-127
10	-5	132	120
10	-4	186	161
10	-3	93	102
10	-2	142	136
10	-1	170	142
11	-9	112	113
11	-7	141	159
11	-6	151	138
11	-2	138	-119
12	-7	123	-124
12	-2	123	108
12	0	112	115
13	-7	152	142
13	-5	192	187
13	-4	135	136
14	-3	140	-108
15	-3	134	132
••• H=6 •••			
-17	-2	100	99
-17	-1	99	98
-17	0	128	121
-17	5	115	124
-17	6	108	104
-16	-1	95	-105
-16	8	116	-103
-15	-2	92	87
-15	-1	99	100
-15	0	116	104
-15	1	193	189
-15	2	114	106
-15	8	94	108
-15	9	115	125
-15	10	141	121
-14	-4	130	137
-14	-2	103	104
-14	-1	111	112
-14	3	129	-135
-14	9	111	-108
-14	12	81	-82
-13	-2	128	-133
-13	2	102	107
-13	3	203	207
-13	5	125	120
-13	9	108	125
-13	11	138	147
-13	12	143	136
-12	-8	137	145
-12	-6	116	115
-12	-5	121	141
-12	-3	134	147
-12	-2	143	152
-12	-1	117	121
-12	0	149	141
-12	1	161	170
-12	5	129	-122
-12	11	124	-117
-12	13	118	-112
-11	-10	101	120
-11	-3	116	-117
-11	0	107	-102
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-11	4	118	132
-11	5	113	112
-11	7	139	132
-11	13	132	144
-10	-5	129	138
-10	-4	136	143
-10	-3	118	110
-10	-1	259	260
-10	0	199	196
-10	1	197	183
-10	2	220	210
-10	3	155	172
-10	5	138	140
-9	-9	151	166
-9	-8	122	140
-9	-4	98	-101
-9	2	129	-118
-9	3	156	-156
-9	4	82	-81
-9	5	170	-181
-9	9	106	92
-8	-9	87	-117
-8	-7	110	-106
-8	-4	135	126
-8	-2	203	209
-8	-1	295	277
-8	1	179	174
-8	2	90	103
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-8	4	308	313
-8	5	125	112
-8	6	103	105
-8	7	140	155
-7	-8	133	127
-7	-7	230	232
-7	-6	270	284
-7	-5	274	260
-7	-4	145	135
-7	-2	136	-117
-7	1	73	-75
-7	3	73	-70
-7	4	152	-154
-7	6	160	-161
-7	7	178	-192
-6	-7	157	-151
-6	-5	222	-222
-6	-4	314	-327
-6	-2	112	-95
-6	0	349	359
-6	1	141	138
-6	3	195	209
-6	6	284	280
-6	7	135	141
-6	8	172	169
-6	9	119	125
-5	-11	106	112
-5	-5	302	311
-5	-4	380	391
-5	-3	235	234
-5	-2	381	387
-5	-1	167	164
-5	1	123	132
-5	2	96	-90
-5	4	146	139
-5	5	68	-54
-5	8	139	-177
-4	-7	235	242
-4	-5	92	-84
-4	-3	356	-361
-4	-2	314	-312
-4	0	332	-347
-4	1	161	156
-4	2	190	208
-4	4	166	177
-4	5	89	88
-4	6	106	-120
-4	8	127	118
-4	10	200	205
-4	11	166	187
-3	-9	118	117
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-3	-5	124	-110
-3	-4	114	140
-3	-3	227	221
-3	-2	126	154
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-3	2	194	203
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-3	6	85	84
-3	8	108	112
-2	-8	105	100
-2	-7	90	-83
-2	-6	128	121
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-1	-3	226	-219
-1	-2	221	208
-1	0	170	165
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-1	2	314	316
-1	3	354	374
-1	4	320	342
0	-7	134	145
0	-4	303	290
0	-2	96	85
0	-1	283	276
0	0	77	65
0	1	143	-150
0	2	123	-131
0	3	215	-215
0	4	201	-200
0	7	86	-102
1	-8	171	-172
1	-7	169	-177
1	-6	134	139
1	-2	213	-203
1	-1	101	-103
1	2	171	177
1	3	236	237
1	4	177	170
1	5	243	276
1	6	183	197
2	-9	114	137
