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The Crystal Structure of Phosphorous Acid

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The crystal structure of phosphorous acid, H_3PO_3, has been determined by X-ray methods. The space group is $Pna2_1$ and there are eight molecules per unit cell. Two of the P—O bonds in the molecule, presumably the P—OH bonds, are found to be about 1.54 Å, whereas the bond to the third oxygen atom is significantly shorter, 1.47 Å. There are two hydrogen bonds for each molecule. These observations are in agreement with the accepted structural formula $H_2(HPO_3)$.

As phosphorous acid, H_3PO_3, is dibasic, it is generally assumed that one of the hydrogen atoms is linked directly to the phosphorus atom. In connection with our work on phosphoric acid [2] we thought it of value to study the structure of this interesting molecule by X-ray crystallographic methods, especially as no such investigation of phosphites was reported in the literature. Only very recently the first crystal structure determination of a phosphite, $MgHPO_3.6H_2O$, was published [1], showing HPO_3^{--} ions with trigonal symmetry.

EXPERIMENTAL

Phosphorous acid was prepared by hydrolysis of phosphorus trichloride and recrystallized from water and alcohol. The best crystals were obtained from the latter solvent. Mp. 73°C (uncorr.). The crystals are hygroscopic and were kept in thinwalled glass capillaries during the exposures. Weissenberg and oscillation diagrams were taken about the *a*- and *c*-axes using Cu$K\alpha$ radiation (λ = 1.542 Å). The intensities were estimated visually, and corrected for Lorentz and polarization effects. Very small crystals with even cross-sections were used and no correction for absorption was made.

CRYSTAL DATA

The crystals are orthorhombic, generally elongated along *a*, with unit cell dimensions a = 7.27 Å, b = 12.06 Å and c = 6.85 Å. These values are probably accurate to within 0.5 %. By flotation in mixtures of carbon tetrachloride and ethylene dibromide a density of 1.806 g/cm^3 was found, corresponding to eight (calc. 7.96) molecules H_3PO_3 in the unit cell.

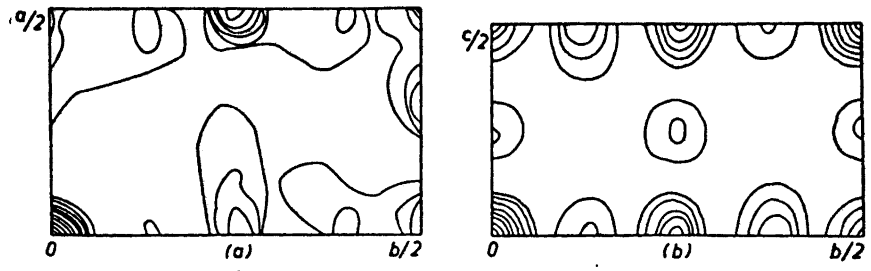

Fig. 1. Patterson projections on the (001) plane (a) and the (100) plane (b).

Systematic absences occur in the $0kl$-reflections for $k+l$ odd and in the $h0l$-reflections for h odd. The space groups $Pna2_1$ and $Pnam$ are both compatible with these observations. The crystals were tested for piezoelectric effects with a sensitive apparatus built by one of us (P.L.), but no effect was found. The space group $Pna2_1$ was nevertheless tentatively assumed on the basis of space considerations, and the subsequent structure analysis showed the choice to be correct. As this space group has four general positions, the asymmetric unit consists of two molecules H_3PO_3. Reflections $0k0$ are extremely weak when k is not 4n, and the crystals have in fact pseudotetragonal symmetry.

THE STRUCTURE DETERMINATION

Projections of the structure along the c and a axes were determined by Patterson, F and $(F_o—F_c)$ syntheses. The c projection was tackled first as it is the only one with apparent centres of symmetry.

