

The Crystal Structure of Phosphoric Acid

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The crystal structure of anhydrous phosphoric acid, H_3PO_4 , has been determined by X-ray methods. Three of the P—O bonds in the molecule, presumably the P—OH bonds, are found to be 1.57 Å, whereas the bond to the fourth oxygen is significantly shorter, 1.52 Å. The PO_4 group deviates slightly, but significantly from tetrahedral symmetry; it has within the limits of error trigonal symmetry. Two hydrogen bonds of length 2.53 Å connect the "keto" oxygen with "hydroxyl" oxygens, whereas the third bond between two "hydroxyl" oxygens is found to be 2.84 Å. Approximate positions derived for the hydrogens show that these atoms probably are ordered.

Phosphoric acid, phosphates, and phosphate esters are compounds of considerable interest from several points of view, and a detailed knowledge of their stereochemistry would appear to be desirable. A number of investigations of KH_2PO_4 have been carried out^{1,2}, but no other detailed structure analysis in this field appears to be reported in the literature. A preliminary note on the structure of phosphoric acid, H_3PO_4 , based on Fourier projections along two axes was published in 1954 by the author³. Recently Smith, Brown and Lehr⁴ have given an account of the structure on the basis of similar evidence. The present paper describes a more comprehensive analysis, the results of which differ in part considerably from those obtained by Smith, Brown and Lehr.

EXPERIMENTAL

Highly purified crystalline phosphoric acid from The British Drug Houses Ltd. was used for the investigation. All the work was carried out at room temperature. The crystals are very hygroscopic and have a low melting point (42° C). They were therefore studied and cut in dry CCl_4 and mounted in thinwalled glass capillaries. Partial melting and recrystallization in the capillaries was difficult to avoid. Weissenberg and oscillation photographs were taken about two crystallographic axes using filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.542$ Å). The intensities were estimated visually.

CRYSTAL DATA

The crystals are monoclinic, elongated along the b axis, usually with (001) dominating. Twinning on (001) was observed in one batch of crystals. The unit cell dimensions are: $a = 5.78$ Å, $b = 4.84$ Å, $c = 11.65$ Å, and $\beta = 95.5^\circ$,

the values being accurate to within 0.5 %. The only systematic absences occur in the $h0l$ reflections for l odd and in the $0k0$ reflections for k odd, and the space group is $P2_1/c$. By flotation in mixtures of carbon tetrachloride and ethylene dibromide a density of about 2.0 g/cm³ was found, corresponding to four molecules in the unit cell. The calculated density is 2.00 g/cm³. The density of pure liquid phosphoric acid is 1.834 g/cm³ at 18° C.

In the literature the crystals are described as orthorhombic (Joly ⁵), and a pseudo-orthorhombic unit cell may in fact be chosen.

THE STRUCTURE DETERMINATION

Projections of the structure in direction of the b - and a -axes were determined independently using Patterson, Fourier and difference methods.

The structure factors. In the b -axis projection all 83 reflections attainable with $\text{CuK}\alpha$ radiation were recorded with measurable intensity. Two different crystals were used with cross-sections 0.12×0.15 mm and 0.20×0.25 mm, respectively. The agreement between the two sets of measurements was good and the mean value taken. The intensities were corrected for Lorentz and polarization effects, but not for absorption. In the a -axis projection a crystal of cross-section 0.14×0.25 mm was used and 66 out of 71 reflections were recorded.

The approximate structure. The positions of the phosphorus and some of the oxygen atoms were derived from Patterson projections, and after four Fourier refinements the electron density maps given in Fig. 1 were obtained. The resolution is not good as one oxygen is close to the phosphorus in both projections. Diffraction effects are also evident in the maps. The reliability index $R = (\sum |F_0 - F_c|) / \sum |F_0|$ was at this stage about 0.20. The coordinates