2	-8	166	158
2	-7	172	162
2	-6	178	154
2	-5	201	206
2	-4	148	152
2	-3	76	81
2	-2	165	163
2	-1	140	141
2	0	202	194
2	1	239	223
2	5	190	-205
2	6	134	-121
3	-10	132	131
3	-6	200	-200
3	-5	87	-84
3	-3	108	-98
3	0	129	-124
3	1	158	-157
3	5	223	226
3	6	127	128
3	7	123	130
3	8	153	166
4	-8	135	-118
4	-6	217	206
4	-5	219	215
4	-4	157	158
4	-3	209	199
4	-1	96	87
4	0	138	127
4	1	128	136
4	2	112	111
4	3	286	279
4	4	112	126
4	5	98	103
4	7	107	-86
5	-9	93	95
5	-8	139	143
5	-3	203	-180
5	-1	145	-142
5	5	157	-160
6	-6	161	-143
6	-3	108	111
6	-2	248	265
6	-1	216	215
6	1	134	136
6	2	115	109
6	5	164	155
6	7	163	156
7	-13	146	162
7	-6	200	181
7	-5	138	134
7	-4	125	114
7	-3	161	157
7	-2	114	-113
7	1	218	-212
8	-13	134	-134
8	0	174	169
8	1	135	122
8	3	119	115
8	6	129	142
9	-10	166	160
9	-5	164	163
9	-4	126	106
9	-2	213	204
10	-2	132	-115
11	-8	96	91
11	-6	117	121
11	-3	138	131
11	-2	106	103
11	-1	151	144
11	0	167	175
••• H=7 •••			
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-14	3	205	187
-14	4	125	102
-14	5	186	151
-13	2	92	-99
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-12	-2	140	139
-12	1	150	154
-12	4	235	233
-12	5	92	111
-12	6	219	224
-12	7	267	237
-11	-4	182	186
-11	6	154	-144
-11	7	131	-127
-11	9	168	-145
-10	-4	108	-124
-10	-2	115	-110
-10	0	139	146
-10	3	110	110
-10	8	226	228
-10	9	171	189
-10	10	154	132
-9	-3	154	151
-9	-2	253	265
-9	-1	144	154
-9	0	192	186
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-9	6	127	122
-9	8	84	-85
-8	-4	142	157
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-8	4	127	110
-8	5	124	127
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-7	-7	134	143
-7	-6	153	170
-7	-3	116	124
-7	-1	137	144
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-7	3	119	138
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-6	2	245	-241
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-5	-5	224	230
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-5	-2	117	123
-5	1	324	329
-5	2	131	134
-5	3	155	151
-5	4	190	198
-5	5	174	190
-4	-10	209	195
-4	-9	216	221
-4	-7	212	220
-4	3	116	-136
-4	4	257	-266
-4	5	140	-143
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-3	-7	259	-258
-3	-5	122	-116
-3	-3	173	188
-3	3	146	151
-3	4	136	133
-3	5	242	250
-3	6	227	241
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-3	8	83	93
-3	9	161	137
-2	-8	157	157
-2	-7	233	217
-2	-6	220	209
-2	-5	392	368
-2	-2	93	102
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-2	8	191	-187
-1	-5	170	-161
-1	-3	317	-305
-1	0	97	97
-1	3	128	-129
-1	10	141	146
0	-4	296	275
0	-2	245	228
0	-1	217	214
0	0	175	168
0	2	99	111
0	3	122	111
0	5	159	160
1	-6	187	168
1	-1	240	-241
1	0	94	-110
1	2	100	-120
1	5	132	-129
2	-2	144	131
2	-1	160	167
2	0	243	250
2	2	169	166
2	4	114	139
2	5	88	95
3	-10	169	168
3	-4	118	135
3	-3	171	173
3	1	135	-138
3	4	94	-127
4	-10	121	-125
