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## Crystal Chemistry of Inorganic Phosphites

BY J. LOUB

*Department of Inorganic Chemistry, Charles University, Hlavova 8/2030, 12840 Praha 2, Czechoslovakia*

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### Abstract

The results of X-ray structural analyses of inorganic phosphites are discussed and the average bond distances and angles of the  $\text{HPO}_3$  group have been calculated by statistical evaluation of the geometry of the structures:  $\text{P}-\text{O}_s = 1.498$  (16),  $\text{P}-\text{O}_m = 1.514$  (12),  $\text{P}-\text{O}_l = 1.548$  (22),  $\text{H}-\text{P} = 1.30$  (8) Å,  $\text{O}_s-\text{P}-\text{O}_m = 114.0$  (2.8),  $\text{O}_s-\text{P}-\text{O}_l = 110.7$  (2.4),  $\text{O}_m-\text{P}-\text{O}_l = 109.8$  (3.1),  $\text{H}-\text{P}-\text{O}_s = 109$  (4),  $\text{H}-\text{P}-\text{O}_m = 107$  (3) and  $\text{H}-\text{P}-\text{O}_l = 106$  (5)° (the subscripts  $s$ ,  $m$  and  $l$  indicate small, medium and large according to the  $\text{P}-\text{O}$  distances  $\text{P}-\text{O}_s \leq \text{P}-\text{O}_m \leq \text{P}-\text{O}_l$ ). The bond-valence parameters  $r_o(\text{HP}^{4+}-\text{O}^{2-}) = 1.626$  (5) and  $r_o(\text{H}_2\text{P}^{3+}-\text{O}^{2-}) = 1.642$  (16) have been obtained. Correlations have been found between the  $\text{P}-\text{O}$  distance and the opposite  $\text{O}-\text{P}-\text{O}$  angle, and between the  $\text{P}-\text{O}$  distance and the  $S(s)$  bond valence of the  $\text{O}(\text{P})$  atom.

### Introduction

The species  $0.5\text{H}^+$  and/or  $0.5\text{H}_2\text{O}$  can formally be gradually dissociated from phosphorous acid,  $\text{H}_3\text{PO}_3$ , yielding the phosphite types given in Table 1.

Some of the phosphite types which are underlined in Table 1 and denoted by the letters  $A$  to  $F$ , have been found in solid phosphites (Loub & Kratochvíl, 1987). The present paper summarizes results of structure determinations of solid phosphites and phosphorous acid (see Table 2).\* The phosphite structural types were systematized and attempts made to find some dependences among their properties so that certain results could be evaluated or predicted on this basis.

### Structural types of phosphites

Substances characterized by a simple chemical formula may sometimes have very complicated structures. Therefore, the structures of some types are briefly characterized below.

#### *Phosphites with a P:O ratio of 1:3*

Phosphorous acid,  $\text{H}_3\text{PO}_3$  (type  $A$ ) (Fig. 1a), primarily belongs in this group. The acid molecules

\* Lists of the full references used in Table 2 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54006 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Phosphite types formed from phosphorous acid by dissociation of the  $0.5\text{H}^+$  and  $0.5\text{H}_2\text{O}$  species

The phosphite types whose structures have been established are denoted by the letters *A* to *F* and are underlined.

P:O	1:3	1:2.5	1:2	1:1.5
$\text{H}_3\text{PO}_3$		$-0.5\text{H}_2\text{O}$	$-\text{H}_2\text{O}$	$-1.5\text{H}_2\text{O}$
	<u><i>A</i> <math>\text{H}_3\text{PO}_3</math></u>	$\text{H}_2\text{PO}_2^-$	$\text{HPO}_2^-$	$\text{PO}_{1.5}$
$-0.5\text{H}^+$	<u><i>B</i> <math>\text{H}_2.5\text{PO}_3^{2.5-}</math></u>	$\text{H}_1.5\text{PO}_3^{2.5-}$		
$-\text{H}^+$	<u><i>C</i> <math>\text{H}_2\text{PO}_3^-</math></u>	<u><i>F</i> <math>\text{HPO}_2^-</math></u>		
$-1.5\text{H}^+$	<u><i>D</i> <math>\text{H}_1.5\text{PO}_3^{1.5-}</math></u>			
$-2\text{H}^+$	<u><i>E</i> <math>\text{HPO}_3^{2-}</math></u>			

are interconnected by hydrogen bonds to form a three-dimensional network.

Type *B* ( $\text{H}_2.5\text{PO}_3^{2.5-}$ ) occurs in one compound in which three hydrogen atoms are always bound to two oxygen atoms (Fig. 1*b*). The structure has three-fold symmetry with the symmetry axis passing through the P—H bond.

