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The Geometry of Polyhedral Distortions. Predictive Relationships for the Phosphate Group

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The shapes of 211 phosphate tetrahedra have been studied. Their dimensions are known precisely from published X-ray and neutron-diffraction investigations. Results: (1) The site symmetry of the P atoms is found in 85% of the cases to be 1. Other observed symmetries are m , 2, 3, $\bar{4}$, mm , $\bar{4}2m$, 222 and 23. (2) The deviations from regular symmetry, $\bar{4}3m$, are pronounced. The distortions can be measured by defining for every phosphate group three distortion indices: $DI(TO) = (\sum |TO_i - TO_m|) / 4TO_m$, $DI(OTO) = (\sum |OTO_i - OTO_m|) / 6OTO_m$ and $DI(OO) = (\sum |OO_i - OO_m|) / 6OO_m$, where TO is the distance P–O, OTO the angle O–P–O, OO the distance O–O, the subscripts m refer to the mean and i to individual values. The average distortion indices for all groups are: $DI(TO) = 0.021$, $DI(OTO) = 0.028$, $DI(OO) = 0.012$. This means that distortions are more pronounced in the P–O distances than in O–O and thus the phosphate group can be viewed, to a first approximation, as a rigid regular arrangement of O atoms, with the P atoms displaced from their centroid. (3) Mean P–O distances of the phosphate groups vary from 1.506 to 1.572 Å. (4) Individual P–O distances are correlated with the bond strengths received by the individual oxygen atoms. (5) The individual O–P–O angles are strongly correlated with the average of the P–O distances on the sides of the angle, and with the opposite O–O distance. The various correlations are strong enough to formulate six equations which are useful for predictive purposes: the mean P–O distances can be calculated from the coordination numbers and the distortion indices; the individual P–O distances follow from the bond strength distribution; the bond angles are based on the normalized bond lengths; the mean O–O distances are a function of the mean P–O distances and the distortion indices; the lengths of shared tetrahedral edges depend on the number of shared edges per tetrahedron. Some of the correlations are affected by the presence of shared edges in the phosphate groups and differ for various subpopulations of the sample (ortho-, di-, ring-, poly-, acid or organic phosphates). The calculated shapes can be used as input to computer simulation of crystal structures.

Introduction

The arrangement of four oxygen atoms around a central pentavalent phosphorus atom is called the tetrahedral phosphate group because the oxygen ligands are distributed over the four corners of a tetrahedron. A regular tetrahedron possesses point group symmetry $\bar{4}3m$ or 23. However, to my knowledge no phosphate tetrahedron observed so far in a crystalline solid is located at a site with $\bar{4}3m$ symmetry. The site symmetries of the phosphate group in Ag_3PO_4 (Helmholz, 1936) and of one of the PO_4^{3-} groups in $Na_6F(OH_2)_{18}(NaH_2O)(PO_4)_2$ (Tillmanns & Baur, in preparation) are 23. However, these data are not used here because in the first case the structure is not determined precisely, while in the second case the phosphate group is disordered and therefore its actual dimensions are not precisely known. The site symmetry of 85% of the

phosphate groups studied in this paper is 1 (Table 1). Most phosphate tetrahedra deviate significantly in their dimensions from the values expected for a regular tetrahedral arrangement. The geometry of these deviations and the extent and the limits of the distortions are the topics of this study. 'Tetrahedron' is used to

Table 1. Site symmetries of a sample of 211 phosphate groups observed in crystalline solids (see Appendix)

Symmetry	Number of groups	% of total
1	179	84.8
m	16	7.6
2	7	3.3
3	4	1.9
$\bar{4}$	2	0.9
mm	1	0.5
222	1	0.5
$\bar{4}2m$	1	0.5

describe any distorted tetrahedral shape. If an *ideal* tetrahedron of point group symmetry $\bar{4}3m$ is meant it will be identified as such.

Corbridge's (1971) recent review of the structural chemistry of phosphates was extended to all classes of compounds which contain a P–O bond. The present study deals only with the tetrahedral PO_4 group. One half of the references to structural data used here are so recent that they were not included in Corbridge's review.

Data

The dimensions of 211 phosphate tetrahedra as found in 129 crystal structures determined by X-ray or neutron diffraction were collected. Data were included only if the mean estimated standard deviation of the four P–O bond lengths in the PO_4 group was equal to or smaller than 0.015 Å. All bond lengths, bond angles and estimated standard deviations have been recalculated from the data in the original papers. In those cases where the values given in Table 15 deviate from those stated in the original papers the discrepancies are most likely due to misprints in the source. The bond lengths were not corrected for thermal motion effects because such corrections can only be meaningfully applied when the joint distribution which describes the motion of the atoms is known or can be reasonably assumed (Busing & Levy, 1964).

Every phosphate group is listed with all of its dimensions in Table 15 in the Appendix. In addition the sums of the bond strengths, $p(\text{O})$, received by the individual oxygen atoms and their coordination numbers are given. The bond strengths were calculated according to Pauling's (1960) second rule for complex ionic compounds. Further details of such calculations and especially the way in which hydrogen bonds and Cu^{2+} ions are accounted for can be found in Baur (1970, 1971). The coordination numbers of the oxygen atoms are given in two parts: under H only those hydrogen atoms are counted which belong to hydrogen bonds donated to the oxygen atom in question (this means that it is a hydrogen-bond acceptor); under C all other coordinated atoms including covalently bonded hydrogen atoms are counted. The complete coordination number of the oxygen atom is the sum of the values given under C and H.

The phosphate tetrahedra are subdivided in Table 15 into two main populations: (1) orthophosphates, PO_4 , where every oxygen atom is bonded to only one phosphorus atom, and (2) condensed phosphates where at least one oxygen atom per phosphate group is shared between different phosphate tetrahedra. The orthophosphates are further subdivided into *i(a)* orthophosphates proper; *i(b)* acid orthophosphates, where one or more oxygen atoms are covalently bonded to hydrogen atoms; and *i(c)* organic phosphates, where one or more oxygen atoms are bonded to carbon atoms. The condensed phosphates are subdivided into *ii(a)* diphosphates, P_2O_7 , where one oxygen atom is shared be-

tween two phosphorus atoms; *ii(b)* ring phosphates, $(\text{PO}_3)_n$, where the phosphate tetrahedra form rings and n assumes values from 3 to 6; and *ii(c)* all other condensed phosphates, which are mainly chain phosphates. Additional information about the data is contained in the Appendix.