4	0	121	118
4	2	155	149
4	3	229	247
4	4	122	128
5	-10	146	146
5	-8	208	195
5	-4	106	109
5	-2	249	252
5	-1	150	155
5	1	117	118
5	3	115	-123
6	-8	137	-147
6	0	154	-165
7	-8	106	133
7	-6	218	195
7	0	175	192
7	2	191	196
8	-8	105	107
9	-4	122	119
••• H=8 •••			
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-14	5	104	113
-13	-2	110	135
-13	0	110	108
-13	1	188	187
-12	0	145	-137
-12	7	109	116
-11	-1	118	143
-11	0	110	128
-11	1	104	118
-11	2	231	240
-11	3	165	166
-11	5	162	163
-10	0	105	98
-10	4	162	-173
-10	5	124	-139
-9	-5	81	108
-9	-2	181	179
-9	3	195	195
-9	4	261	264
-9	5	123	153
-9	6	185	197
-9	7	160	152
-8	-7	195	217
-8	-5	116	128
-8	2	110	108
-8	6	204	-210
-8	7	192	-161
-7	-5	180	-200
-7	0	167	156
-7	6	170	204
-7	7	188	207
-7	9	110	123
-6	-8	106	116
-6	-5	209	220
-6	-4	204	202
-6	-3	208	205
-6	-2	141	147
-6	4	105	120
-6	8	176	-172
-6	9	104	-117
-5	-3	128	-134
-5	0	88	-84
-4	-4	132	141
-4	-3	152	159
-4	-2	130	150
-4	-1	200	207
-4	0	251	255
-4	5	91	111
-4	6	171	175
-3	-1	169	-170
-3	0	132	-141
-3	2	113	-108
-3	8	143	-115
-2	-2	127	135
-2	1	192	202
-2	2	196	202
-2	4	139	154
-2	7	151	152
-1	-10	230	21
-1	-9	126	14
-1	-8	137	12
-1	-4	96	7
-1	-1	151	15
-1	1	175	-17
-1	3	108	-12
-1	4	103	-12
0	-10	148	-16
0	-8	178	-16
0	-7	168	-16
0	-3	186	16
0	3	145	14
0	5	135	13
0	6	141	15
1	-9	173	14
1	-8	264	24
1	-7	245	22
1	-6	129	13
1	-5	158	16
1	-2	108	10
1	1	178	18
1	5	203	-18
2	-6	274	-24
2	-5	174	-168
2	3	91	-100
3	-6	278	261
3	-5	178	169
3	-4	162	177
3	-3	236	237
3	-1	92	92
3	2	121	122
3	3	155	141
3	5	102	100
4	-9	109	122
4	-8	138	149
4	-4	149	-165
4	0	150	107
5	-4	149	123
5	-3	136	148
5	-2	249	266
5	-1	126	140
5	1	139	120
6	-7	167	170
6	-6	172	154
6	-2	104	-127
7	-5	86	-109
••• H=9 •••			
-13	0	121	112
-13	1	133	142
-11	-4	129	-153
-11	0	123	132
-11	2	161	154
-10	-5	93	118
-10	-3	195	211
-10	-2	189	226
-10	0	112	102
-9	-3	181	-177
-9	-1	149	-159
-9	0	201	-199
-9	4	125	131
-8	-3	147	131
-8	-1	219	211
-8	0	185	209
-8	1	186	176
-8	2	201	212
-7	1	217	-212
-7	2	138	-162
-6	1	258	271
-6	2	170	187
-6	3	166	168
-6	4	185	185
-5	-8	139	130
-5	-7	144	170
-5	3	184	-166
-5	4	164	-180
-4	-7	125	-126
-4	-5	105	-122
-4	3	184	177
-4	4	179	168
-4	5	205	211
-4	6	172	183
-3	-7	159	153
-3	-6	172	166
-3	-5	225	217
-3	-4	88	108
-3	-2	92	108
-3	1	189	191
-3	5	127	-126
-2	-5	129	-142
-2	-3	163	-188
-1	-4	208	182
-1	-3	290	297
-1	-2	153	156
-1	-1	170	172
-1	0	107	112
-1	5	131	133
0	-6	139	146
0	-1	195	-206
1	-2	166	164
1	-1	151	156
1	0	131	153
1	1	194	204
1	4	133	125
2	-4	190	173
2	0	121	-141
3	2	96	136
4	-2	211	216
••• H=10 •••			
-7	-3	113	132
-7	-2	124	140
-6	-3	161	-149
-5	-3	125	130
-5	-2	97	123
-5	-1	190	221
-5	0	170	185
-5	2	122	102
-4	-1	164	-158
-3	-2	152	124
-3	0	134	138
-3	1	217	226
-3	2	119	146
-3	3	140	143
-2	-4	94	109
-2	-1	113	102
-2	3	147	-157
0	-2	106	118
0	0	104	121