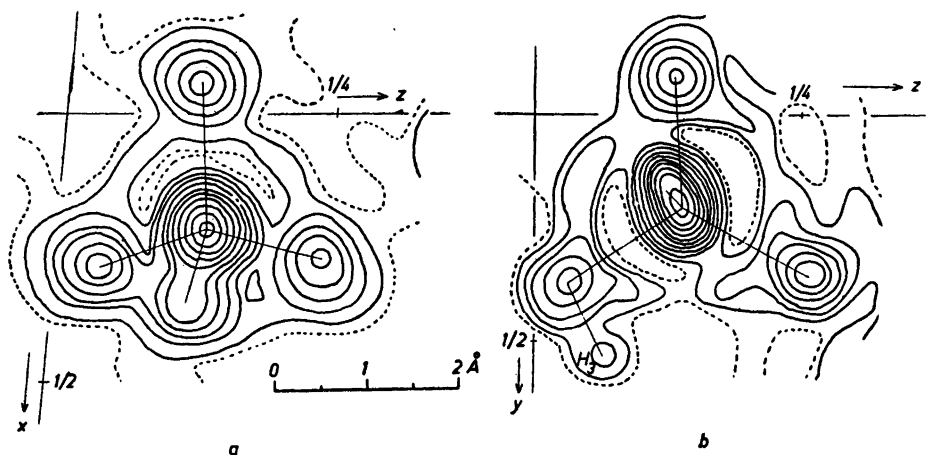


Fig. 1. Electron density projections on the (010) plane (a) and the (001) plane (b). Contours at 2, 4, 6, $e \cdot \text{Å}^{-2}$, every second contour being omitted above $12 e \cdot \text{Å}^{-2}$. The broken line corresponds to $1 e \cdot \text{Å}^{-2}$. Calculated at $1/60$ of c and $1/30$ of a and b .

derived from the maps differed in part considerably from those finally obtained by $(F_0 - F_c)$ syntheses.

$(F_0 - F_c)$ refinement. The structure was further refined by successive $(F_0 - F_c)$ syntheses (Cochran ⁶). The refinement was continued until at all atomic centres the synthesis and its slope were nearly zero, whereas only an approximate correction was made for anisotropy in the thermal vibrations.

In the b -projection eight successive difference syntheses were calculated. Corrections to the positional and vibrational parameters were derived partly from the difference maps, partly by plotting F_0/F_c against $\sin^2\Theta$. One adjustment of scale and temperature factors was also carried out by least squares calculation, in which 75 linear equations, one for each reliable reflection, were solved for four unknowns in groups corresponding to different directions in the reciprocal lattice. In the temperature factor $\exp(-B \sin^2 \Theta/\lambda^2)$ finally chosen B was 3.1 \AA^2 for the oxygen atoms and $1.7 - 0.4 \sin^2\varphi$ for the phosphorus atom, where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom. This direction lies about 40° from c in the obtuse angle. In addition, the vibrations of the molecule as a whole appear to be slightly asymmetric with maximum vibration in a direction about 15° from a in the obtuse angle. This was corrected for by applying a factor $\exp(-0.5 \sin^2\varphi' \cdot \sin^2\Theta/\lambda^2)$. The final difference map is given in Fig. 2a. The highest peaks are probably due to hydrogen atoms, which were not included in F_c at this stage. Atomic coordinates are given in Table 1.

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

Atom	x	y	z
P	211	202	1402
O ₁	282	346	2538
O ₂	328	910	1295
O ₃	277	371	0330
O ₄	942	157	1205

The a -projection was less completely refined. Five difference syntheses were calculated, but in the last map, which is given in Fig. 2b, there are still irregularities of considerable magnitude. Probably the intensity measurements were less accurate in this zone. A temperature factor with $B = 0.9 - 0.5 \sin^2\varphi''$ was applied to the oxygen atoms and $B = 0.9 - 1.4 \sin^2\varphi''$ to the phosphorus atom, where φ'' is the angle between b and the normal to the reflecting plane. It will be seen that the values of B are much lower in this projection. The temperature factors probably have little significance in terms of thermal motion of the atoms; rather, they represent also other effects such as absorption and variation in spot shape.

