

correct value for a titanium–oxygen bond, and the bonds must therefore lie close to the plane of projection, perpendicular to (001). As the atom O(16) is shared by TiO_6 octahedra on either side of the sheet of alkali atoms the tetrahedral layers are related by an approximate mirror plane parallel to (001). The potassium atoms, site K(1), are therefore each bonded to two rings of six oxygen atoms, as in the micas, and also to O(16) in the plane of the alkali atoms. The sodium atoms are in tenfold coordination, bonded to four atoms on each side of the alkali atom plane and two atoms, O(16) in the plane.

There are a number of possible variations in the structure:

(a) *Rotation of the TiO_6 octahedron.* In any layer of the structure there are two possible arrangements, as shown in Fig. 8. The differences between these are small and probably restricted to the atoms Si(2,3) and O(9,10,11,12).

(b) The relative rotation of the TiO_6 octahedra in adjacent layers could make the structure centrosymmetric or asymmetric. These variations would have small differences in the arrangement of the oxygen atoms around the alkali atoms.

(c) In this specimen the corrugation of the octahedral layer limits the number of polymorphs produced by the relative positions of the tetrahedral layers on either side to two, the atoms differing in x coordinates only. These can be distinguished by the value of the angle β (90° or 101°).

(d) The possible occurrence of many more varieties of astrophyllite is suggested by the specimen studied by Пэн & Ма (1963). This has the formula $(\text{K}_2\text{Na}_2)(\text{Fe}_5\text{Mg}_2)\text{Ti}_2\text{Si}_8(\text{O},\text{OH})_{31}$. The structure consists of the same ‘octahedral’, ‘tetrahedral’ and alkali atom layers but the presence of magnesium in the octahedral layer has produced a more symmetrical stacking of the units.

In this specimen the octahedral layer is flat and the positions of attachment of the titanium and silicon chains of the tetrahedral layer are apparently associated with the different sizes of the MgO_6 and FeO_6 octahedra and not with alterations in size produced by curvature. As a result the TiO_6 octahedra on either side are attached to the same octahedron of the Fe, Mg layer. The mirror lines perpendicular to (001) shown in Fig. 3(b) become in this specimen mirror planes running continuously through the now monoclinic lattice. The extra sodium atoms in this specimen are accommodated by replacing the atom in site K(2) by an atom on either side of this position, spaced at right-angles to the x axis.

The fact that the variations in ‘repeat distance’ of a composite TiO_6 – SiO_4 layer can be matched to a flat octahedral layer by the replacement of iron by magnesium suggests that with appropriate compositions of the octahedral layer continuous ‘tetrahedral’ layers with other ratios of titanium to silicon may be possible. The ratio 1:2 has already been found in bafertisite and some other minerals.

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The Crystal and Molecular Structure of Dimethylphosphinic Acid

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The crystal structure of dimethylphosphinic acid, $(\text{CH}_3)_2\text{PO}(\text{OH})$, has been determined from three-dimensional X-ray data. Crystals of this compound are monoclinic, space group $C2/c$, with 8 molecules in the unit cell. Cell dimensions are $a = 15.78$, $b = 6.76$, $c = 10.94$ Å; $\beta = 125^\circ 40'$. The structure has been refined by the method of least squares. The final R index for 852 observed reflexions is 0.078. The phosphorus atom has the expected tetrahedral configuration. The P–C bond lengths are equal within experimental error, with a mean value of 1.78 Å. The two P–O bond lengths are 1.50 and 1.56 Å. Strong O–H \cdots O hydrogen bonds, 2.48 Å in length and arranged around twofold screw axes, hold the molecules together to form chains along the b axis.

As a part of a series of investigations of Zn(II) and Co(II) di- n -alkylphosphinate polymers, which were found to be chains of tetrahedral metal atoms bonded with phosphinate bridges both in non-coordinating

solvents and in the solid state (Crescenzi, Giancotti & Ripamonti, 1965; Rose & Block, 1965; Giancotti & Ripamonti, 1966), the structure of dimethylphosphinic acid, $(\text{CH}_3)_2\text{PO}(\text{OH})$, was determined by a single-

crystal X-ray diffraction analysis. This study was undertaken not only to provide a standard for comparison between the geometry of the phosphinate group in the aforementioned coordination polymers and that of the free acids, but also because of the intrinsic interest of the molecular packing in the crystalline state. The presence in solution of hydrogen bonded dimers of phosphinic acids, like those formed by carboxylic acids, has been suggested on the basis of molecular weight determinations (Kosolapoff & Powell, 1950) and infrared spectra have provided evidence for the formation of strong hydrogen bonds (Detoni & Hadži, 1964). However, there is no accurate structural information available on the state of association of these acids of phosphorus in the solid phase.