Distortion indices

Deviations from $\bar{4}3m$ symmetry of the phosphate tetrahedra can affect the P–O distances, $d(\text{P–O})$, the O–P–O angles, $\angle(\text{O–P–O})$, or the O–O distances, $d(\text{O–O})$. A measure of the degree of distortion can be obtained by calculating for every tetrahedron the three distortion indices (DI):

$$\text{DI}(\text{TO}) = \left(\sum_{i=1}^4 |\text{TO}_i - \text{TO}_m| \right) / 4\text{TO}_m \quad (1)$$

$$\text{DI}(\text{OTO}) = \left(\sum_{i=1}^6 |\text{OTO}_i - \text{OTO}_m| \right) / 6\text{OTO}_m \quad (2)$$

$$\text{DI}(\text{OO}) = \left(\sum_{i=1}^6 |\text{OO}_i - \text{OO}_m| \right) / 6\text{OO}_m, \quad (3)$$

where TO_i stands for the individual distances from the tetrahedral cation to the oxygen atom, OTO_i for the individual angles O–T–O, OO_i for the individual lengths of the tetrahedral edges and m signifies the mean value for the polyhedron. The distortion indices express the average deviation of $d(\text{T–O})$, $\angle(\text{O–T–O})$ and $d(\text{O–O})$ from their means. Analogous expressions can be formulated for other types of polyhedra as well. In the case of polyhedra, such as the tetrahedron, the octahedron or the cube, for which ideal shapes are defined by symmetry it will not matter whether the distortion index $\text{DI}(\text{OTO})$ is defined by comparison with the *mean* values or with the *ideal* values for the polyhedron. If the shape of a polyhedron is not defined by its symmetry (trigonal prism and many others) it would be appropriate to define first an ideal shape and then express $\text{DI}(\text{OTO})$ as a deviation from this predefined shape. For a useful discussion and a listing of various coordination polyhedra, including possible definitions of their ideal shapes, see King (1970) and his earlier papers on this subject.

Shapes of phosphate tetrahedra

A regular tetrahedron would have zero values for all three distortion indices (case I, Table 2). Among the groups in Table 15 one comes close to this: one of the phosphate groups in $\text{Na}_6\text{F}(\text{OH}_2)_{18}(\text{NaH}_2\text{O})(\text{PO}_4)_2$ (No. 111, Table 15) which has $\bar{4}$ symmetry. It is not possible for a tetrahedral group to have two distortion indices equal to zero and one different from zero. Whenever one of them deviates from zero at least one of the other two distortion indices must also be different from zero. Therefore five cases can be distinguished (Table 2). Strictly speaking most phosphate

tetrahedra belong to case V. However, it is instructive to inspect the three cases II, III and IV, because they demonstrate extreme possibilities. Case II illustrates a tetrahedral group in which the oxygen atoms are equidistant from each other and outline a regular tetrahedron, and the central cation is moved away from the centroid of the tetrahedron [Fig. 1(a)]. Case III occurs when the tetrahedral angles are exactly preserved at 109.471° , while the T-O and O-O distances vary [Fig. 1(b)]. Case IV means that the four T-O distances are all of equal length, but the ideal tetrahedral angles are not preserved [Fig. 1(c)].

Table 2. Possible combinations of distortion indices which define different distortion cases

Case	I	II	III	IV	V
DI(TO)	=0	≠0	≠0	=0	≠0
DI(OTO)	=0	≠0	=0	≠0	≠0
DI(OO)	=0	=0	≠0	≠0	≠0

Very few of the *individual* phosphate tetrahedra are close to the pure cases I to IV. However, different phosphate group *populations* (Table 4) show tendencies towards some of the pure cases. The average distortion

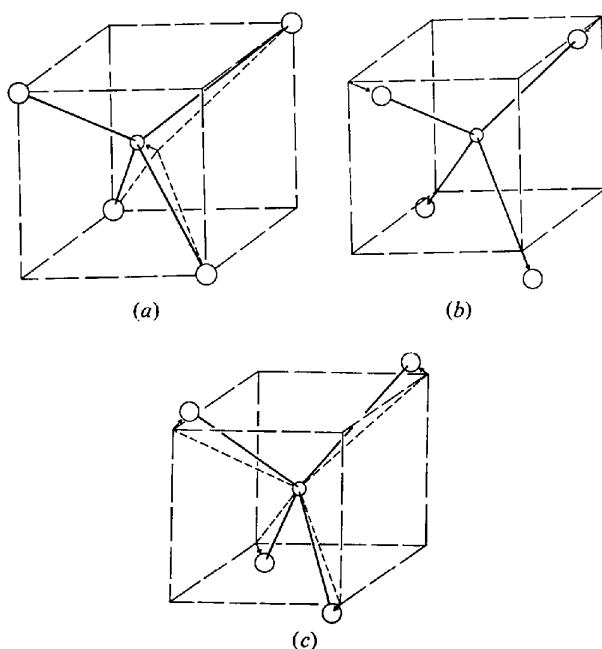


Fig. 1. Three pure cases of distortion of a tetrahedral shape. (a) Case II of Table 2; $d(\text{O-O})$ remains constant, $d(\text{T-O})$ varied by moving T out of centroid; therefore $\angle(\text{O-T-O})$ must deviate from ideal tetrahedral angle. In this example symmetry $3m$ is preserved. (b) Case III: $\angle(\text{O-T-O})$ constant at ideal value, $d(\text{T-O})$ and $d(\text{O-O})$ must vary. Symmetry of this example mm . (c) Case IV: $d(\text{T-O})$ remains constant, while $\angle(\text{O-T-O})$ varies; therefore $d(\text{O-O})$ must vary too. Symmetry of this example $\bar{4}2m$. It has to be emphasized that the symmetries as shown are examples. The same types of distortions could also occur with other symmetries. Only $\bar{4}3m$ and 23 are impossible for any of the distortions.