Some chemical evidence exists to support the single-bond character of the imidazole-phosphate bond. Jencks & Gilchrist (1965) have pointed out that 'the kinetically determined *pK* of (mono)phosphoimidazole is essentially the same as that of imidazole itself, which shows that... there is no significant electron-withdrawing effect of the phosphate group on the imidazole ring'.

In sodium phosphoramidate, $NaPO_3NH_3$ (Hobbs, *et al.*, 1953), the phosphorus–nitrogen bonding is $O_3P{-}NH_3$. Cruickshank (1964*a*) refined this structure[*] and obtained 1·769 ± 0·019 Å for the P–N bond. He observed: 'Since the nitrogen is bonded to three hydro-

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[*] Final $R=0{\cdot}064$ for 119 non-zero reflections; anisotropic thermal parameters and assumed H positions were used.

gen atoms, there can be no π character in the P–N bond. Consequently we may take 1·77 ± 0·02 Å as the value of the P–N single-bond length.' Herriott (1967) has recently reported the crystal structure of *N*-phosphoryl creatine, where he finds a P–N distance of 1·735 ± 0·004 Å.

P–N bonds having substantially greater double-bond character have been reported and discussed by Migchelsen, Olthof & Vos (1965) in studies of metaphosphimates and phosphonitrilics. Average P–N distances in these compounds are approximately 1·67 and 1·57 Å, respectively.

The difference between the two P–N distances in DPI is 0·023 Å, the e.s.d. in the P–N bond, 0·006 Å. According to the usual criterion, this difference is significant at the 0·01 level. It may be worth noting that the phosphoryl group associated with the shorter P–N bond has a very Ca^{2+}-rich environment.

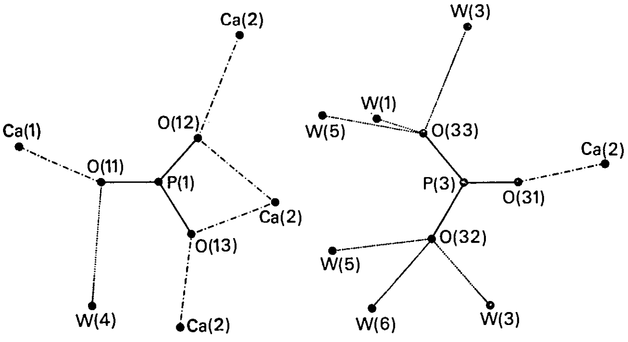


Fig. 3. Phosphoryl group environments. Projections showing the arrangement of the nearest neighbors for each phosphoryl group.

The P–O *bonds*

The bond distances and angles involving the phosphorus atoms are shown in Fig. 2. None of the six oxygen atoms is covalently bonded to an atom other than phosphorus. (These oxygen atoms will subsequently be referred to as covalently unshared.)

At least eighteen other P–O bonds of this type have been reported to date in precise determinations of structures containing phosphate groups. All of these P–O bond distances have been listed in Table 8. Kraut & Jensen (1963) have reviewed the results of structures 4, 5, 6 in Table 8. The current tabulation of 24 distances averages 1·494 Å, with an r.m.s. deviation of 0·016 Å. The average P–O distance in DPI is 1·492 Å.

Some comment regarding the relation of the individual P–O distances in DPI to the respective oxygen environments may be justified. In the P(1) group, P–O deviations from the average of 1.492 Å are 0·0, 0·3, and 1·0 times the e.s.d. (0·006 Å) in the P–O bond length. The environments of these oxygen atoms are similar (Fig. 3). Analogous deviations in the P(3) group are 1·6, 3·0 and 3·7 times the P–O e.s.d. The oxygen atoms with the two longest bonds, 1·502 and 1·510 Å, each accept 3 hydrogen bonds; the one with the short bond, 1·470 Å, coordinates to single Ca^{2+}. These relations may be in part fortuitous; however, there is apparently a relation between the P–O bond length and the nature of the interactions between oxygen and its environment.

O–P–O *and* N–P–O *angles*

The average O–P–O angle in each phosphoryl group is 115°. The angles in the P(3) group deviate from this average by 1°, −2°, and 2°. There is more variation in the P(1) group, which has bidentate coordination to Ca(2). Here the deviations are 1°, −5°, and 4°.

Table 6. *Comparison of the* DPI *imidazole ring and the imidazole molecule*

Imidazole results from Martinez-Carrera (1966).
Standard deviations are in parentheses.

	Distances in Å			Angles in degrees	
	DPI	Imidazole*		DPI	Imidazole
N(1)–C(2)	1·344 (8)	1·349 (5)	C(5)–N(1)–C(2)	107·4 (5)	107·2 (3)
N(3)–C(2)	1·345 (7)	1·326 (5)	C(2)–N(3)–C(4)	107·8 (5)	105·4 (3)
N(1)–C(5)	1·385 (7)	1·369 (5)	N(3)–C(4)–C(5)	107·8 (5)	109·8 (3)
N(3)–C(4)	1·372 (8)	1·378 (5)	C(4)–C(5)–N(1)	107·5 (5)	106·3 (3)
C(4)–C(5)	1·362 (9)	1·358 (5)	N(1)–C(2)–N(3)	109·6 (5)	111·3 (3)

* Refinement by differential synthesis with e.s.d. calculated by Cruickshank's method. $R = 11·2\%$.