Experimental

Dimethylphosphinic acid was prepared according to Reinhardt, Bianchi & Mölle (1957). Monoclinic crystals were grown from solutions in benzene and crystallographic data were obtained from precession photographs taken with Cu $K\alpha$ radiations. The unit cell parameters were found to be

$$a = 15.78, b = 6.76, c = 10.94 \text{ \AA}; \beta = 125^\circ 40'.$$

Eight molecules per unit cell give a calculated density of 1.317 g.cm^{-3} . The systematic absences, hkl with $(h+k)$ odd, $h0l$ with h and l odd, indicated that the crystals belong to space group Cc or $C2/c$.

Equi-inclination Weissenberg intensity data were collected with Cu $K\alpha$ radiation from a crystal (cross-section of about $0.2 \times 0.2 \text{ mm}$) sealed in a thin-walled capillary tube because of its hygroscopicity and mounted about $[010]$. The $h0l \cdots h6l$ layers were accessible. The zero layer of a crystal mounted about $[101]$ was

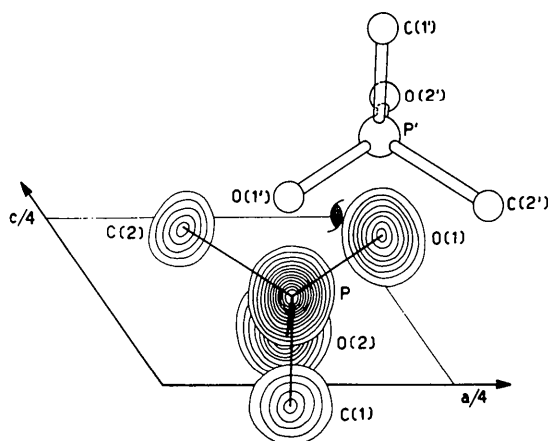


Fig. 1. Composite diagram of the three-dimensional electron density function viewed along b . Contours are at intervals of $1 \text{ e.}\text{\AA}^{-3}$ around the oxygen and carbon atoms and at intervals of $2 \text{ e.}\text{\AA}^{-3}$ around the phosphorus atom, beginning with the $2 \text{ e.}\text{\AA}^{-3}$ contour. A perspective drawing of the molecule related to that at x, y, z by the twofold screw axis is also shown.

recorded to provide cross-correlation terms. The multiple-film technique was used throughout. The intensities of 852 independent reflexions, which correspond to approximately 82% of the Cu $K\alpha$ sphere, were measured by eye-estimation and scaled with the aid of the cross-correlation terms. The intensities were corrected for change of spot shape on upper layers (Phillips, 1954) and reduced to structure amplitudes by a data-reduction program written for an IBM 1620 computer (Damiani, De Santis, Giglio & Ripamonti, 1962). No absorption or extinction corrections were applied.

Determination and refinement of the structure

Because there are eight molecules in the unit cell, the space group was assumed to be $C2/c$ and not Cc . This was confirmed later by structure analysis.

From the phosphorus position, determined from the Patterson projections on (010) and (101) , a trial structure was obtained in which the molecules which were hydrogen bonded together were related by the twofold screw axis. This model was refined by Fourier methods until R_{h0l} and $R_{hk\bar{k}}$ were reduced to 0.13 and 0.15 respectively. Structure factors, calculated with the atomic coordinates thus obtained, gave $R = 0.20$ for all observed reflexions.

The three-dimensional refinement of the structure was then carried out by the block diagonal least-squares method, using the weighting scheme $w = [a + bkF_o + c(kF_o)^2]^{-1}$ where $a = 5.0$, $b = 1.0$, $c = 0.01$. The positions and the isotropic temperature factors of the heavy atoms were initially refined and subsequently anisotropic factors were included. R dropped to 0.091.