The  $\text{H}_2\text{PO}_3^-$  anion is denoted as type *C* (Fig. 1*c*). The hydroxyl hydrogen which permits hydrogen bonding causes various connections of ions and molecules in the structures, e.g. the formation of infinite  $(\text{H}_2\text{PO}_3)_n^{n-}$  chains in the compound  $\text{KH}_2\text{PO}_3$ . If other molecules or ions capable of hydrogen bonding are present in the compounds, then the hydrogen bonds cause more complicated connections between the molecules or ions.

The  $\text{H}_1.5\text{PO}_3^{1.5-}$  ion (type *D*) has been found in two compounds in which it forms dimeric anions  $\text{H}_3\text{P}_2\text{O}_6^{3-}$  (Fig. 1*d*).

The type *E* compounds include relatively isolated  $\text{HPO}_3^{2-}$  anions, especially when they do not contain water molecules or other compounds capable of hydrogen bonding (Fig. 1*e*).

#### Phosphites with a P:O ratio of 1:2.5

Compounds of this type include condensed pyrophosphite (diphosphite) anions  $\text{H}_2\text{P}_2\text{O}_5^{3-}$ , i.e. anions with an oxygen bridge (Fig. 1*f*). They have been described by, for example, Zipp (1988).

#### Compounds with P:O ratios of 1:2 and 1:1.5

The hypothetical metaphosphorous acid,  $\text{HPO}_2$ , and phosphorous oxide,  $\text{P}_4\text{O}_6$ , belong in this group. The structure of the latter compound is well known. The oxide is the final product of a formal dissociation of the  $0.5\text{H}^+$  and  $0.5\text{H}_2\text{O}$  species from phosphorous acid,  $\text{H}_3\text{PO}_3$ .

The phosphites with a P:O ratio of 1:3 were selected for further studies. 32 out of the 50 references on 44 compounds exhibiting this ratio were used. The reasons for not considering the remaining compounds are given in Table 2. Of the 32 compounds studied, ten crystallize in space group  $P2_1/c$  (No. 14),

Table 2. Chemical formulae, symbols of the compounds and references to the phosphite and hypophosphite crystal structures

The symbol of the compound consists of the number of the compound, the phosphite type and the serial number of the given phosphite type. The references denoted by superscript letters were not analyzed in detail for the following reasons: (a) the work was inaccessible, (b) the work was outdated, (c) the work was identical to that in the previous reference, (d) the work contained controversial data and the correct coordinates were not obtained from the authors, (e) coordinates were not given in the work and were not obtained from the authors, (f) isomorphous character was found but without specification of the coordinates, (g) the structure was obtained from powder data and no quantitative criterion of agreement was given, (h) the work was a review on pyrophosphites and (n) the work consisted of neutron data.