index DI(OO) for all phosphate groups is about half as large as DI(TO) or DI(OTO). This becomes even more pronounced when we consider only those 145 tetrahedra that do not share polyhedral edges with other coordination polyhedra in the structures. For those phosphate tetrahedra that share edges with other polyhedra DI(TO) and DI(OTO) are not very different from the overall values, while DI(OO) is slightly higher because shared edges tend to be shorter than unshared edges (Pauling, 1960). Consequently the distortion in terms of $d(\text{O-O})$ is increased. On balance the average DI-values for all 211 tetrahedra indicate that the average phosphate group corresponds approximately to case II of Table 2. Among the different sub-populations only the orthophosphates proper do not follow this trend [i(a) in Table 4]. Orthophosphates *without* shared edges have small values for all three distortion indices and conform best to case I, while the orthophosphates *with* shared edges constitute the only example that comes close to case IV. None of the sub-populations corresponds to case III. Obviously the most variable parts of a phosphate tetrahedron are its angles and the least variable ones are its edges. This is also apparent from an inspection of the extreme values of the dimensions of the phosphate tetrahedra (Table 3).

Mean tetrahedral P-O distances

The mean distances, $d(\text{P-O})_m$, in the 211 phosphate tetrahedra range in length from 1.506 to 1.572 Å, with a mean value of 1.537 Å. Because only precisely determined structures have been included the spread over 4% of the value is too large to be explained by experimental error alone. The question of the constancy of the mean $d(\text{T-O})$ in tetrahedral oxyanions has been much debated. An excellent summary of the previous views on this subject has been presented by Shannon & Calvo (1973), who also investigated the factors contributing to the variation in the mean interatomic distances in tetrahedral PO_4^{3-} , AsO_4^{3-} and VO_4^{3-} groups. They considered mainly the coordination numbers of the oxygen atoms (see Shannon & Prewitt, 1969) and the electronegativities of cations other than the tetrahedral cation bonded to oxygen. However, they ignored the effects of the degree of distortion of the tetrahedra, a significant effect in a number of coordination octahedra (Brown & Shannon, 1973).

Regressions were calculated (for information on the computer program see Appendix) of $d(\text{P-O})_m$ on the mean coordination number, CN_m , of the oxygen atoms. Extremely low correlation coefficients were obtained whether or not the hydrogen bonds accepted by the hydrogen atoms were included in CN_m (Table 5, lines 1 and 2). Different results, however, are obtained after the sample has been subdivided into two populations, one containing the orthophosphates proper, the acid orthophosphates and the diphosphates (lines 3 and 4, Table 5); the other consisting of the organic phos-

Table 3. *Extreme individual and extreme average values of $d(\text{P-O})$, $\angle(\text{O-P-O})$, $d(\text{O-O})$, $p(\text{O})$ and maximal values of the distortion indices occurring in the 211 phosphate groups*

The numbers in square brackets are references to phosphate groups (in Table 15) which display these extreme values.

	Individual values		Average values for tetrahedron		DI _{max}
	Min	Max	Min	Max	
$d(\text{P-O})$	1.412 Å [721]	1.662 Å [555]	1.506 Å [271]	1.572 Å [555]	0.054 [555]
$\angle(\text{O-P-O})$	96.6° [961]	123.4° [1121]	109.0° [555]	109.6° [1291]	0.069 [961]
$d(\text{O-O})$	2.317 Å [961]	2.620 Å [121]	2.458 Å [271]	2.552 Å [555]	0.029 [1291]
$p(\text{O})$	1.25 v.u. [1031]	2.786 v.u. [72]	1.750 v.u. [361]	2.250 v.u. [1151]	0.265 [1121]

Table 4. *Phosphate groups*

Mean values of $d(\text{P-O})$, $\angle(\text{O-P-O})$, $d(\text{O-O})$ and the coordination number. Mean distortion indices DI(TO), DI(OTO), DI(OO) and DI($p\text{O}$) (for definitions see text). The number of phosphate groups used in the averaging is N . Every population is subdivided into those coordination tetrahedra which do not share edges with other polyhedra in the crystal structures (nsh) and in those which share polyhedral edges (sh).

	N	$d(\text{P-O})$	DI(TO)	$\angle(\text{O-P-O})$	DI(OTO)	$d(\text{O-O})$	DI(OO)	CN _m	DI($p\text{O}$)
i (a), ortho, all	64	1.536 Å	0.006	109.45°	0.015	2.507 Å	0.009	3.31	0.035
ortho, nsh	35	1.533	0.005	109.47	0.009	2.504	0.006	3.15	0.034
ortho, sh	29	1.539	0.006	109.44	0.022	2.512	0.014	3.49	0.035
i (b), acid, all	31	1.536	0.018	109.41	0.026	2.506	0.012	3.04	0.114
acid, nsh	23	1.536	0.017	109.41	0.025	2.506	0.011	2.91	0.112
acid, sh	8	1.537	0.018	109.41	0.027	2.507	0.014	3.41	0.119
i (c), carbon, all	30	1.538	0.030	109.31	0.038	2.506	0.016	2.53	0.167
carbon, nsh	28	1.539	0.030	109.30	0.038	2.507	0.015	2.46	0.171
carbon, sh	2	1.525	0.025	109.36	0.038	2.486	0.019	3.50	0.102
i (a), i (b), i (c), all	125	1.536	0.015	109.41	0.023	2.507	0.011	3.05	0.086
nsh	86	1.536	0.017	109.40	0.023	2.505	0.010	2.86	0.100
sh	39	1.538	0.010	109.43	0.024	2.509	0.014	3.47	0.055
ii (a), di, all	42	1.534	0.020	109.37	0.028	2.501	0.012	2.71	0.121
di, nsh	30	1.531	0.019	109.37	0.028	2.497	0.011	2.43	0.118
di, sh	12	1.541	0.024	109.38	0.028	2.513	0.013	3.42	0.131
ii (b), ring, all	26	1.544	0.041	109.19	0.041	2.512	0.014	2.93	0.208
ring, nsh	17	1.544	0.041	109.18	0.040	2.512	0.014	2.79	0.205
ring, sh	9	1.545	0.042	109.20	0.041	2.514	0.015	3.19	0.213
ii (c), poly, all	18	1.542	0.037	109.20	0.040	2.510	0.015	2.78	0.190
poly, nsh	12	1.542	0.035	109.19	0.040	2.509	0.014	2.67	0.188
poly, sh	6	1.543	0.039	109.21	0.042	2.511	0.015	3.00	0.194
ii (a), ii (b), ii (c), all	86	1.539	0.030	109.28	0.034	2.506	0.013	2.79	0.162
nsh	59	1.537	0.029	109.28	0.034	2.503	0.013	2.59	0.157
sh	27	1.543	0.033	109.28	0.035	2.513	0.014	3.25	0.172
all, all	211	1.537	0.021	109.35	0.028	2.506	0.012	2.95	0.117
nsh	145	1.536	0.022	109.35	0.027	2.505	0.011	2.75	0.123
sh	66	1.540	0.019	109.37	0.029	2.511	0.014	3.38	0.103