At this stage a three-dimensional Fourier synthesis of electron density, shown in Fig. 1, and a difference synthesis based upon low angle reflexions were calculated. The $(F_o - F_c)$ map showed hydrogen atom peaks at the expected positions for a staggered orientation of the methyl groups and a broad peak between the hydrogen bonded oxygen atoms. Since an ordered position of the hydrogen atom in the $\text{O-H} \cdots \text{O}$ bond seemed reasonable because of the different values of the two P-O bond lengths, the contribution of all the hydrogen atoms was included at positions calculated by assuming staggered methyl groups, with C-H bond lengths 1.09 \AA , and an $\text{O-H} \cdots \text{O}$ linear hydrogen bond, with O-H distance of 1.07 \AA . An average isotropic B value of 5.0 \AA^2 was assigned to the hydrogen atoms. In the final cycles of calculations all parameters, except those of the hydrogen atoms, were further refined until the residual shifts were, on average, smaller than the corresponding estimated standard deviations. The final reliability index for observed reflexions was 0.078.

The coordinates and the temperature parameters of heavier atoms with their estimated standard deviations are given in Table 1 and Table 2 respectively. The standard deviations were calculated from the residuals and diagonal elements of the normal equations of the least squares procedure. Table 3 lists the observed

amplitudes and calculated structure factors based on the final atomic parameters.

The atomic scattering factors used were those of Hanson, Herman, Lea & Skillman (1964) for C, O and H and that reported in *International Tables for X-ray Crystallography* (1962) for P. The calculations were performed on an IBM 1620 computer with the programs of Van der Helm (1961*a, b*) for structure factors and Fourier synthesis and on an IBM 7040 computer with programs written by Albano, Domenicano & Vaciego (1966) for structure factors, least squares and by Domenicano & Vaciego for Fourier synthesis.

Discussion

Bond lengths and angles calculated from the atomic coordinates, listed in Table 1, are shown in Fig. 2 and given in Table 4 together with their standard deviations (Cruickshank & Robertson, 1953).

The bond angles at the phosphorus atom are close to the tetrahedral value. The P-C bond lengths are equal within experimental error, the mean value being 1.78 Å. This value is somewhat smaller than those observed earlier for this type of bond. In an electron diffraction study of the molecular structure of trimethylphosphine oxide Wang (1965) found a P-C bond length of 1.81 Å, which is in agreement with the values found by X-ray in 2-aminoethylphosphonic acid (Okaya, 1966) and in diphenylphosphinic acid (Liang & Chi, 1965).

It is deduced that the values of 1.50 and 1.56 Å correspond to the P-O and P-OH bonds respectively. These values are in good agreement with the average P-OH bond length of 1.568 Å and the average P-O of 1.505 Å found in organic phosphates and recently reported by Karle & Britts (1966).

The crystals are built up from infinite chains of molecules held together by strong O-H...O hydrogen bonds around the twofold screw axes parallel to the *b* axis. The hydrogen bond length of 2.48 Å and the P-OH...O angle of 112.3° compare well with the values found in the phosphate structure. Earlier pub-

lished values have been tabulated by Calleri & Speakman (1964) and by Liminga (1965). All the other intermolecular contacts (Table 5) are greater than the normal van der Waals distances. Similar spiral shaped chains of molecules linked by means of hydrogen bonds of length 2.74 Å were found in the crystals of diphenylphosphinic acid (Liang & Chi, 1965). If the values thus far obtained for the O-H...O bonds between phosphorus atoms and the infrared spectroscopic evidence (Detoni & Hadži, 1964) are considered, the O-H...O distance reported by Liang & Chi (1965) appears surprisingly long. However, the poor accuracy of the two-dimensional analysis of the structure does not allow much significance to be attached to this value.

9,10-Dihydro-9-hydroxy-9-phosphaphenanthrene-9-oxide, a cyclic phosphinic acid, is also associated in the form of long chains of molecules linked across a

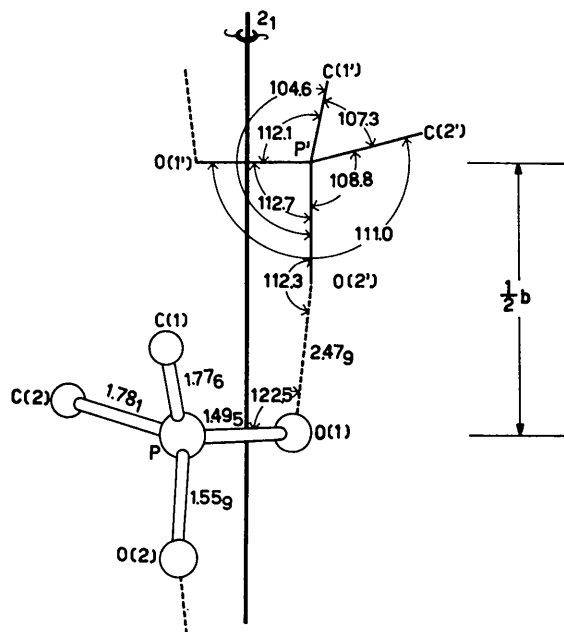


Fig. 2. Diagrammatic representation of two hydrogen bonded molecules with bond lengths and angles.