Table 7. *Least-squares plane displacements*

Equation of the plane: $0·996X - 0·271Y + 0·046Z - 0·395 = 0$, where X, Y, Z are in Å and refer to the triclinic axes. The last term is the plane-to-origin distance in Å.

Atoms determining the plane	Displacement (Å)	Displacements of other atoms (Å)			
N(1)	0·002	P(1)	0·08	P(3)	0·15
C(2)	−0·005	O(11)	−0·12	O(31)	0·10
N(3)	0·006	O(12)	1·38	O(32)	1·47
C(4)	−0·005	O(13)	−1·04	O(33)	−1·02
C(5)	0·002				

Table 8. *Phosphorus–oxygen distances where no other atom is covalently bonded to the oxygen*

Environment of Oxygen	Reference	P–O	Average
2 Ca	2	1·472 Å	1·490 Å
	2	1·475	
	5	1·486	
	1	1·486	
	1	1·490	
	2	1·494	
	2	1·505	
	5	1·514	
3 H	5	1·474	1·500
	3	1·495	
	1	1·502	
	1	1·510	
	9	1·517	
2 H	7	1·477	1·495
	7	1·486	
	4	1·493	
	4	1·503	
	3	1·514	
1 Ca	1	1·470	
1 Ca, 1 H	1	1·492	
2 Na, 1 H	9	1·504	1·513
	8	1·522	
2 Na, 2 H	9	1·507	
1 H	6	1·469	
(r.m.s. deviation for all the above, 0·016 Å)			1·494 (all)

1. Diphosphoimidazole, this work.
2. Ca 1-naphthylphosphate trihydrate (Li & Caughlan, 1965).
3. Adenosine 5′-phosphate (Kraut & Jensen, 1963).
4. 2-Aminoethanol phosphate (Kraut, 1961).
5. Ca thymidylate (Trueblood, *et al.* 1961).
6. Dibenzylphosphoric acid (Dunitz & Rollett, 1956).
7. Adenosine 3′-phosphate (Sundaralingam, 1966).
8. Sodium phosphoramidate (Cruickshank, 1964*a*).
9. *N*-Phosphorylcreatine (Herriott, 1967).

Enlargement of the O–P–O angle relative to RO–P–O and RO–P–OR angles has been observed in several phosphate structures, where O–P–O angles of 113° to 117° are reported. When the group includes three covalently unshared oxygen atoms, this leads to a flattening of the PO_3 pyramid, as seen in each of the six groups listed in Table 9. In DPI, all six N–P–O angles are within 2° of the average value, 103°. The smallest angle in each phosphoryl group is 101° and involves the singly coordinated oxygen atom, the one which lies in the plane of the imidazole ring.

Table 9 shows a comparison of the N–PO_3 geometry in DPI with other phosphate groups in which there is one covalently shared atom and three covalently unshared oxygen atoms. It appears that the degree of flattening, as manifested by comparison of the N–P–O or RO–P–O angles *versus* the O–P–O angles, may be slightly greater in the N–PO_3 than in the RO–PO_3 groups.

Calcium coordination

There are two crystallographically independent calcium ions in the structure. One, Ca(1), lies at a center of symmetry and coordinates to six oxygen atoms which form a slightly distorted octahedron. Two of the three independent oxygen atoms belong to water molecules; these lie 2·34 and 2·36 Å from the calcium. The third oxygen belongs to a phosphoryl group, and its distance is 2·26 Å. The average of the three is 2·32 Å. The three unique obtuse O–Ca–O angles in this group are 90·2°, 91·0°, and 93·0°, subtended by *W*(1)–*W*(2), O(11)–*W*(1), and O(11)–*W*(2), respectively.

The second calcium atom, Ca(2), has sevenfold coordination, with the oxygen atoms forming a slightly

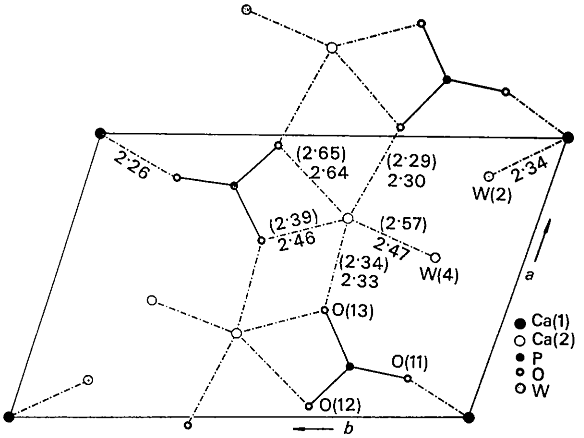


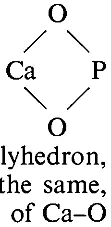
Fig. 4. The calcium-phosphorus-oxygen chain. Calcium coordination to atoms lying near $z=0$. Calcium–oxygen distances for CaDPI are shown together with (in parentheses) similar distances in calcium thymidylate (Trueblood *et al.*, 1961).