The c-projection. The Patterson synthesis reproduced in Fig. 1a indicates that one phosphorus atom lies at $y = 1/8$ and the other at $y = 3/8$, and that approximately $x = 0$ for one or both of them. Coordinates (0, 1/8) and (0, 3/8) were chosen for the first Fourier synthesis, from which some information on the positions of the oxygen atoms was obtained. Because of the pseudotetragonal symmetry a difference of $b/4$ in the y coordinates of corresponding atoms in the two crystallographically independent molecules was assumed. Some agreement between F_o and F_c was obtained by Fourier refinement. However, the value of F_c remained very small for some strong reflections. The likely signs of these were then derived by the "multiplication rule" (Sayre [3]). The corresponding Fourier map indicated clearly radical shifts in the x coordinates of some of the oxygen atoms, and by further refinement the final electron density map given in Fig. 2a was obtained. Four further refinements of the atomic coordinates were carried out by $(F_o—F_c)$ synthesis. The same temperature factor $\exp(-2.2 \sin^2\Theta/\lambda^2)$ was used for all the atoms, although the final difference map shows this to be only approximately correct. The atomic scattering factors employed are those given by Viervoll and Øgrim [4]. No attempt was made to derive the positions of the hydrogen atoms from the difference maps, and their contribution to the structure factors was calculated from assumed positions. The final value of the reliability index $R = (\Sigma|F_o—F_c|)/\Sigma|F_o|$ is

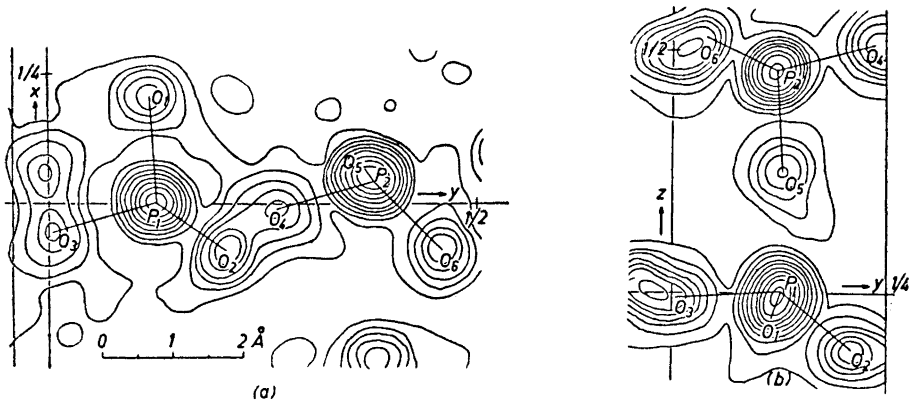

Fig. 2. Electron density projections on the (001) plane (a) and the (100) plane (b). Contours at 2, 4, 6, . . . e . Å^{-2}, every second contour being omitted above 12 e . Å^{-2}. Calculated at 1/60 of b and 1/30 of a and c.

0.10. The strongest reflection, 200, which evidently suffers from extinction (as well as 002 in the a projection), is not included in the calculation of R. Reflections not observed are only taken into account when F_c exceeds the observable limit.

The a-projection. The Patterson synthesis (Fig. 1b) shows that the difference in z-coordinates of the two phosphorus atoms probably is near $c/2$. Approximate z-coordinates for the oxygen atoms were derived from the known coordinates and the P—O distances found in phosphoric acid [2]. Two different mutual orientations of the molecules were possible, which both gave $R = 0.33$. The one chosen changed in the course of the refinement to the other possibility. Three Fourier refinements brought R down to 0.20, followed by five difference syntheses which made R drop to 0.10. As this projection is non-centrosymmetric, the atoms were in each refinement moved approximately twice the amount indicated by the Fourier- and difference-maps. The process would have been speedier if the atoms had been moved even more than this in each refinement. The final electron density map is shown in Fig. 2b, and the atomic coordinates are given in Table 1. The temperature factor is the same as in the c-projection. In Table 3 observed and calculated structure factors are given.

Table 1. Atomic coordinates as fractions of the corresponding cell edge.

Atom	x	y	z
P_1	0.002	0.1265	0.003
P_2	0.046	0.378	0.461
O_1	0.208	0.116	0.951
O_2	0.910	0.209	0.874
O_3	0.940	0.004	0.985
O_4	0.994	0.259	0.518
O_5	0.075	0.369	0.241
O_6	0.909	0.459	0.518

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

From the atomic coordinates in Table 1 the bond lengths and bond angles given in Table 2 were calculated.