The atomic scattering curves given by Viervoll and Øgrim ⁷ were used in all the calculations. When the seven reflections suffering from extinction (see below) are not included, the reliability index R is 0.08 for the b projection and 0.13 for the a projection. In Table 5 observed and calculated structure factors are given (hydrogen contribution included).

The hydrogen atoms. The standard deviation in electron density is about $0.25 \text{ e} \cdot \text{\AA}^{-2}$ for the $(h0l)$ zone and $0.6 \text{ e} \cdot \text{\AA}^{-2}$ for the $(0kl)$ zone. Only the highest

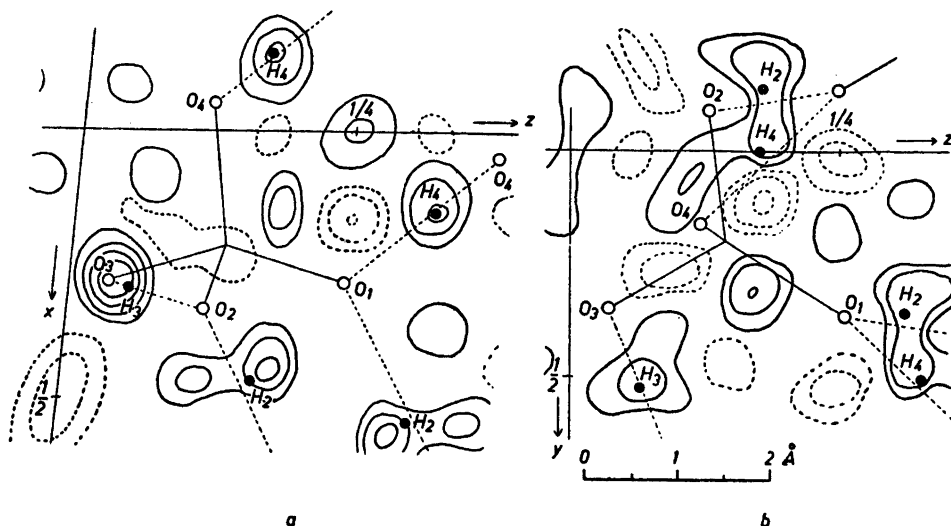


Fig. 2. Difference-syntheses on the (010) plane (a) and the (100) plane (b). In (a) the contour interval is $0.2 e \cdot \text{\AA}^{-2}$, in (b) $0.5 e \cdot \text{\AA}^{-2}$. Hydrogen contribution not included in F_c . Negative contours are broken and zero contour omitted. Hydrogen bonds are broken. The filled circles show the positions assigned to the hydrogen atoms.

peaks in the *b* projection (Fig. 2a) are therefore likely to be significant. They can reasonably be interpreted as indicating the positions of the three hydrogens, and show that these atoms probably are associated with oxygen atoms O₂, O₃ and O₄. There are no significant peaks near O₁. The hydrogen atom H₄ gives a well-defined peak, whereas H₂ is associated with a broad area near O₂. H₃ lies almost directly above O₃ and its height depends therefore on the choice of temperature factor for O₃. In the *a* projection (Fig. 2b), where the peaks are not significant, H₃ is well resolved, whereas H₂ and H₄ are poorly defined. H₃ also appears as a separate peak on the electron density map (Fig. 1b). The peak positions are very sensitive to changes in atomic coordinates and temperature factors, but it is believed that the assignment of the hydrogens is qualitatively correct. The following coordinates, which obviously are inaccurate, were derived: H₂ (0.46, -0.15, 0.18); H₃ (0.30, 0.54, 0.062); H₄ (0.15, 0.50, 0.33). The coordinates of H₃ and the *x*, *z* coordinates of H₄ were found directly from the maps. The others were deduced by taking the position of the hydrogen bonds into account. When the hydrogen contribution to the structure factors was included *R* dropped by about 0.01 to 0.07 and 0.12 for the two projections, respectively. Atoms H₂ and H₄ were given half weight as they take part in strong hydrogen bonds (Cochran⁹, Bernal¹⁰).