Table 9. *Average distances and angles in tetrahedra about phosphorus atoms in which* 1 *atom* (N *or* RO) *is covalently shared and* 3 *are not*

	Compound	Reference	N–O	RO–O	O–O	N–P–O	RO–P–O	O–P–O
N–PO_3	DPI	1	2·57 Å	—	2·52 Å	103°	—	115°
	N-Phosphorylcreatine	2	2·57	—	2·53	105°	—	114°
	Sodium phosphoramidate	3	2·60	—	2·57	104°	—	114°
RO–PO_3	Calcium thymidylate	4	—	2·45 Å	2·49	—	106°	113°
	β-$Ca_2P_2O_7$	5	—	2·45	2·53	—	105°	113°
	$Na_4P_2O_7.10H_2O$	6	—	2·49	2·53	—	105°	113°

1. This work
2. Herriott (1967)
3. Cruickshank (1964*a*)
4. Trueblood *et al.* (1961)
5. Webb (1966)
6. Cruickshank (1964*b*); MacArthur & Beevers (1957).

distorted pentagonal bipyramid. The detailed geometry of this bipyramid is given in Table 10. The five oxygen atoms forming the base of the bipyramid lie in an infinite chain of calcium, phosphorus, and oxygen atoms, as shown in Figs. 4 and 6. An identical arrangement exists in calcium thymidylate, as reported by Trueblood, Horn & Luzzati (1961). (In thymidylate there is a crystallographic screw axis along the chain, whereas in DPI there is an inversion center.) Similar chains exist in $CaHPO_4$ and $CaH_2PO_4 . H_2O$ (MacLennan & Beevers, 1955, 1956) where the calcium ions are 7 and 8 coordinated.

These chains all involve bidentate coordination. Table 11 summarizes the Ca–O coordination distances in these and several other structures containing 7-coordinate calcium. The geometry of all these  groups is strikingly similar. In each calcium polyhedron, the largest Ca–O distance is approximately the same, and involves a bidentate oxygen. The range of Ca–O distances is much smaller in calcium naphthyl phosphate, which does not contain a bidentate ligand. Li & Caughlan (1965) attribute this small range to the relative lack of constraints on the coordinated oxygen atoms.

The water molecules and hydrogen bonding

There are six crystallographically independent water molecules in the structure; their hydrogen bonds are summarized in Table 12. Four of them participate in hydrogen-bonded 'cages'. These cages are very reminiscent of similar configurations in clathrate compounds. The main differences are that, in DPI, there are fewer water molecules participating, and there is no space for an entrapped molecule. (The *W*(5)–*W*(5′) distance is 3·78 Å across the center of the cage.)

This arrangement is depicted by an idealized projection in Fig. 5 and in the stereoscopic view, Fig. 6. The cages are centrosymmetric, with sixteen edges (H-bonds) and twelve corners (atoms). The range of the 8 crystallographically independent H-bonds in the cage is 2·74 to 2·82 Å; the average, 2·784 Å. Eight of the corners are occupied by water molecules (4 independent) and 4 by phosphate oxygen atoms (2 independent).

The hydrogen bond arrangement about the two phosphoryl oxygen atoms in the cage, O(32) and O(33), is roughly tetrahedral. These bonds are quite symmetric with respect to the P–O axes; the P–O-water angles are 117°, 127°, 128°, and 121°, 123°, and 122°, respectively. Phosphoryl oxygen atoms have been observed to accept three hydrogen bonds in at least three other structures (see Table 8). In all three cases, howvere, there is much less symmetry about the P–O axis.

As Table 12 shows, all hydrogen atoms but one are used in hydrogen bonding. The free hydrogen atom is attached to *W*(2) which has three potential hydrogen bond acceptors nearby: *W*(3), 3·15 Å; *W*(4), 3·11 Å; and *W*(5), 2·97 Å. The difference map indicates possible hydrogen atom sites between *W*(2)–*W*(4) and *W*(2)–*W*(5). However, the *W*(4)–*W*(2)–*W*(5) angle is 140°. If one concludes that *W*(2) forms a hydrogen bond only to its nearest neighbor, *W*(5), then all six water molecules in the structure satisfy their lone-pair electron regions by either accepting two hydrogen

Table 10. *Distances and angles in the* Ca(2) *bipyramid*

The apices of all angles in the table are at Ca(2).