Table 2. Bond lengths (in Å units) and bond angles.

Molecule I		Molecule II	
P_1-O_1	1.544	P_2-O_5	1.526
P_1-O_2	1.485	P_2-O_6	1.451
P_1-O_3	1.552	P_2-O_4	1.535
$O_1-P_1-O_2$	111°	$O_5-P_2-O_6$	114°
$O_1-P_1-O_3$	101°	$O_5-P_2-O_4$	103°
$O_2-P_1-O_3$	117°	$O_6-P_2-O_4$	114°

The standard deviation of the atomic coordinates were estimated by applying the formula given by Cruickshank [5]. The following values were found: $\sigma(x) = 0.004$ Å, $\sigma(y) = 0.003$ Å, $\sigma(z) = 0.005$ Å for the phosphorus atoms; $\sigma(x) = 0.016$ Å, $\sigma(y) = 0.012$ Å, $\sigma(z) = 0.024$ Å for the oxygen atoms. In the case of $\sigma(z)$ the lack of a centre of symmetry is taken into account by multiplication by 2. The standard deviation in the bond lengths vary between 0.013 Å for the bond $P_1—O_3$ and 0.024 Å for $P_2—O_5$. Unfortunately, an oxygen atom is very close to a phosphorus atom in each projection (O_5 and O_1, respectively), and the error in the position of these atoms may be considerably greater than should be expected from the calculated standard deviations. This does not influence the bond lengths appreciably, but makes the values derived for the bond angles rather uncertain. The maximum error is estimated to about 5° for the angles $O_1—P_1—O_2$ and $O_5—P_2—O_6$ and to about 3° for the other angles.

It will be seen that the two crystallographically independent molecules are found to be identical within the limits of error. The differences observed in the bond angles may also partly be due to deformation by van der Waals forces [6]. In each of the molecules there is one shorter and two longer P—O bonds, and one of the bond angles is considerably smaller than the others. The mean dimensions of the two molecules are given in Fig. 3. The short P—O bond, which presumably corresponds to the "lone" oxygen, has the length of 1.47 Å, and is significantly shorter than the two bonds to the "hydroxyl" oxygens, for which values close to 1.54 Å are found. The angle between the two P—OH bonds is as small as 102°, whereas all the angles involving the short P—O bond are greater than the tetrahedral angle, their mean value being 114°. The O—O distance across the small angle is only 2.39 Å in both molecules. Approximate positions for the hydrogen atoms of the hydroxyl groups may be derived from the directions of the hydrogen bonds. All O—H bonds lie roughly in the plane of the two P—OH bonds, and the whole molecule has thus approximately a plane of symmetry. These molecular dimensions are, as might be expected, somewhat different from those reported for the phosphite ion, which is found to have threefold symmetry about the P—H bond direction with P—O bonds of length 1.51 Å and O—P—O bond angles of 110°.

Table 3. Observed and calculated structure factors. The values given are one quarter of the absolute values.