Table 5. *Results of weighted regression analysis involving the dependence of $d(\text{P-O})_m$ on CN_m and distortion indices*

Not corrected for = n.c.; corrected for = c.; accepted hydrogen bonds included in CN_m = w.H.; accepted hydrogen bonds excluded from CN_m = wo.H.; intercept of regression equation = a ; slope of regression equation = b ; correlation coefficient = r ; percent variation explained = %; sample size = N . The different subpopulations i (a) etc., ii (a) etc., are as defined in the text (see data). In parentheses following the values are the e.s.d.'s in units of the least significant digits.

Dependent variable	Independent variable	a	b	r	%	N
1. $d(\text{P-O})_m$	CN _m , wo.H.	1.534 (2)	0.0015 (6)	0.16	3	211
2. $d(\text{P-O})_m$	CN _m , w.H.	1.532 (2)	0.0019 (8)	0.16	3	211
3. $d(\text{P-O})_m$, i (a), i (b), ii (a)	CN _m , wo.H.	1.529 (2)	0.0025 (7)	0.31	10	137
4. $d(\text{P-O})_m$, i (a), i (b), ii (a)	CN _m , w.H.	1.521 (3)	0.0047 (9)	0.42	18	137
5. $d(\text{P-O})_m$, i (c), ii (b), ii (c)	CN _m , wo.H.	1.538 (3)	0.0013 (15)	0.10	1	74
6. $d(\text{P-O})_m$, i (c), ii (b), ii (c)	CN _m , w.H.	1.543 (5)	-0.0010 (19)	-0.06	0	74
7. $d(\text{P-O})_m$, n.c.CN _m	DI(TO)	1.534 (1)	0.19 (4)	0.34	12	211
8. $d(\text{P-O})_m$, c.CN _m	DI(TO)	1.493 (1)	0.41 (4)	0.57	32	211
9. $d(\text{P-O})_m$, n.c.CN _m	DI(TOSQ)	1.535 (1)	0.63 (12)	0.34	12	211
10. $d(\text{P-O})_m$, c.CN _m	DI(TOSQ)	1.496 (1)	1.46 (13)	0.60	36	211
11. $d(\text{P-O})_m$, c.DI(TOSQ)	CN _m , wo.H.	1.525 (2)	0.0031 (6)	0.33	11	211
12. $d(\text{P-O})_m$, c.DI(TOSQ)	CN _m , w.H.	1.514 (2)	0.0059 (7)	0.49	24	211

phates, the ring- and the polyphosphates (lines 5 and 6). A correlation with a coefficient of 0.42, while it certainly does not account for all the variation in $d(\text{P-O})_m$, is nevertheless significant for a sample size of 137. The two populations differ mainly in that the first has a mean distortion index $\text{DI}(\text{TO})=0.013$, while the second has a mean $\text{DI}(\text{TO})=0.035$, almost three times as large. Consequently, the dependence of $d(\text{P-O})_m$ on $\text{DI}(\text{TO})$ was tested in two ways: first by using the raw $d(\text{P-O})_m$ data (line 7) and secondly, after reduction of the $d(\text{P-O})_m$ values to an assumed coordination number of zero, by subtracting from each $d(\text{P-O})_m$ value CN_m multiplied by 0.012 Å. The value of the slope was not taken from line 4 (0.0047 Å) but was taken instead from Fig. 5 of Shannon & Prewitt (1969) because the latter value is based on a larger number of more diverse data, and is therefore more reliable. In addition the regression equation was calculated for $d(\text{P-O})_m$ on $\text{DI}(\text{TOSQ})$, the distortion index as defined by Brown & Shannon (1973):

$$\text{DI}(\text{TOSQ}) = \left[\sum_{i=1}^4 (\text{TO}_i - \text{TO}_m)^2 \right] / 4\text{TO}_m^2 \quad (4)$$

The correlation coefficient improved slightly (compare line 10, Table 5, with line 8). Then the procedure was reversed and the correlation was tested between CN_m and $d(\text{P-O})_m$ after it was corrected for its dependence on $\text{DI}(\text{TOSQ})$ (Figs. 2 and 3). The correlation coefficients improved greatly (lines 11 and 12 as compared with lines 1 and 2).

From this discussion it emerges that:

(1) In the case of the phosphate groups the hydrogen bonds donated to an oxygen atom have to be counted as coordinating contacts when the coordination number is determined (Fig. 2). Whether or not this is also true for oxygen atoms in other bonding situations re-

mains to be seen. If it is generally true, it would be preferable to evaluate the mean coordination numbers of the oxygen atoms of every single coordination polyhedron individually and to count the donated hydrogen bonds as coordinating contacts as has been done here, instead of using the general formula employed by Shannon & Prewitt (1969) which yields a *single* average anion coordination number for *all* the oxygen atoms in all cation coordination polyhedra within a crystal structure.

(2) Both the mean coordination number of the oxygen atoms and the distortion index of the phosphate group contribute significantly to the variation in mean distance P-O in this sample of 211 phosphate tetrahedra (Fig. 2 and 3). This statement does not contradict Shannon & Calvo's (1973) opinion that the distortions of the tetrahedral groups can be ignored. For their sample of phosphate groups (61 crystal structures) this was true because it contained only 4 structures of ring- and polyphosphate groups and no organic phosphates.

(3) The mean coordination number and the distortion index still account for all the variation in mean P-O distances. Otherwise, the correlation coefficients would have to be higher (lines 10 and 12, Table 5). Additional factors must be at work. One of these may be the average electronegativity of the cations bonded to the oxygen atoms, as discussed by Shannon & Calvo (1973) but ignored in the present treatment.