Distances		Angles Apex-to-base		Angles Apex-to-base		Base	
Ca(2)–O(31′)	2·27 Å	O(31′)–O(13)	85·9°	*W*(3‴)–O(13)	98·4°	O(13)—O(13″)	72·4°
Ca(2)–*W*(3‴)	2·42	O(31′)–O(13″)	89·5	*W*(3‴)–O(13″)	86·4	O(13″)–O(12″)	57·0
Ca(2)–O(13)*	2·33	O(31′)–O(12″)	80·2	*W*(3‴)–O(12″)	92·7	O(12″)–O(12^{iv})	77·8
Ca(2)–O(13″)*	2·46	O(31′)–O(12^{iv})	85·9	*W*(3‴)–O(12^{iv})	92·8	O(12^{iv})–*W*(4)	79·8
Ca(2)–O(12″)*	2·64	O(31′)–*W*(4)	106·0	*W*(3‴)–*W*(4)	80·7	*W*(4)——O(13)	76·4
Ca(2)–O(12^{iv})*	2·30						
Ca(2)–*W*(4)*	2·47						

* atoms which form the pentagonal base of the bipyramid

(′) = 1 − *x*, 1 − *y*, 1 − *z* (‴) = *x*, *y*, *z* − 1
(″) = 1 − *x*, 1 − *y*, − *z* (^{iv}) = 1 + *x*, *y*, *z*

Table 11. *Calcium–oxygen distances for seven-coordinated calcium ions*

Compound	Reference	Range	Average	Bidentate legs	
DPI	1	2·27–2·64 Å	2·41 Å	2·46 Å	2·64 Å
Ca thymidylate	2	2·29–2·65	2·42	2·39	2·65
β-Ca_2PO_7	3	2·32–2·69	2·43	2·46	2·69
β-Ca_2PO_7	3	2·34–2·78	2·45	2·42	2·78 (bridge)
$CaHPO_4$	4	2·29–2·69	2·44	2·44	2·69
Ca naphthyl phosphate	5	2·36–2·45	2·42	none	

1. This work
2. Trueblood, *et al.* (1961)
3. Webb, (1966)
4. MacLennan & Beevers (1955)
5. Li & Caughlan (1965)

bonds, or coordinating to one calcium ion (see Clark, 1963). As expected (Templeton, 1960 and Clark, 1963), no hydrogen bonds were found along cation polyhedron edges.

Description of the crystal structure

A very good notion of the crystal structure is conveyed by the stereoscopic view* of the unit cell, Fig. 6. The structure might be described as a three-dimensional network held together by interactions between four gross structural elements; the DPI molecule, the hydrogen-bonded cage, and the two coordination polyhedra of the calcium atoms. These elements interact to form a very cohesive structure as evidenced by the hardness of the crystals and their stability under ordinary laboratory conditions. Interactions between these groups are few and may be best seen in Fig. 6.

The imidazole rings are normal to the *a* axis with the planes of adjacent rings 3·40 and 3·50 Å apart. The rings are staggered, so the intermolecular distances are larger than the interplanar distances. The shortest intermolecular contact is 3·42 Å, between C(4) and C(4″). Other intermolecular distances are listed in Table 13.

It is interesting to compare the twinning in CaDPI with that found in $Ca(H_2PO_4)_2.H_2O$ (MacLennan & Beevers, 1956). This compound also forms twinned crystals in the space group $P\bar{1}$. The environments of the twinning planes are very similar in the two structures, with a bidentate $\mathrm{Ca}\begin{smallmatrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\mathrm{P}$ chain running along

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* This illustration was photographically reduced from a drawing prepared by a mechanical plotter. We thank Dr Carroll Johnson for setting up and running the OR TEP program (Johnson, 1965).

Table 13. *Intermolecular atomic separations less than* 4·0 Å

Only imidazole atoms are shown.

Atoms*	Distance	Atoms*	Distance
N(1)–C(4′)	3·84 Å	N(3)–C(4″)	3·81 Å
N(3)–C(4′)	3·90	N(3)–C(5″)	3·81
N(3)–C(5′)	3·72	C(4)–C(4″)	3·42
C(4)–C(4′)	3·55	C(4)–C(5″)	3·60
C(4)–C(5′)	3·52		
C(5)–C(5′)	3·98		

* $( )=x,y,z$; $(')=1-x,1-y,1-z$; $('')=-x,1-y,1-z$.