hkl	F_o	F_c	*hkl*	F_o	F_c
011	1.8	1.5	0 14 0	<0.8	+ 0.1
031	8.8	6.5	110	0.9	− 0.9
051	12.2	12.4	120	0.7	+ 0.5
071	2.7	3.1	130	1.2	+ 1.1
091	3.9	3.9	140	6.0	+ 5.5
0 11 1	2.2	2.3	150	7.1	+ 7.3
0 13 1	2.3	2.1	160	<1.0	− 0.2
0 15 1	1.2	1.5	170	1.3	+ 1.5
002	18.0	38.4	180	1.4	− 1.2
022	5.8	6.4	190	2.8	+ 2.1
042	4.8	5.8	1 10 0	<1.2	− 0.6
062	2.2	1.2	1 11 0	2.6	+ 3.0
082	13.5	14.7	1 12 0	<1.2	− 0.6
0 10 2	3.6	3.4	1 13 0	1.5	+ 1.6
0 12 2	5.7	5.9	1 14 0	<1.0	− 0.4
0 14 2	1.5	1.3	1 15 0	2.3	+ 2.3
013	8.1	8.3	200	16.8	+34.6
033	5.8	5.4	210	2.3	− 2.2
053	8.3	8.4	220	2.7	− 2.7
073	2.2	1.8	230	9.4	− 9.4
093	<1.2	0.3	240	4.6	− 4.8
0 11 3	<1.2	0.3	250	10.6	+11.0
0 13 3	1.3	0.7	260	<1.2	+ 0.7
004	17.4	21.1	270	8.9	+ 8.4
024	4.9	5.1	280	12.8	+12.9
044	11.3	11.3	290	3.5	− 2.9
064	1.8	0.9	2 10 0	<1.2	− 1.1
084	11.8	12.5	2 11 0	<2.1	− 1.1
0 10 4	2.6	3.2	2 12 0	5.4	+ 5.3
0 12 4	4.6	4.2	2 13 0	<1.0	+ 0.9
015	4.2	4.5	310	3.7	+ 1.8
035	5.0	5.1	320	12.4	+13.9
055	7.4	8.1	330	3.7	+ 2.7
075	3.1	3.3	340	5.5	− 5.4
095	1.4	1.9	350	<1.2	+ 1.3
0 11 5	2.4	2.5	360	8.7	− 8.5
006	7.8	6.8	370	4.4	+ 3.2
026	2.9	2.8	380	4.3	− 3.5
046	5.8	5.5	390	<1.2	− 0.9
066	1.1	0.7	3 10 0	5.6	+ 5.2
086	5.3	4.9	3 11 0	<1.2	− 0.8
0 10 6	1.6	1.7	3 12 0	<1.2	+ 0.9
017	2.2	2.2	3 13 0	<1.0	+ 0.4
037	2.1	1.9	3 14 0	2.6	− 2.5
057	3.4	3.8	400	10.0	+10.4
077	1.8	1.8	400	10.0	+10.4
008	4.9	4.3	410	1.2	− 0.9
028	1.1	1.0	420	3.3	− 3.0
048	3.4	2.7	430	5.1	− 4.5
020	0.6	− 0.5	440	9.4	− 8.5
040	12.2	−13.9	450	7.5	+ 7.5
060	<0.8	+ 0.4	460	2.5	− 2.1
080	18.4	+19.6	470	5.5	+ 5.0
0 10 0	1.2	− 1.6	480	9.8	+ 9.6
0 12 0	8.9	− 9.3	490	2.2	− 2.7

Table 3. Continued.

hkl	F_o	F_c	*hkl*	F_o	F_c
4 10 0	<1.2	− 0.6	660	1.6	− 1.9
4 11 0	<1.2	− 0.7	670	3.7	+ 3.8
4 12 0	2.9	− 2.0	680	3.4	+ 3.3
4 13 0	1.6	+ 1.5	690	1.9	− 2.0
510	7.3	+ 7.6	6 10 0	1.1	− 1.3
520	6.0	+ 6.8	6 11 0	2.8	− 3.1
530	3.7	− 3.0	710	3.2	+ 3.2
540	<1.2	− 0.7	720	3.3	+ 2.7
550	7.4	− 7.3	730	3.7	− 3.7
560	5.1	− 5.1	740	1.9	+ 1.9
570	6.3	+ 5.7	750	3.8	− 4.7
580	<1.2	− 0.5	760	2.4	− 2.1
590	1.8	+ 0.8	770	2.9	+ 3.5
5 10 0	3.6	+ 3.6	780	0.9	+ 1.0
5 11 0	3.2	− 3.1	790	0.9	+ 0.1
5 12 0	<1.0	+ 0.5	800	<1.0	− 0.7
600	<1.2	− 0.1	810	1.9	− 1.7
610	5.5	− 5.3	820	1.3	− 2.0
620	2.0	− 2.7	830	<1.0	− 1.1
630	5.9	− 5.7	910	2.3	+ 2.5
640	5.4	− 3.4	920	1.2	+ 0.9
650	4.0	+ 3.9	930	3.3	− 4.4