Keeping the foregoing limitations in mind the values of line 10 of Table 5 and the dependence on CN_m (Shannon & Prewitt, 1969) can be used for a predictive equation for the mean P-O distance:

$$d(\text{P-O})_m = [1.496 + 0.012\text{CN}_m + 1.46\text{DI}(\text{TOSQ})] \text{ \AA} \quad (5)$$

The mean deviation between the 211 observed values and the values calculated by equation (5) is 0.007 Å and the maximum deviation is 0.028 Å. Some of the more pronounced deviations may be explained by the systematic influence of large thermal motion on the observed bond lengths. An example is $\text{AgPO}_2(\text{OC}_2\text{H}_5)_2$ (No. 87, Table 15) where the observed $d(\text{P-O})_m = 1.513$ Å, while equation (5) yields $d(\text{P-O})_m = 1.533$ Å. All temperature factors of the phosphate group oxygen atoms are high; therefore, $d(\text{P-O})_m$ corrected for riding motion is 1.523 Å, which is in better agreement with the calculated value.

Individual tetrahedral P-O distances

A study (Baur, 1970, 1971) of a large number of borates, silicates, phosphates, sulfates and titanates has shown that the *individual* bond lengths $d(\text{A-X})$ within a polyhedron around a cation A vary with $p(\text{X})$, the sum of the bond strengths (Pauling, 1960) received by the anion X.

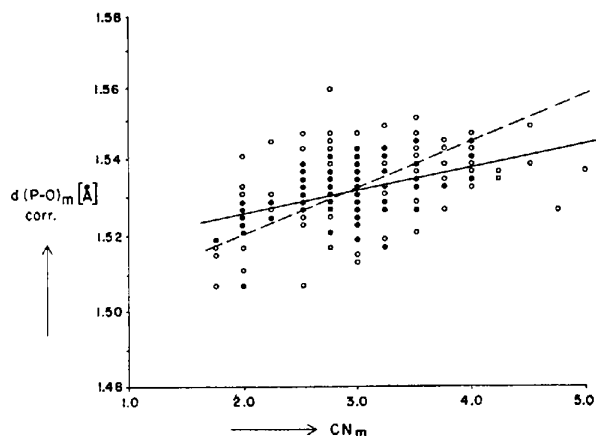


Fig. 2. Scatter diagram of mean P-O distances, corrected for dependence on $\text{DI}(\text{TOSQ})$, versus mean coordination number. Full circles represent multiple points, open circles single points, see Table 5, line 12. The regression line is drawn solid, the line with a slope of 0.012 (Shannon & Prewitt, 1969) is dashed.

Individual bond lengths can be predicted using regression equations of the form:

$$d(A-X) = [a + bp(X)] \text{ \AA} \quad (6)$$

and

$$d(A-X) = [d(A-X)_m + b\Delta p(X)] \text{ \AA} \quad (7)$$

where $d(A-X)_m$, a and b are empirically derived constants for given pairs of A and X in a given coordination, $\Delta p(x)$ is the difference between the individual $p(X)$ and the mean $[p(X)_m]$ for the coordination polyhedron, and A and X are atoms with formal positive or negative charges. For the P-O bond the value of b was determined (Baur, 1970) to be 0.109(5) (based on equation (6) and using 174 pairs of values; correlation coefficient 0.87). It is possible to use either an experimental mean value $d(P-O)_m$ or to calculate it from equation (5) [the required value of DI(TOSQ) can be estimated from equation (16)].

Based on equation (7) an improved value of b for the P-O bond was determined from the data from Table 15, by finding the regression equation between $\Delta d(om)$ and $\Delta p(O)$, where $\Delta d(om)$ is the bond length variation within the phosphate tetrahedron [difference between observed individual $d(P-O)$ and mean $d(P-O)$, $\Delta d(om) = d(P-O) - d(P-O)_m$]. The correlation between $\Delta d(om)$ and $\Delta p(O)$ is good (Table 6, Fig. 4) and the mean difference between calculated and observed values is only 0.010 Å. Even the organic phosphates fit equation (7) reasonably well. In the calculation of the bond strengths the carbon atoms were given a formal charge of 4+, a procedure which may appear extreme. However, it is no more extreme than to assume a charge of 5+ on a phosphorus atom. In both cases the formal charges refer to the core of the atom without its valence electrons [compare on this point the excellent discussions by Bent (1970) and Brown & Shannon (1973)].

Brown & Shannon (1973) have shown that the relationship between bond length and bond strength is exponential. However, the relationship between $\Delta p(O)$ and $\Delta d(om)$ is essentially linear (Fig. 4). This linearity can be taken as a reasonable approximation of the exponential form as long as the investigated range of bond lengths is relatively small and the coordination polyhedron is well defined.

Deviations from Pauling's postulate

Individual $p(O)$ values received by the oxygen atoms range from 1.25 to 2.79 v.u. (valence units), which means that Pauling's (1960) postulate, according to which the sum of the bond strengths should equal (with opposite sign) the formal charge of the oxygen ion, is not well obeyed in the 211 phosphate tetrahedra studied here. The deviations from the postulate are compensated by the variations observed in the individual bond lengths [equation (7)]. The amount of variation in $p(O)$ can be expressed by a discrepancy index

$$DI(pO) = \left(\sum_{i=1}^4 |p(O) - p(O)_m| \right) / 4p(O)_m \quad (8)$$

The distortion indices DI(TO) and DI(OTO) are strongly correlated with DI(pO), while the correlation with DI(OO) is less pronounced (Table 6, Figs. 5-7). The correlation between DI(pO) and DI(TO) is not affected by separating the phosphate tetrahedra into populations that contain and that do not contain shared edges. However, there is no correlation between DI(pO) and DI(OO) for the group of tetrahedra with shared edges, while the correlation is fair for the tetrahedra without shared edges. Naturally, the relationship between DI(pO) and DI(OTO) falls between these extremes because the angle O-P-O depends on both $d(P-O)$ and $d(O-O)$. Therefore, it appears that for phosphate tetrahedra with no shared edges the shape is affected mostly by DI(pO) [*i.e.* by $\Delta p(O)$] while for those with shared edges the influence of edge shortening on DI(OO) is also appreciable.