Formula	Symbol	Reference*
$\text{H}_3\text{PO}_3$	01A01,02	ACAPCT 11 1505 Loopstra (1958a) <sup>a</sup>
$\text{H}_3\text{PO}_3 \cdot 2\text{K}_2\text{H}_3\text{PO}_3$	02A03,C04,05	ASBSDK 37 2058
$\text{Na}_6\text{O}_5\text{H}_2\text{P}_2\text{O}_5$	03B01	ASBSDK 38 1267 Albrand (1972) <sup>b</sup>
$\text{LiH}_2\text{PO}_3$	04C01	ACAPCT 24 2803 CHDCAQ 270 1395 <sup>c</sup> ASBSDK 32 412 <sup>n</sup>
$\text{KH}_2\text{PO}_3$	05C02,03	ACSCEE 39 326
$\text{KH}_2\text{PO}_3 \cdot \text{HF}$	06C06	ASBSDK 27 1982
$\text{NH}_4\text{H}_2\text{PO}_3$	07C07	ACSCEE 40 720
$\text{NaMn}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$	08C08,09,10	ACSCEE 42 1281
$\text{NaCo}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$	09C11,12,13	ASBSDK 38 2436
$\text{RbUO}_2(\text{H}_2\text{PO}_3)_2 \cdot (\text{HPO}_3)_2 \cdot 3\text{H}_2\text{O}$		KOKHDC 11 1393 <sup>d</sup>
$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$	10C14,15	ZAACAB 508 154
$\text{Cu}(\text{H}_2\text{PO}_3)_2$	11C16,17	CHZVAN 26 494
$\text{Zn}(\text{H}_2\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$	12C18,19	INOCJ 28 2608
$\text{Cd}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$	13C20,21	ASBSDK 34 32
$\text{La}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$	14C22,23,24	ACSCEE 44 2048
$\text{U}(\text{H}_2\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$		Butman, Nikolajev & Sokol (1977) <sup>e</sup>
$\text{UO}_2(\text{H}_2\text{PO}_3)(\text{HPO}_3) \cdot (\text{CH}_3)_2\text{NH}_2$		ZNOKAQ 26 1011 <sup>f</sup>
$\text{UO}_2(\text{H}_2\text{PO}_3)_2 \cdot 2\text{OC}[\text{N}(\text{CH}_3)_2] \cdot \text{H}_2\text{O}$		ZNOKAQ 26 1011 <sup>f</sup>
$\text{Mn}_6\text{O}_5\text{H}_1.5\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$	15D01	KOKHDC 9 981 <sup>e</sup>
$\text{Nd}_6\text{O}_5\text{H}_1.5\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$	16D02,03	ASBSDK 38 1687
$\text{Ln}_6\text{O}_5\text{H}_1.5\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$		ACSCEE 44 6
$\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$	17E01	Durand, Loukili, Tijani, Rafiq & Cot (1988) <sup>f</sup>
$\text{K}_2(\text{HPO}_3)_2 \cdot (\text{Mg}_2\text{O}_7)$	18E02,03	ZAACAB 439 265
$(\text{NH}_4)_2\text{HPO}_3 \cdot \text{H}_2\text{O}$	19E04	JCSJAP 1971 1207 <sup>b</sup>
$\text{LiTiHPO}_3$	20E05	BCSJA8 61 4455
$\text{Na}_2\text{Zn}_3(\text{HPO}_3)_4$	21E06,07,08	ZAACAB 484 187
$\text{K}_2\text{Zn}_3(\text{HPO}_3)_4$	22E09,10,11,12	RVCMA8 18 1
$\text{K}_2\text{UO}_2(\text{HPO}_3)_2 \cdot 2\text{H}_2\text{O}$		INOCJ 28 2608
$(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$	23E13,14	INOCJ 28 2608
$\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$	24E15	KOKHDC 11 1393 <sup>d</sup>
$\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$	25E16	ASBSDK 38 1441
$\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$	26E17	ACCRA9 9 991
$\text{Zn}_2(\text{HPO}_3)_2 \cdot 5\text{H}_2\text{O}$	27E18,19	CCCCAK 52 1742
$\text{Zr}(\text{HPO}_3)_2$		CHZVAN 26 494
$\text{Zr}(\text{HPO}_3)_{1.15} \cdot (\text{HPO}_3)_{0.85} \cdot 0.5\text{H}_2\text{O}$		INOCJ 28 2608
$\text{SnHPO}_3$	28E20	JSSCBI 63 455 <sup>e</sup>
$\text{BaZn}_3(\text{HPO}_3)_4 \cdot 6\text{H}_2\text{O}$	29E21,22	INOCJ 19 1237
$\text{Sb}_2(\text{HPO}_3)_2$	30E23,24,25	INOCJ 28 2608
$\text{UO}_2\text{HPO}_3 \cdot \text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{SO}$	31E26	ASBSDK 37 1106
$\text{UO}_2\text{HPO}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_2\text{OCN}(\text{CH}_3)_2$	32E27	KOKHDC 8 1561
$\text{UO}_2\text{HPO}_3 \cdot 2\text{H}_2\text{O} \cdot \text{CO}(\text{NH}_2)_2$		KOKHDC 8 1561
$\text{UO}_2\text{HPO}_3 \cdot 2\text{CO}(\text{NH}_2)_2$		IVNMAW 15 947 <sup>f</sup>
$\text{UO}_2\text{HPO}_3 \cdot \text{H}_2\text{O} \cdot \text{HCON}(\text{CH}_3)_2$		IVNMAW 15 947 <sup>f</sup>
$\text{UO}_2\text{HPO}_3 \cdot \text{CH}_2(\text{CONH}_2)_2$		ZNOKAQ 26 1011 <sup>f</sup>
$\text{HPO}_2^-$	<i>F</i>	ZNOKAQ 26 1011 <sup>f</sup>
$\text{NaH}_2\text{PO}_3 \cdot 0.8\text{H}_2\text{O}$		CCHRAM 84 47 <sup>b</sup>
$\text{KH}_2\text{PO}_2$		ACBCAR 35 1041
$\text{NH}_4\text{H}_2\text{PO}_2$		Akimoto (1965)
$\text{NaCa}(\text{H}_2\text{PO}_2)_2$		JCPA6 2 34
$\text{Ca}(\text{H}_2\text{PO}_2)_2$		ACBCAR 25 1932
$\text{Zn}(\text{H}_2\text{PO}_2)_2$		Loopstra (1958 <i>b</i> )
$\text{Zn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$		ACBCAR 35 42
$\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$		ACBCAR 35 42
$\text{Mg}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$		ACBCAR 35 42
$\text{GeClH}_2\text{PO}_2$		Pedrazuela, Garcia-Blanco & Rivoir (1953)
$\text{Ge}_2(\text{H}_2\text{PO}_2)_6$		ACBCAR 35 3023
$\text{SnClH}_2\text{PO}_2$		JCSJD 5 279
$\text{La}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$		ACBCAR 35 3023
		KRISAJ 18 403

\* See Notes for Authors (1983) for a description of journal Codens.

seven in  $P\bar{1}$  (No. 2) and three in  $P2_12_1$  (No. 19). The remaining 12 compounds crystallize in 10 other space groups.