Extinction. In Table 2 the observed uncorrected intensity (I_{obs}) and F_0 and F_c of the seven strongest reflections are listed. It will be seen that the F_c values in all cases are much too high. The effect is thought to be due mainly to extinction. It presented a serious difficulty in the structure determination, making the calculation of scale and temperature

factors uncertain and preventing an experimental determination of the hydrogen contribution to these reflections. The reflections were not included in the calculation of the difference maps and their calculated values were used in deriving the electron density maps.

Table 2. *The strongest reflections.*

Reflection	I_{obs}	F_0	F_c	$0.11 F_0 \sqrt{I_{\text{obs}}}$
102	352	8.2	17.6	16.9
012	320	8.6	14.2	16.9
102	304	8.0	17.0	15.3
200	248	8.8	18.3	15.3
013	214	7.7	12.8	12.4
004	175	7.2	10.8	10.5
302	125	8.3	10.8	10.2

Assuming the F_c values to be nearly correct, it was found empirically that the extinction error could be roughly corrected for by multiplying F_0 by a factor $k\sqrt{I_{\text{obs}}}$ where k is a constant. The values of k varied from 0.10 to 0.13 and the mean value, 0.11, was used to derive the last column in Table 2. According to this the structure factors of the strongest reflections are approximately proportional to I_{obs} rather than to $\sqrt{I_{\text{obs}}}$ in the present case.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Accuracy of the structure. The standard deviations of the atomic coordinates were estimated by applying the formula given by Cruickshank⁸. The following values were found: $\sigma(x) = \sigma(z) = 0.008 \text{ \AA}$, $\sigma(y) = 0.024 \text{ \AA}$ for the oxygen atoms; $\sigma(x) = \sigma(z) = 0.002 \text{ \AA}$, $\sigma(y) = 0.005 \text{ \AA}$ for the phosphorus atom. An experimental check on the accuracy is provided by the two independent determinations of the z coordinates. They differed by 0.005 \AA for the phosphorus atom and by 0.004 \AA , 0.023 \AA , 0.012 \AA and 0.010 \AA for the oxygen atoms O_1 , O_2 , O_3 and O_4 , respectively. These values give a standard deviation of 0.009 \AA in the z coordinates of the oxygen atoms, about the same as found by Cruickshank's formula. From these results the standard deviations in the P—O bond lengths given in Table 3 were computed. The standard deviation of O—P—O bond angles were calculated to be approximately 0.7°. The standard deviation of electron density was found to be about $0.25 \text{ e} \cdot \text{\AA}^{-2}$ in the b projection and $0.6 \text{ e} \cdot \text{\AA}^{-2}$ in the a projection.

The molecular structure. From the coordinates in Table 1 the distances and angles given in Tables 3 and 4 and Fig. 3 were calculated. The bond P— O_1 is found to be 1.52 \AA , considerably shorter than the other three P—O bonds, which are all close to 1.57 \AA . The difference is significant. The bond lengths found by Smith, Brown and Lehr are also given in Table 3. As there appears to be hydrogen atoms attached only to O_2 , O_3 and O_4 , O_1 is the "keto" oxygen, in accordance with the shortness of the bond P— O_1 .

The bond angles show small, but significant deviations from the tetrahedral angle. Those involving the bond P— O_1 are greater than 109.5°, their mean value being 112°, whereas the angles between two P—(OH) bonds all are near 106°. Correspondingly, the distances from the "keto" oxygen to the "hydroxyl" oxygens (2.56—2.59 \AA) are somewhat greater than the distances

Table 3. Bond lengths.

Bond	Length (Å)	Standard deviation	Values from Ref. ⁴
P—O ₁	1.517	0.013	1.57
P—O ₂	1.577	0.024	1.59
P—O ₃	1.570	0.013	1.55
P—O ₄	1.568	0.008	1.52

Table 4. Bond angles and O—O distances.