Table 1. Final fractional atomic coordinates and their standard deviations (Å)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
P	0.1640	0.1673	0.1303	0.0016	0.0014	0.0011
O(1)	0.2790	0.2035	0.2241	0.0032	0.0041	0.0033
O(2)	0.1348	-0.0490	0.0702	0.0032	0.0041	0.0033
C(1)	0.0961	0.3172	-0.0338	0.0064	0.0068	0.0055
C(2)	0.1117	0.2198	0.2336	0.0047	0.0074	0.0055

Table 2. Final temperature factors

Temperature factors are of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. The standard deviations given in parentheses are expressed in units of the last digit stated.

	<i>b</i> ₁₁	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₂	<i>b</i> ₂₃	<i>b</i> ₃₃
P	0.0053 (1)	0.0013 (2)	0.0087 (1)	0.0190 (3)	0.0005 (2)	0.0097 (1)
O(1)	0.0060 (1)	0.0001 (6)	0.0109 (3)	0.0259 (9)	-0.0054 (9)	0.0157 (3)
O(2)	0.0072 (2)	0.0009 (7)	0.0081 (3)	0.0240 (9)	-0.0044 (9)	0.0128 (3)
C(1)	0.0094 (3)	0.0084 (11)	0.0148 (5)	0.0366 (18)	0.0148 (14)	0.0146 (4)
C(2)	0.0079 (2)	-0.0058 (10)	0.0155 (3)	0.0427 (19)	-0.0063 (15)	0.0138 (4)

Table 3. Observed and calculated structure factors
Columns are $h, k, 10F_o, 10F_c$.

Table with multiple columns representing observed and calculated structure factors for various h, k indices. The table is organized into a grid with rows of indices (h, k) and columns of numerical values. Some rows have labels like l=0, l=1, l=2, l=3, l=5, l=6, l=7, l=8, l=10, l=11, l=12, l=13 indicating the layer index. The values are arranged in a regular grid format.

Table 4. Bond lengths and angles and their standard deviations

	l	$\sigma(l)$		α	$\sigma(\alpha)$
P-O(1)	1.495 Å	0.004 Å	O(1)-P-O(2)	112.7°	0.2°
P-O(2)	1.559	0.004	C(1)-P-O(1)	112.1	0.3
P-C(1)	1.776	0.006	C(1)-P-O(2)	104.6	0.3
P-C(2)	1.781	0.006	C(1)-P-C(2)	107.3	0.3
O(1)-O(2')	2.479	0.005	C(2)-P-O(1)	111.0	0.2
			C(2)-P-O(2)	108.8	0.2
			P-O(1)-O(2')	122.5	0.2
			O(1)-O(2')-P'	112.3	0.2

Table 5. Intermolecular distances less than 4.0 Å

From	to	in molecule at	
O(1)	P	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	3.39 Å
P	O(1)		3.85
O(1)	O(1)		3.63
C(1)	O(1)		3.79
C(2)	O(1)		3.60
P	O(2)		3.52
C(2)	O(2)		3.61
O(1)	C(2)		3.80
P	O(2)	$-x, -y, -z$	3.95
O(2)	O(2)		3.64
C(1)	O(2)		3.88
C(2)	O(2)		3.53
O(2)	C(2)	$x, -y, -\frac{1}{2}+z$	3.67
C(1)	O(1)	$\frac{1}{2}-x, \frac{1}{2}-y, -z$	3.61
C(2)	C(2)	$-x, y, \frac{1}{2}-z$	3.75

glide plane by means of hydrogen bonds of length 2.53 Å (Wheatley, 1962). From these results it seems that phosphinic acids as well as organophosphoric acids of the type $(RO)_2PO(OH)$ (Calleri & Speakman, 1964; Dunitz & Rollett, 1956) have a common tendency towards formation, in the solid state, of long chains of molecules held together by strong hydrogen bonds.

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