### Geometry of the phosphite group

The primary data for the calculations of the distances and angles were the lattice parameters and the atomic coordinates. The distances and angles were recalculated using the modified part of the *ORTEP* program (Johnson, 1965). The 32 compounds contain 58  $\text{HPO}_3$  species. The phosphites *E01*, *06* and *07* have symmetry  $m$ , the phosphites *B01* and *E15* have symmetry  $3m$  and the remaining 53 phosphites have symmetry 1. Other data on the symmetry of the phosphites are given in Table 3.

Fig. 2 depicts histograms for the P—O distances and O—P—O angles. The average P—O distances and O—P—O angles are given in Table 4. The phosphite oxygen atoms are differentiated according to the P—O distances into  $O_s$ ,  $O_m$  and  $O_l$ , where the indices  $s$ ,  $m$  and  $l$  indicate small, medium and large, i.e.  $\text{P—O}_s \leq \text{P—O}_m \leq \text{P—O}_l$  (Fig. 3a).

The H(P) coordinates were determined for 46 phosphites, of which seven were excluded here by the

Table 3. Symmetry of 58 phosphites of types *A* to *E*

	Phosphite type				
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
Symmetry	$\text{H}_3\text{PO}_3$	$\text{H}_{2.5}\text{PO}_3^{0.5-}$	$\text{H}_2\text{PO}_3^-$	$\text{H}_{1.5}\text{PO}_3^{1.5-}$	$\text{HPO}_3^{2-}$
Possible	$m, 1$	$3m, 3m, 1$	$m, 1$	$m, 1$	$3m, 3m, 1$
Found	1	$3m$	1	1	$3m, m, 1$
Number of phosphites with the found symmetry	3	1	24	3	1.3.23
Number of compounds with the found symmetry	2	1	12	2	1.2.13

Compound 02 is given as types *A* and *C*.

elimination criteria  $1.56 < \text{H—P} < 0.99 \text{ \AA}$  and/or  $123 < \text{H—P—O} < 91^\circ$ . The average H—P distance is  $1.30 (8) \text{ \AA}$ , the average H—P—O angles are  $109 (4)$  for  $O_s$ ,  $107 (3)$  for  $O_m$  and  $106 (5)^\circ$  for  $O_l$ . These three angles are not statistically different.

### Distortion indices

Regular configurations occur very rarely in nature and thus also in phosphite structures, as pointed out in the previous section. When evaluating the deviations from the ideal or average geometry, more or less distorted configurations are encountered. It is advantageous to quantify these deviations. We use the DISQ distortion index according to Baur (1974), defined by

$$\text{DISQ} = \left[ \frac{\sum_{n=s,m,l} (P_n - X_n)^2}{\sum_{n=s,m,l} P_n^2} \right] K$$