	Angle		Length (Å)
O ₁ —P—O ₂	112.8°	O ₁ —O ₂	2.59
O ₁ —P—O ₃	112.2°	O ₁ —O ₃	2.57
O ₁ —P—O ₄	110.9°	O ₁ —O ₄	2.56
O ₂ —P—O ₃	105.3°	O ₂ —O ₃	2.50
O ₂ —P—O ₄	106.8°	O ₂ —O ₄	2.52
O ₃ —P—O ₄	105.3°	O ₃ —O ₄	2.50

between "hydroxyl" oxygens (2.50—2.52 Å). The PO₄ group thus deviates slightly from tetrahedral symmetry, but has within the limits of error trigonal symmetry with the shortest bond as trigonal axis.

Smith, Brown and Lehr⁴ found an irregularly distorted tetrahedron with one O—O distance as short as 2.34 Å.

It was found from the maps in Figs. 1a and 2a that the number of electrons in the phosphorus peak is 15.2 and in the oxygen peaks near 8.0. It is difficult to estimate the error because of partial overlap of atoms, uncertainties in the areas assigned to the atoms, and the extinction effect. The values indicate, however, that transfer of electrons, if any, only takes place to a small extent.

The values given by Pauling¹¹ for the length of single- and double-bonds P—O are 1.76 Å and 1.55 Å, respectively. Thus a very large amount of double-bond character is indicated for the three long P—O bonds of 1.57 Å. It is, however, less pronounced than for the shortest bond, which is only 1.52 Å. This bond is presumably a nearly pure double-bond, and it is possible that the

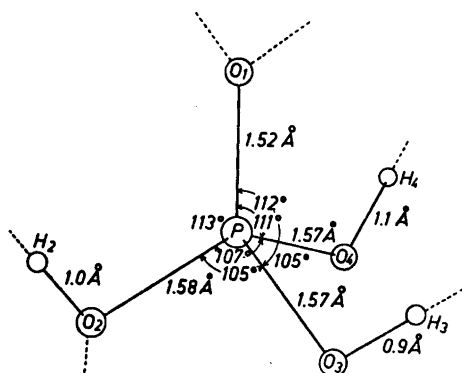


Fig. 3. The molecular structure of H₃PO₄. The broken lines indicate hydrogen bonds.

Table 5. Observed and calculated structure factors. The values given are one quarter of the absolute values. F_o 's suffering from extinction in brackets.

hkl	F_o	F_c	hkl	F_o	F_c
002	2.9	- 2.6	400	6.3	6.4
004	(7.2)	-10.8	402	4.7	4.3
006	2.3	1.9	404	3.1	- 3.2
008	10.3	11.7	406	4.2	- 3.6
0 0 10	7.0	- 7.0	408	3.8	3.8
0 0 12	4.2	- 3.9	4 0 10	1.1	- 1.0
0 0 14	1.8	2.1			
			$\bar{4}02$	5.7	- 5.3
100	3.7	3.2	$\bar{4}04$	3.0	2.6
102	(8.0)	-17.0	$\bar{4}06$	5.7	5.9
104	5.9	- 6.3	$\bar{4}08$	1.4	1.2
106	5.9	6.2	$\bar{4} 0 10$	4.8	- 4.8
108	5.8	- 5.9	4 0 12	1.9	2.1
1 0 10	5.2	- 5.1			
1 0 12	2.6	2.6	500	0.9	1.3
1 0 14	2.3	2.0	502	0.9	- 0.6
			504	4.5	- 4.6
$\bar{1}02$	(8.2)	17.6	506	1.9	2.0
$\bar{1}04$	5.4	- 5.2	508	1.0	- 0.3
$\bar{1}06$	4.3	- 4.7			
$\bar{1}08$	9.7	9.9	$\bar{5}02$	1.4	- 1.0
$\bar{1} 0 10$	5.2	5.1	$\bar{5}04$	5.1	- 5.1
$\bar{1} 0 12$	4.6	- 4.6	$\bar{5}06$	4.7	4.3
$\bar{1} 0 14$	0.7	- 0.5	$\bar{5}08$	3.1	3.2
			$\bar{5} 0 10$	1.9	- 2.0
200	(8.8)	- 18.3			
202	5.5	5.8	600	1.2	- 1.1
204	2.7	2.7	602	2.7	- 1.1
206	3.0	- 2.5	604	1.6	1.7
208	6.3	- 6.4	606	2.7	2.7
2 0 10	6.3	6.7			
2 0 12	3.5	3.6	$\bar{6}02$	2.5	2.7
			$\bar{6}04$	3.2	- 2.8
$\bar{2}02$	2.7	- 2.7	$\bar{6}06$	2.7	- 2.9
$\bar{2}04$	3.8	- 3.2	608	1.7	1.5
$\bar{2}06$	2.0	- 1.5			
$\bar{2}08$	4.3	- 4.4	700	2.8	- 2.6
$\bar{2} 0 10$	5.7	5.6	702	0.9	0.1
$\bar{2} 0 12$	1.1	- 1.0	$\bar{7}02$	1.1	0.9
2 0 14	1.4	- 1.5	704	4.1	4.1
300	4.3	3.9	011	4.6	4.1
302	(8.3)	10.8	012	(8.6)	-14.2
304	3.4	3.1	013	(7.7)	-12.8
306	7.5	- 7.6	014	1.5	- 0.8
308	4.8	4.1	015	6.1	- 5.9
3 0 10	5.2	5.3	016	6.2	6.2
3 0 12	1.8	- 1.7	017	6.5	5.7
			018	7.3	- 7.2
$\bar{3}02$	7.7	- 8.8	019	4.0	3.2
$\bar{3}04$	2.6	2.4	0 1 10	6.3	- 6.0
$\bar{3}06$	1.0	1.2	0 1 11	3.8	- 3.6
308	4.1	- 3.9	0 1 12	4.5	4.1
$\bar{3} 0 10$	2.8	- 2.5	0 1 13	< 1.0	0.7
3 0 12	1.7	1.9	0 1 14	2.2	2.4