While the individual $d(P-O)$ vary with $p(O)$, there is no correlation between the mean $p(O)$ received by

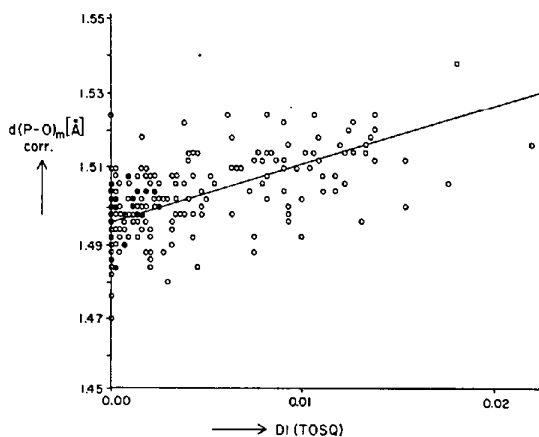


Fig. 3. Scatter diagram of mean P-O distances, $d(P-O)_m$, corrected for dependence on CN_m , versus DI(TOSQ), see Table 5, line 10.

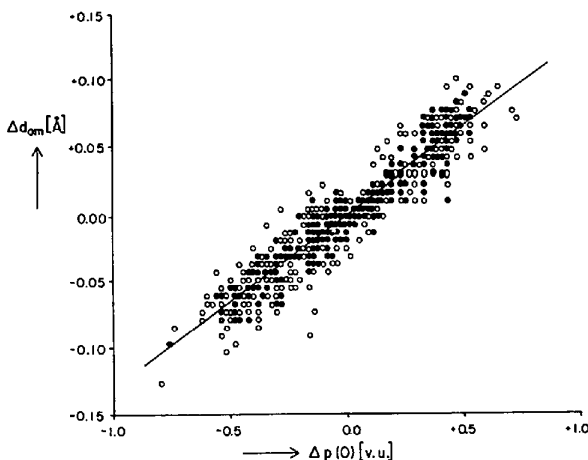


Fig. 4. Scatter diagram of $\Delta d(om)$ versus $\Delta p(O)$ (Table 6).

the four oxygen atoms in a tetrahedron and the mean tetrahedral distance $d(P-O)_m$. The correlation coefficient between $p(O)_m$ and $d(P-O)_m$ is 0.05 (compare rule 3, Baur, 1970).

Bond angles

As in any triangle the angle O(1)–P–O(2) in a tetrahedron is determined by its sides P–O(1) and P–O(2), and by the length of the opposite distance O(1)–O(2). Since $d(P-O)$ and $d(O-O)$ vary from tetrahedron to tetrahedron the angles must be affected accordingly. These variations, however, are not always random, as has been recognized by McDonald & Cruickshank (1967) in the case of condensed phosphates for which $d[O(1)–O(2)]$ decreases in length as the mean of the distances P–O(1) and P–O(2) increases [$d(P-O)_s$]. Furthermore, Baur (1970) pointed out that: ‘The values of the averaged angles $\alpha = \angle(X-A-X)$ around a cation tend to vary inversely with the mean bond length $d(A-X)_s$ of the two sides of the angles. The geometrical relationship is:

$$\log [\sin (\alpha / 2)]=a+b \log [d(A-X)]_s . \quad (9)$$

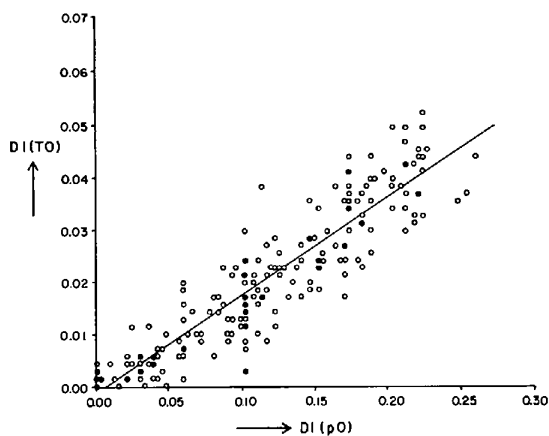


Fig. 5. Scatter diagram of DI(TO) versus DI(pO), all phosphate tetrahedra (Table 6).

The values a and b derived from the regression analysis tend to be not very different from those theoretically expected: $a = \log [\sin (\beta / 2) d_1]$ and $b = -1.0$, where d_1 is the grand mean of $d(A-X)$ observed for a given pair A and X in a given coordination. The ‘theoretically expected’ values refer to a coordination polyhedron in which the anions outline an ideal polyhedron, where the angle X–A–X is β when the central cation is centered in the polyhedron, and where X–A–X has the value α when the cation is not in the center of the polyhedron [this corresponds for a tetrahedron to case II of Table 2, see Fig. 8(a)]. For orthophosphate tetrahedra the slope b was found to be -1.08 (12) and for condensed phosphates it was -1.49 (7). The difference in the values is significant and is related to McDonald & Cruickshank’s (1967) observation of the dependence of $d(O-O)$ on $d(P-O)_s$ in condensed phosphates. A slope different from -1.0 means that this population of tetrahedra does not conform to case II of Table 2. The presence of shared and therefore shortened tetrahedral edges often masks the $\angle(O-P-O)$ versus $d(P-O)_s$ relationship. In order to offset this effect partially the correlations were calculated previously (Baur, 1970) for the values averaged over angles formed by bonds with similar $d(P-O)_s$ values within each tetrahedron and not for the individual angles.

The regression analyses of the present sample were performed on the non-averaged, individual pairs of values of $\log [\sin (\alpha / 2)]$ and $\log [d(P-O)_s]$. The influence of shared edges was excluded by treating tetrahedra with and without shared edges separately (Table 7). In addition the dependence of $d(O-O)$ on $d(P-O)_s$ as well as the dependence of $\angle(O-P-O)$ on the length of the edge O–O were investigated [see Fig. 8(b)]:

$$\log [\sin (\alpha / 2)]=a+b \log [d(O-O) / 2] . \quad (10)$$

This equation is analogous to equation (9). A similar equation was used by Louisnathan & Gibbs (1972). A geometrically simple model to which this equation could be applied would be one in which it is assumed that $d(P-O)_s$ stays constant while the distances O–O and the angle O–P–O vary (case IV of Table 2). For

Table 6. Results of weighted regression analyses involving the dependence on $\Delta p(O)$ and $DI(pO)$

Only tetrahedra without shared edges included = nsh; only tetrahedra containing shared edged included = sh; for other explanations see Table 5.