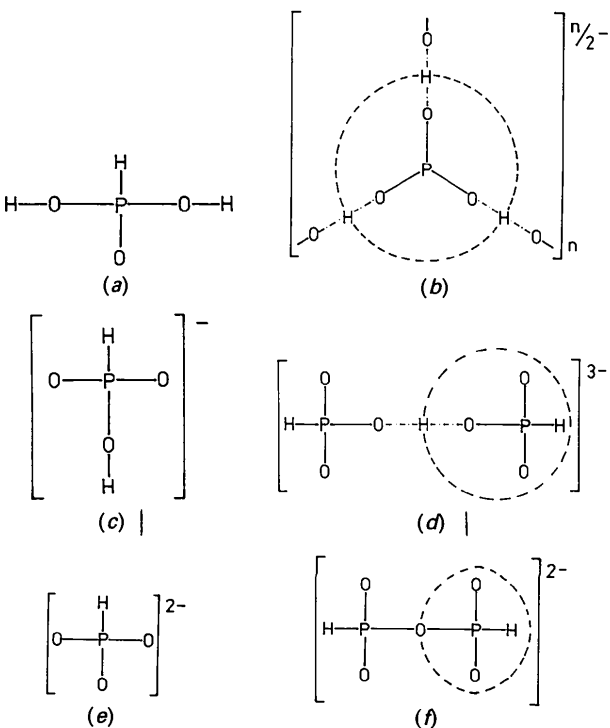


Fig. 1. Schematic representation of structural types: (a)  $\text{H}_3\text{PO}_3$ , (b)  $\text{H}_{2.5}\text{PO}_3^{0.5-}$  [the type is limited by the dashed-line circle, the H(P) atom is not shown,  $n$  is the number of phosphorus atoms], (c)  $\text{H}_2\text{PO}_3^-$ , (d)  $\text{H}_{1.5}\text{PO}_3^{1.5-}$  (the type is limited by the dashed-line circle), (e)  $\text{HPO}_3^{2-}$  and (f)  $\text{HPO}_{2.5}$  (the type is limited by the dashed-line circle).

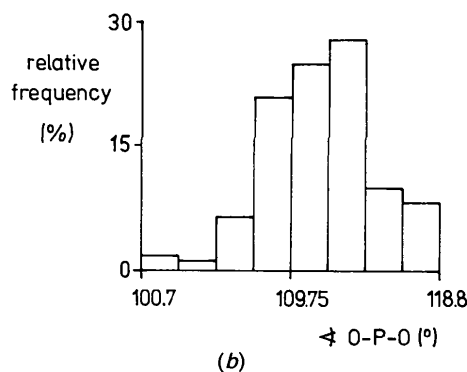
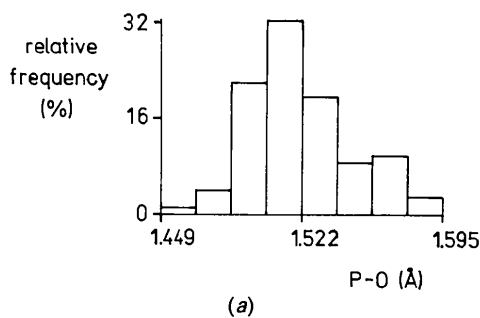


Fig. 2. (a) A histogram of the P—O distances. The class width is  $0.01825 \text{ \AA}$ . (b) A histogram of the O—P—O angles. The class width is  $2.6225^\circ$ .

Table 4. Average P—O distances (Å) and O—P—O angles (°) with the e.s.d.'s of the arithmetic means in parentheses

Type	<i>n</i>	P—O <sub>s</sub>	P—O <sub>m</sub>	P—O <sub>l</sub>	O <sub>s</sub> —P—O <sub>m</sub>	O <sub>s</sub> —P—O <sub>l</sub>	O <sub>m</sub> —P—O <sub>l</sub>
A H <sub>3</sub> PO <sub>3</sub>	3	1.470 (20)	1.539 (11)	1.544 (8)	113.0 (2.0)	115.2 (2.1)	102.9 (2.4)
B H <sub>2</sub> PO <sub>3</sub> <sup>3-</sup>	1	1.529	1.529	1.529	112.8	112.8	112.8
C H <sub>2</sub> PO <sub>3</sub>	24	1.494 (11)	1.507 (8)	1.566 (13)	116.0 (1.8)	109.9 (2.0)	108.6 (2.7)
D H <sub>2</sub> PO <sub>3</sub> <sup>5-</sup>	3	1.515 (21)	1.529 (13)	1.574 (25)	113.2 (2.2)	108.4 (2.7)	108.6 (5)
E HPO <sub>3</sub> <sup>2-</sup>	27	1.503 (13)	1.516 (9)	1.531 (12)	112.4 (2.5)	111.2 (2.0)	111.6 (1.8)
PO <sub>3</sub>	58	1.498 (16)	1.514 (12)	1.548 (22)	114.0 (2.8)	110.7 (2.4)	109.8 (3.1)
PO <sub>3</sub>	174		1.520 (27)			110 (11)	

where the values of  $P_n$  are the average values taken from Table 4 for the individual types, the values of  $X_n$  are the values of the phosphites under evaluation and  $K$  is a constant equal to  $10^5$  for the distances and  $10^4$  for the angles. The greater the index value, the more the phosphite differs from the average value ( $0 \leq \text{DISQ} < \infty$ ). The distortion indices characterize the deviations from ideal or average geometry better than the arithmetic means, as, amongst other things, the same arithmetic mean may be exhibited by geometries with very different individual values. The DISQ distortion indices are given in Table 5 for the P—O distances and O—P—O angles.