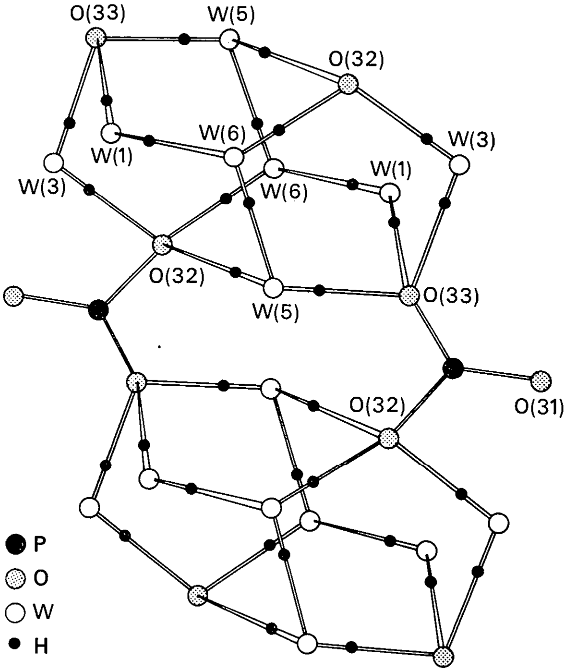

Fig. 5. Hydrogen-bonded 'cages'. The hydrogen bonding between some of the oxygen atoms in the calcium DPI structure as seen in an idealized projection approximately along [11$\bar{1}$].

Table 12. *Bonding to the water molecules in* DPI

Atoms in negative region of donor	H-bond donor (O_d)	Bonding H	H-bond acceptor (O_a)	O_d–O_a (Å)	O_a–O_d–O_a	ϱ_o–ϱ_c at hydrogen position (e.Å^{-3})
Ca(1)	†**W*(1)	H(11)	*O(33)	2·79	100°	0·53
		H(12)	**W*(6)	2·80		0·52
Ca(1)	†*W*(2)	H(21)	**W*(5)	2·97	—	0·47
		H(22)	none	—		0·48
Ca(2)	†**W*(3)	H(31)	*O(32)	2·81	104°	0·50
		H(32)	*O(33)	2·82		0·37
Ca(2)	†*W*(4)	H(41)	**W*(6)	2·81	105°	0·41
		H(42)	†O(11)	2·99		0·50
H(21)	**W*(5)	H(51)	*O(32)	2·78	119°	0·59
H(62)		H(52)	*O(33)	2·77		0·32
H(11)	**W*(6)	H(61)	*O(32)	2·77	105°	0·35
H(41)		H(62)	**W*(5)	2·74		0·39

* Denotes a member of the 'cage'.
† Denotes an oxygen coordinated to calcium

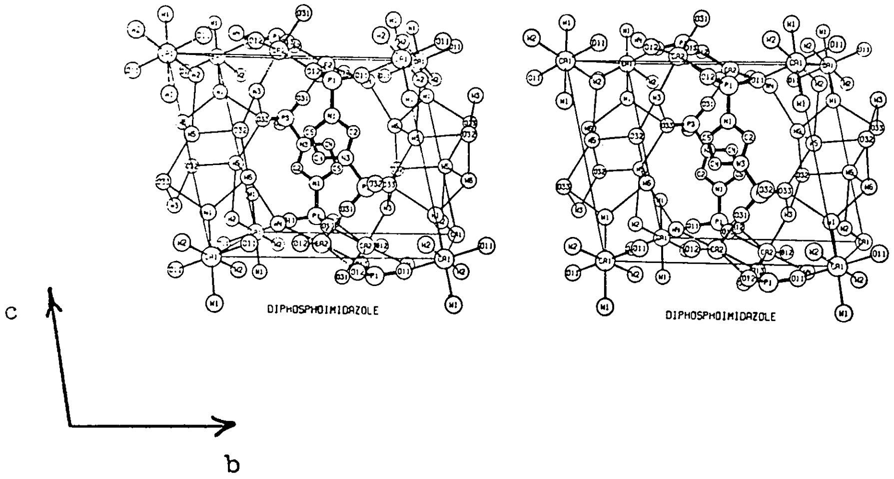

Fig. 6. CaDPI stereoscopic pair viewed nearly along *a*.

the plane, and with adjacent links related by a center of symmetry. The twinning is examined in some detail by MacLennan & Beevers in comparison with twinning found in brushite and gypsum, and the reader is referred to their discussion.

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