It would seem to be of interest to compare the molecule of phosphorous acid with that of phosphoric acid [2]. In phosphoric acid the short P—O bond is found to be 1.52 Å and the P—OH bonds to be 1.57 Å. Values of 106° and 112° were found for the two types of bond angles. Phosphorous acid may be derived from phosphoric acid by substituting a hydroxyl group by a hydrogen atom. It is seen that this change appears to make all the bond angles deviate more from the tetrahedral angle and all the P—O bonds shorter, especially the short P—O bond. Correspondingly, the angles involving this bond are greater in H_3PO_3 than in H_3PO_4, and the angles between P—OH bonds smaller. Although these differences are small, they are probably significant in view of the agreement in the dimensions of the two independent molecules of H_3PO_3.

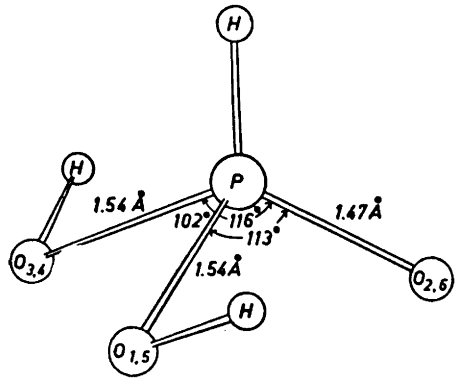

Fig. 3. Bond lengths and bond angles in H_3PO_3.

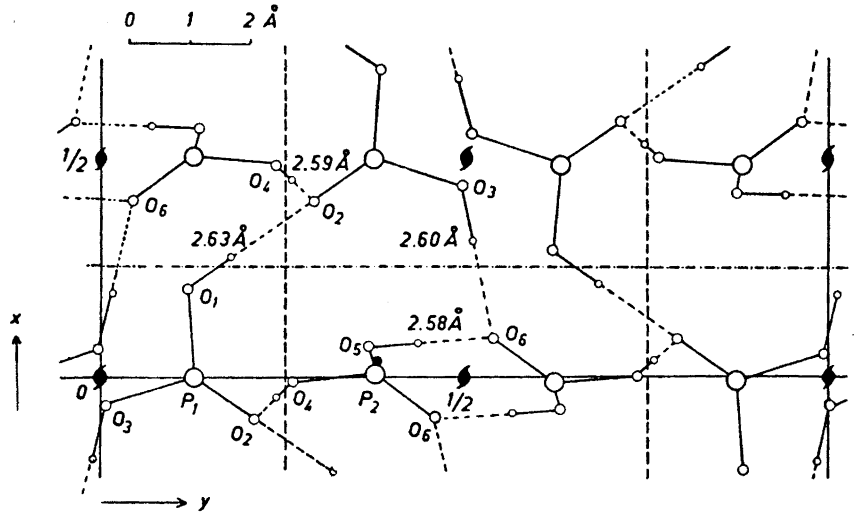

Fig. 4. The c projection of the structure. Broken lines indicate hydrogen bonds.

The molecules are linked together by hydrogen bonds, as shown in Fig. 4. There are two such bonds for each molecule, as to be expected from the formula $HPO(OH)_2$, but not from $P(OH)_3$. The four bonds are of nearly equal length, the values 2.59 Å, 2.63 Å, 2.58 Å and 2.60 Å being found. All other intermolecular O—O distances are greater than 3.0 Å. The two "lone" oxygen atoms O_2 and O_6 each take part in two hydrogen bonds, whereas each of the other oxygen atoms is involved in only one such bond. As generally found in crystal structures, the angles between the hydrogen bonds and the P—O bonds are least distorted at the oxygen atoms to which the hydrogen atoms are bonded. The two hydrogen bonds to the "lone" oxygen atom in H_3PO_4 are 2.53 Å of length, somewhat shorter than in the present case.

The structure has pseudo-tetragonal symmetry, with an approximate 4_1 axis roughly at (0, y, 1/4). This holds not only for the atomic coordinates and the molecular dimensions, but also for the hydrogen bonding scheme.

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