### Hydrogen bonds

Hydrogen bonding occurs wherever possible in all phosphites. The distance between the donor oxygen atom  $O^d$  and the acceptor oxygen atom  $O^a$ ,  $O^d \cdots O^a \leq 3.17$  Å, was taken as the criterion for the possibility of hydrogen bonding. This distance corresponds to the value  $\bar{x} + 3\sigma$  for  $\bar{x} = 2.72$  and  $\sigma = 0.15$  Å, given by Kuleshova & Zorkii (1981) as a value

calculated from 1019 hydrogen bonds. The average distances and angles for the  $P^d-O^d-H^d \cdots O^a-P^a$  and  $P^a-O^a \cdots H_w^d-O_w^d$  hydrogen bonds are given in Table 6. The shortest hydrogen bond, symmetrical  $O^d \cdots O^a = 2.438$  (7) Å, was found in compound 15D. The  $F^d \cdots O^a = 2.2383$  (4) Å distance, corresponding to a strong  $F^d-H^d \cdots O^a$  hydrogen bond, was found in compound 06C.

### Bond valences in phosphites

Interatomic distances and angles may give an accurate geometrical picture of the structure of substances, but not a lucid picture of the bonding conditions. Therefore, the concept of bond valence (Brown & Altermatt, 1985) is advantageous. The bond valence  $s$  is calculated from the relationship

$$s = \exp[(r_o - r)/B]$$

where  $r$  is an interatomic distance and  $r_o$  and  $B$  are calculated parameters,  $B = 0.37$ . As Brown & Altermatt (1985) do not give the bond-valence parameter  $r_o(\text{HP}^{4+}-\text{O}^{2-})$ , the value was calculated using the least-squares method obtaining 1.626 (5) for  $n = 174$ .

The hydrogen-bond valences were determined from the graph of the  $s(\text{H}^d-\text{O}^a)$  dependence on  $r(\text{O}^d-\text{O}^a)$ . It holds that  $s(\text{O}^d-\text{H}^d) = 1 - s(\text{H}^d-\text{O}^a)$ .

In an ideal case,  $V_i = \sum_j s_{ij}$  where  $V_i$  is the oxidation state of cation  $i$  and  $s_{ij}$  is the bond valence between cation  $i$  and anion  $j$ . Thus, the calculated  $V_i$  value can serve as a criterion for the correctness of interatomic distances. The  $j$  value corresponds to the coordination number (Baur, 1974; Brown & Shannon, 1973). For the same cation and anion it then holds that the shorter the distance  $r$ , the greater the bond valence expressed in terms of the bond-valence unit.

The average bond valences  $s(\text{P}-\text{O})$  are given in Table 8 for various phosphite types. An ideal  $\sum_{n=s,m,l} s(\text{P}-\text{O}_n)$  value is equal to 4.

### Discussion

Most phosphites deviate greatly from a symmetrical arrangement (Tables 3 and 4). For steric reasons the hydrogen atom directly bonded to phosphorus makes it possible for the H—P—O angles to be

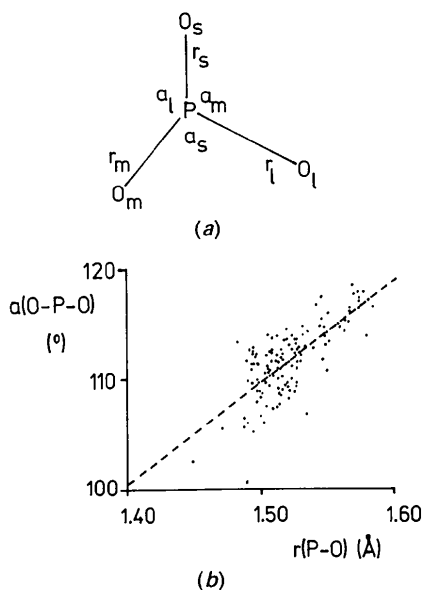


Fig. 3. (a) Labelling scheme for the atoms, distances and angles in PO<sub>3</sub>, (b) correlation between the P—O distances and O—P—O angles.

Table 5. DISQ distortion indices for the P—O distances ( $K = 10^5$ ) and O—P—O angles ( $K = 10^4$ ) with the e.s.d.'s of the arithmetic means in parentheses

Type	n	Distances			Angles		
		Minimum	Average	Maximum	Minimum	Average	Maximum
A $H_3PO_3$	3	0.90	6 (5)	10.0	1.62	3 (1)	3.97
C $H_2PO_3^-$	24	0.06	5 (7)	27.9	0.30	4 (4)	18.9
D $H_1PO_3^{5-}$	3	8.73	12 (3)	15.2	3.88	23 (18)	40.8
E $HPO_3^{2-}$	27	0.42	6 (7)	32.8	0.58	3 (5)	27.8

Table 6. Average distances (Å) and angles (°) of hydrogen bonds in phosphites, water molecules and  $LiH_2PO_3$ 

The values for types A and C ( $P^d-O^d-H^d \cdots O^e-P^e$ ,  $n = 17$ ,  $d$  and  $e$  denote donor and acceptor atoms) and for types C, E and water molecules ( $O^d-H^d \cdots O^e-P^e$ ,  $n = 28$ ,  $w$  denotes a water atom) are given with the e.s.d.'s of the arithmetic means in parentheses. The values for  $LiH_2PO_3$ , which were obtained by neutron diffraction (Johansson & Lindquist, 1976) are given with e.s.d.'s in parentheses.