Dependent variable	Independent variable	Remarks	<i>a</i>	<i>b</i>	<i>r</i>	%	<i>N</i>
$\Delta d(om)$	$\Delta p(O)$	all	0.000 (0)	0.130 (2)	0.95	90	844
DI(TO)	DI(pO)	all	-0.001 (1)	0.183 (6)	0.92	84	211
DI(TO)	DI(pO)	nsh	-0.001 (1)	0.183 (7)	0.91	83	145
DI(TO)	DI(pO)	sh	0.000 (1)	0.187 (9)	0.94	88	66
DI(OTO)	DI(pO)	all	0.011 (1)	0.145 (8)	0.78	60	211
DI(OTO)	DI(pO)	nsh	0.006 (1)	0.173 (9)	0.84	71	145
DI(OTO)	DI(pO)	sh	0.018 (2)	0.105 (14)	0.69	48	66
DI(OO)	DI(PO)	all	0.008 (1)	0.032 (5)	0.42	18	211
DI(OO)	DI(pO)	nsh	0.005 (1)	0.050 (5)	0.66	43	145
DI(OO)	DI(pO)	sh	0.013 (1)	0.006 (9)	0.09	1	66
DI(TOSQ)	DI(pO)	all	-0.002 (0)	0.053 (3)	0.82	68	211
DI(TOSQ)	DI(pO)	nsh	-0.002 (0)	0.055 (3)	0.81	66	145
DI(TOSQ)	DI(pO)	sh	-0.002 (1)	0.052 (4)	0.84	71	66

Table 7. Results of weighted regression analyses involving the dependence of $\log [\sin (\alpha/2)]$ on $\log [d(P-O)_s]$, of $\log [\sin (\alpha/2)]$ on $\log [d(O-O)/2]$ and of $d(P-O)_s$ on $d(O-O)$

In these expressions $d(P-O)_s$ is the normalized mean of the two sides of the angle (except in the case of the first three lines). Not normalized = n.n.; normalized = n.; dependent variable = d.v.; independent variable = i.v.; for other explanations see Tables 5 and 6.

	N	d(P-O) _s on d(O-O)			log [sin (α/2)] on log [d(P-O) _s]			log [sin (α/2)] on log [d(O-O)/2]			d(P-O) _s on d(O-O)		
		a	b	r	a	b	r	a	b	r	a	b	r
i (a), ortho, n.n., all	384	0.055 (20)	-0.77 (11)	-0.34	-0.181 (2)	0.95 (2)	0.90	2.0 (3)	0.3 (2)	0.09	0.8 (2)	0.3 (2)	
nsh	210	-0.017 (16)	-0.39 (8)	-0.30	-0.154 (4)	0.67 (5)	0.71	0.8 (2)	1.1 (1)	0.51	1.1 (1)	0.51	
sh	174	0.184 (43)	-1.45 (23)	-0.43	-0.192 (2)	1.05 (2)	0.96	4.0 (6)	-1.0 (4)	-0.18	-1.0 (4)	-0.18	
i (a), ortho, n., all	384	0.232 (30)	-1.72 (15)	-0.50	-0.194 (2)	1.08 (2)	0.96	4.8 (4)	-1.5 (3)	-0.27	-1.5 (3)	-0.27	
nsh	210	0.121 (24)	-1.12 (13)	-0.52	-0.191 (4)	1.04 (4)	0.89	2.8 (4)	-0.2 (2)	-0.07	-0.2 (2)	-0.07	
sh	174	0.313 (50)	-2.15 (27)	-0.52	-0.195 (2)	1.09 (2)	0.97	5.8 (7)	-2.1 (5)	-0.34	-2.1 (5)	-0.34	
i (b), acid, n., nsh	138	0.168 (18)	-1.37 (9)	-0.78	-0.214 (7)	1.28 (7)	0.84	3.4 (3)	-0.6 (2)	-0.29	-0.6 (2)	-0.29	
nsh	48	0.178 (45)	-1.43 (24)	-0.66	-0.202 (8)	1.16 (9)	0.90	3.7 (6)	-0.7 (4)	-0.26	-0.7 (4)	-0.26	
sh	168	0.161 (12)	-1.34 (7)	-0.84	-0.226 (8)	1.40 (8)	0.81	3.3 (2)	-0.5 (1)	-0.35	-0.5 (1)	-0.35	
i (c), carbon, n., nsh	12	0.152 (68)	-1.29 (37)	-0.75	-0.207 (26)	1.20 (26)	0.82	3.2 (9)	-0.4 (6)	-0.23	-0.4 (6)	-0.23	
nsh	516	0.162 (8)	-1.34 (4)	-0.81	-0.219 (4)	1.33 (4)	0.82	3.3 (1)	-0.5 (1)	-0.31	-0.5 (1)	-0.31	
sh	234	0.210 (28)	-1.60 (15)	-0.58	-0.198 (3)	1.11 (3)	0.94	4.1 (4)	-1.0 (3)	-0.27	-1.0 (3)	-0.27	
i (a), i (b), i (c), n., nsh	180	0.180 (14)	-1.44 (7)	-0.83	-0.224 (6)	1.38 (6)	0.85	3.6 (2)	-0.7 (1)	-0.45	-0.7 (1)	-0.45	
nsh	72	0.106 (18)	-1.04 (10)	-0.78	-0.191 (14)	1.05 (15)	0.65	2.7 (2)	-0.2 (1)	-0.12	-0.2 (1)	-0.12	
sh	102	0.169 (11)	-1.39 (6)	-0.92	-0.264 (12)	1.79 (12)	0.83	3.5 (1)	-0.7 (1)	-0.59	-0.7 (1)	-0.59	
ii (b), ring, n., nsh	54	0.143 (16)	-1.25 (8)	-0.90	-0.243 (19)	1.58 (20)	0.75	3.1 (2)	-0.4 (1)	-0.37	-0.4 (1)	-0.37	
nsh	72	0.194 (13)	-1.52 (7)	-0.94	-0.271 (11)	1.87 (11)	0.89	3.8 (2)	-0.9 (1)	-0.68	-0.9 (1)	-0.68	
sh	36	0.167 (20)	-1.37 (10)	-0.91	-0.258 (20)	1.73 (21)	0.82	3.5 (3)	-0.7 (2)	-0.55	-0.7 (2)	-0.55	
ii (a), ii (b), ii (c), nsh	354	0.177 (7)	-1.43 (4)	-0.89	-0.246 (5)	1.61 (6)	0.84	3.6 (1)	-0.7 (1)	-0.54	-0.7 (1)	-0.54	
sh	162	0.137 (10)	-1.21 (6)	-0.87	-0.225 (10)	1.40 (10)	0.73	3.0 (1)	-0.4 (1)	-0.30	-0.4 (1)	-0.30	