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
020	7.9	— 9.0	040	4.7	— 4.7
021	3.2	2.2	041	5.3	5.5
022	4.3	3.2	042	2.1	— 0.9
023	4.6	— 4.6	043	5.9	6.6
024	4.4	4.7	044	2.6	— 2.2
025	8.5	0.2	045	7.5	— 9.0
026	2.7	— 2.0	046	2.4	1.9
027	2.9	1.6	047	2.1	— 1.5
028	5.8	— 5.6	048	1.7	— 1.6
029	< 1.5	0.7	049	5.5	5.6
0 2 10	5.4	5.0	0 4 10	< 0.7	0.3
0 2 11	< 1.5	— 0.1	0 4 11	0.8	1.0
0 2 12	1.8	1.8			
0 2 13	4.8	4.6	051	3.8	3.5
			052	2.9	2.3
031	4.7	— 4.4	053	3.7	— 2.7
032	6.9	6.7	054	1.8	1.4
033	7.9	9.4	055	< 0.9	— 0.6
034	4.4	— 3.5	056	1.0	— 0.8
035	5.0	4.8	057	4.1	3.8
036	6.4	— 7.2	058	1.0	1.1
037	5.9	— 6.3			
038	3.0	2.0	060	2.5	2.3
039	2.7	— 2.4	061	3.5	— 3.7
0 3 10	3.1	2.9	062	1.0	— 1.1
0 3 11	5.6	5.2	063	2.3	— 2.0
0 3 12	4.4	— 4.6			

value for a double-bond P—O should be revised slightly downwards from 1.55 Å. The values observed for the bond angles are in accordance with the different degree of double-bond character of the P—O bonds. One would expect a smaller bond angle between two bonds with partial single-bond character than between one such bond and a pure double-bond.

In the phosphorus oxyhalides a P—O distance of 1.55 ± 0.03 Å and bond angles of 106° (Cl—P—Cl) and 112° (Cl—P—O) are found¹². The angles are thus the same as in the present structure. In crystals of KH_2PO_4 all P—O bonds are reported to be equal, 1.56 Å, at room temperature, whereas below the Curie point, where ordering of the hydrogens is assumed, two sets of bonds of lengths 1.53 Å and 1.58 Å are found (Frazer and Pepinsky³). These values are close to those found in the present investigation (1.52 Å and 1.57 Å), where the hydrogens also appear to be ordered.