	A, C	C, E, W	$LiH_2PO_3$
$P^d-O^d$	1.566 (10)		1.586 (2)
$O^e-H^d$	0.94 (10)	0.86 (10)	1.018 (4)
$H^d \cdots O^e$	1.67 (12)	2.01 (13)	1.546 (4)
$O^e-P^e$	1.505 (9)	1.536 (24)	1.506 (2)
$O^d \cdots O^e$	2.58 (5)	2.84 (1)	2.558 (4)
$P^d \cdots O^e$	3.51 (12)		3.35 (1)
$P^d \cdots O^d$	3.64 (12)	3.78 (21)	3.63 (1)
$P^d-O^d-H^d$	112 (6)		110.1 (2)
$O^e-H^d \cdots O^e$	168 (7)	163 (11)	171.6 (3)
$H^d \cdots O^e-P^e$	125 (8)	118 (11)	124.0 (3)
$P^d-O^d \cdots O^e$	115 (8)		105.7 (4)
$P^d-O^e \cdots O^d$	129 (15)	117 (12)	124.8 (3)

smaller than the tetrahedral angle,  $109.47^\circ$ . The O—P—O angles differ even more from the tetrahedral angle, mostly being larger. This is also demonstrated by the DISQ distortion indices, which are substantially larger for the angles than for the distances (Table 5).

For the compounds in which the hydrogen-atom positions H(O) were not determined, the hydrogen bonds were estimated from the values given in Table 6. The use of the given average distances and angles P—O, O $\cdots$ O, P $\cdots$ O and P—O $\cdots$ O as criteria for the existence of hydrogen bonding is much better than the mere criterion of the O $\cdots$ O distance.

Various correlations between the P—O and (P)O $\cdots$ O(P) distances, the O—P—O angles and the bond valences were studied further. In the calculations those compounds whose DISQ and/or  $\sum_n s(P-O_n)$  values were outside the interval  $\bar{x} \pm 1.96\sigma$  were excluded, where  $\bar{x}$  is the arithmetic mean and  $\sigma$  is the e.s.d. of the arithmetic mean given in Tables 5 and 7.

Two correlations are significant, primarily that between the P—O distance and the opposite O—P—O angle [e.g. between distance  $P-O_s = r_s$  and  $O_m-P-O_t = a_s$ , etc. (Fig. 3a)]. The correlation is described by  $a = 92 (7)r - 28 (11)^\circ$  where  $n = 141$  and the correlation coefficient equals 0.74 (Fig. 3b). The test of the linear correlation gives the value  $F(68,71) = 1.338$  [theoretical value  $F(60,60)_{0.99} =$

1.836]. The correlation indicates that a smaller O—P—O angle is located opposite a shorter P—O distance.

Furthermore, there is also the correlation between the P—O distance and the  $S(s)$  bond valence defined as a sum of the bond valences between the phosphite oxygen atom and the other non-phosphite cations [e.g.  $H^+$ ,  $M^{n+}$  but not  $HP^{4+}$  (Fig. 4a)],  $S(s) = \sum_n s(O-c_n)$ . In an ideal case,  $S(s) + s(P-O) = 2$ . Some of the compounds were not included in the correlation calculation because the  $r_o$  parameters have not been published or the  $S(s)$  values were not realistic. This correlation is described by  $S(s) = 4.1 (3)r - 5.6 (5)$  where  $n = 102$  and the correlation coefficient equals 0.80 (Fig. 4b). The test of linear correlation gives the value  $F(61,39) = 1.823$  [theoretical value  $F(60,40)_{0.99} = 2.019$ ]. The correlation demonstrates the dependence of the P—O distance on the bond-valence  $S(s)$ : the greater the P—O distance, the greater is the  $S(s)$  value.

Higher order polynomials were also tested in these regression procedures, but linear regression was found to be the most suitable.

All the O(P) atoms but only 58% of the (H)O(P) atoms are coordinated to metal cations. It follows from the bond-valence values that cations are substantially more strongly bonded to the O(P) atoms than to the PO(H) atoms. The highest bond valence (0.981) was found in compound 30E for the O $\cdots$ Sb bond.

Hydrogen bonding occurs wherever possible in phosphites. The average distance of the (P)O $^d \cdots O^e(P^e)$  hydrogen bonds, 2.58 (5) Å (Table 6), corresponds to the bond valence,  $s(H^d \cdots O^e) = 0.26$ , which is a relatively strong hydrogen bond. The average distance of the (P $^e$ )O $^a \cdots O_w^d$  hydrogen bonds, 2.84 (1) Å (Table 6), corresponds to a weaker hydrogen bond with  $s(O^a \cdots H_w^d) = 0.17$ . Hence hydrogen bonding is important for the stabilization of the phosphite structures.

Finally, the P—O distances, O—P—O angles and bond valences were compared in phosphates, phosphites and hypophosphites (Table 8). The distances and angles for phosphates were taken from the paper of Baur (1974), the values for hypophosphites from the works listed in Table 2.\* As a value of

\* See deposition footnote.

Table 7. Average  $s(\text{P—O})$  bond valences and  $\sum s(\text{P—O})$  values in phosphites with the e.s.d.'s of the arithmetic means in parentheses

Type	$n$	$s(\text{P—O}_s)$	$s(\text{P—O}_m)$	$s(\text{P—O}_l)$	Minimum	Average	Maximum
A $\text{H}_2\text{PO}_3$	3	1.53 (12)	1.266 (38)	1.247 (27)	3.922	4.04 (14)	4.201
B $\text{H}_2\text{P}_2\text{O}_3^{3-}$	1	1.299	1.299	1.299		3.897	
C $\text{H}_2\text{PO}_3^-$	24	1.428 (41)	1.380 (31)	1.175 (41)	3.907	3.983 (59)	4.110
D $\text{H}_2\text{P}_2\text{O}_3^{3-}$	3	1.351 (76)	1.300 (46)	1.153 (79)	3.612	3.80 (17)	3.902
E $\text{HPO}_3^{2-}$	27	1.396 (52)	1.345 (35)	1.294 (43)	3.933	4.036 (97)	4.335
A + B + C + D + E	58					4.00 (10)	
A + B + C + D + E	174		1.332 (24)				

Table 8. Comparison of the P—O distances (Å), O—P—O angles ( $^\circ$ ) and  $s(\text{P—O})$  bond valences for phosphates, phosphites and hypophosphites with the e.s.d.'s of the arithmetic means in parentheses

	Phosphates* ( $\text{PO}_4$ )	Phosphites ( $\text{HPO}_3$ )	Hypophosphites ( $\text{H}_2\text{PO}_2$ )
P—O Minimum	1.412	1.449	1.423
P—O Average	1.537	1.520 (27)	1.493 (22)
P—O Maximum	1.662	1.595	1.549
$s(\text{P—O})$ Average	1.241	1.332 (24)	1.496 (22)
$n$	844	174	48
O—P—O Minimum	96.6	100.7	114.6
O—P—O Average	109.35	110 (11)	117.4 (2.8)
O—P—O Maximum	123.4	118.8	122.1
$n$	1266	174	24

\* The values for the phosphates are taken from the paper of Baur (1974) where no e.s.d.'s are supplied.

$r_o(\text{H}_2\text{P}^{3+}—\text{O}^{2-})$  was not available in the literature, it was calculated by the least-squares method and found to be 1.642 (16) ( $n = 48$ ). It is evident (Table 8) from the distances and bond valences that the strongest bonds between phosphorus and oxygen atoms are in the hypophosphites and the weakest in phosphates. The O—P—O angles are closest to the tetrahedral angle in phosphates and the greatest deviation, towards higher values, occurs in hypophosphites. This can be explained by steric effects: one oxygen atom in phosphites and two oxygen atoms in hypophosphites are replaced by smaller hydrogen atoms. The remaining oxygen atoms thus have more space available and can form greater O—P—O angles.

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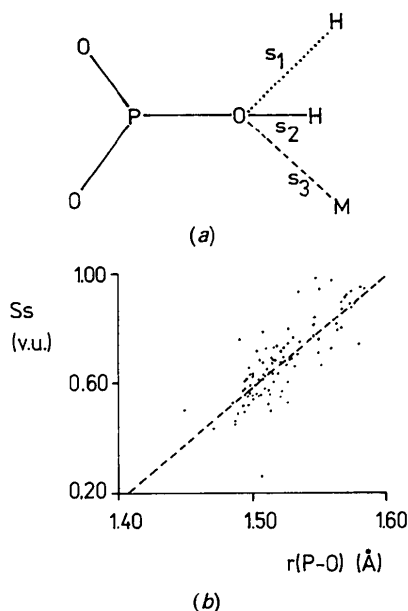


Fig. 4. (a) Possible bond valences,  $S(s) = \sum_r s(\text{O—}c_n)$ . (b) Correlation between the P—O distances and bond valences  $S(s)$ .