The hydrogen bonds. Only three intermolecular oxygen-oxygen separations are shorter than 3.0 Å, and as they all involve a hydrogen atom, they correspond to hydrogen bonds. Two of these are very short, 2.53 Å, connecting the "keto" oxygen O_1 with "hydroxyl" oxygens O_2 and O_4 in different neighbouring molecules. They firmly connect molecules related by screw axes into sheets parallel to the (001) plane. The third hydrogen bond is longer, 2.84 Å, forming a link between "hydroxyl" oxygens O_3 and O_2 in molecules related by b translation, thus further connecting the molecules within the sheets. There are no hydrogen bonds between the sheets. The two short bonds have the same length

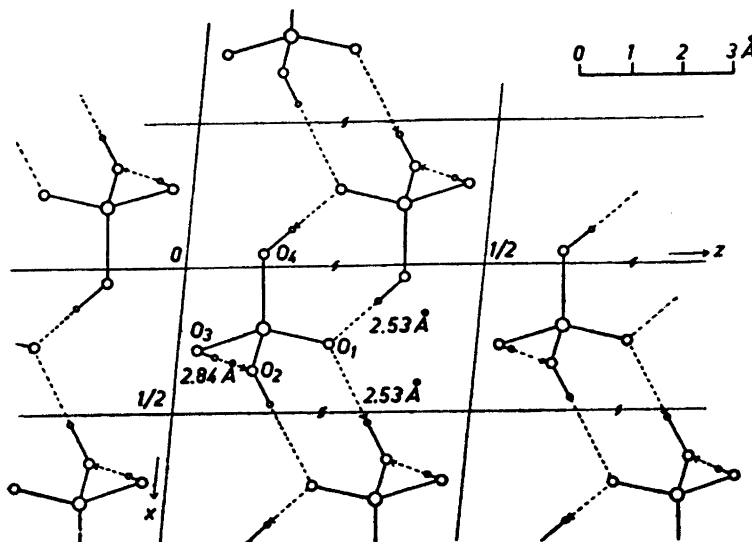


Fig. 4. The b projection of the structure. Arrows indicate that the hydrogen bonds (broken) terminate at atoms related to those shown by b translation.

as the hydrogen bonds found in KH_2PO_4 at room temperature (2.53 Å). The hydrogen bonds are shown in Fig. 4. (In Fig. 1 in the author's preliminary note³ the hydrogen bond from O_3 is erroneously drawn.)

The formation of the strong hydrogen bonds does not seem to influence the state of the molecule to any great extent. The P—(OH) bonds are found to be nearly equal, and the two strong hydrogen bonds have the same length.

According to Bernal¹⁰ the electronic charge around the proton will decrease from about 0.6 electrons for the weaker "hydroxyl" bonds of length 2.75—2.85 Å to about 0.3 for the stronger bonds of length 2.65—2.4 Å. He also assumes that the O—H bond may lengthen from 0.85 Å to about 1.10 Å as the hydrogen bonds increase in strength. The charge distribution and O—H distances indicated by the difference maps in Fig. 2 appear to be in general agreement with this view, although little significance can be attached to the values derived. In the weak bond between two hydroxyls (2.84 Å) the $\text{O}_3\text{—H}_3$ distance is found to be 0.89 Å and the charge 0.45 el., whereas in the short bond involving H_4 the $\text{O}_4\text{—H}_4$ distance is 1.1 Å and the charge only 0.3 el. The hydrogen atom of the other strong bond (H_2) is very poorly defined (see above), but the coordinates assumed correspond to an O—H distance of 1.0 Å. The charge on H_2 is 0.25 el. The number of electrons associated with the hydrogens were computed from the ($h0l$) difference map (Fig. 2a) after adding to the map the calculated hydrogen contribution to the reflections suffering from extinction.

To locate the hydrogen atoms more precisely better intensity measurements are required, as well as a more careful refinement of both projections of the structure.

The author wishes to thank *Nansenfondet og de dermed forbundne fond* for a grant.

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Received September 26, 1955.