case IV to be ideally fulfilled for a population of phosphate tetrahedra, a has to equal $\log [\sin (\beta / 2) / 0.5 e_1]$, where e_1 is the edge length in an undeformed polyhedron [Fig. 8(b)] and b must equal 1.0.

Both the correlation coefficients and the coefficients a and b of the regression equations are affected by the large spread in $d(\text{P-O})_m$ values in the different tetrahedra. Therefore, the individual $d(\text{P-O})_s$ and $d(\text{O-O})$ values were normalized to a standard mean P-O bond length of 1.537 Å by multiplying the individual values by the factor $1.537/d(\text{P-O})_m$ separately for every tetrahedron. The angles O-P-O were left at the values of the unnormalized tetrahedra. As a rule the effect of the normalization procedure is for all three relations [equations (9) and (10), and the $d(\text{O-O})$ versus $d(\text{P-O})_s$ relationship] to increase the correlation coefficient and to steepen the slope b of the regression equation. There is only one exception to this rule: the trivial case of the relatively undistorted orthophosphate groups prop-

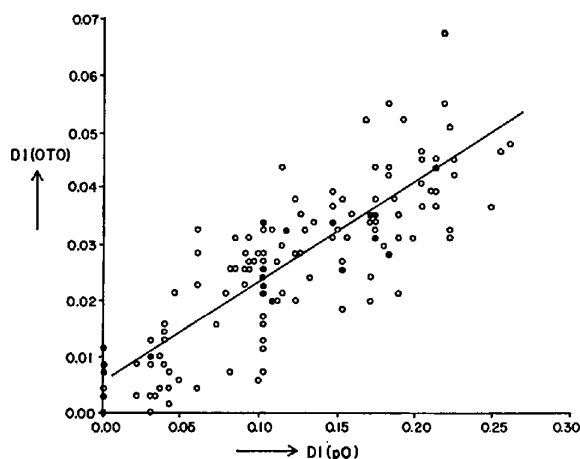


Fig. 6. Scatter diagram of DI(OTO) versus DI(pO), phosphate groups without shared edges only (Table 6).

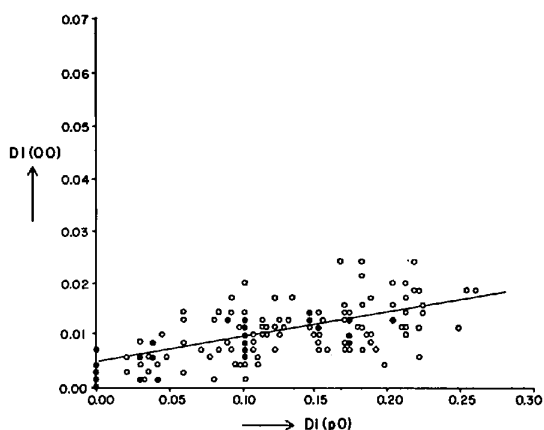


Fig. 7. Scatter diagram of DI(OO) versus DI(pO), phosphate groups without shared edges only (Table 6).

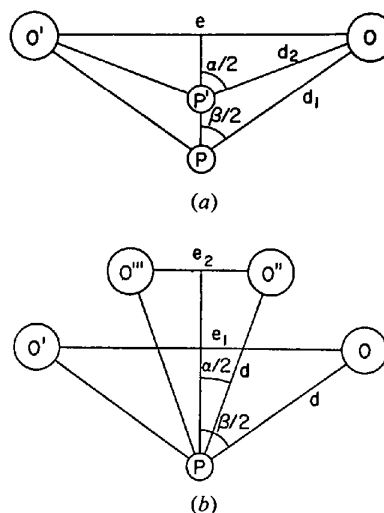


Fig. 8. Distortions of bond angle geometry. The special cases of $\text{P-O}=\text{P-O}'$ are treated. (a) Case II of Table 2: $d_1=d(\text{P-O})_m=\text{P-O}$; $d_2=\text{individual } d(\text{P-O})=\text{P}'\text{-O}=\text{P}'\text{-O}'$; $e=d(\text{O-O})=\text{O-O}'=\text{tetrahedral edge}$; $\alpha=\angle(\text{O-P}'\text{-O}')$ =distorted bond angle; $\beta=\angle(\text{O-P-O})$ =undistorted angle in ideal tetrahedron. (b) Case IV of Table 2: $d=d(\text{P-O})_m=\text{P-O}=\text{P-O}'=\text{P-O}''=\text{P-O}'''$ =individual and mean P-O distance; $e=d(\text{O-O})=\text{O-O}'$ =undistorted tetrahedral edge in an ideal tetrahedron; $e_2=d(\text{O-O})=\text{O}''\text{-O}'''$ =distorted tetrahedral edge; $\alpha=\angle(\text{O-P-O}')$ =distorted bond angle; $\beta=\angle(\text{O}''\text{-P-O}''')$ =undistorted bond angle in ideal tetrahedron.

er [i(a) in Tables 4 and 7]. In the unnormalized case a positive correlation exists between $d(\text{O-O})$ and $d(\text{P-O})_s$ because the distance O-O must increase proportionally to $d(\text{P-O})_s$ in an undistorted polyhedron. However, once the tetrahedra are normalized this correlation has to disappear. The orthophosphates proper represent the only population for which the regression equations are given for the combined data of tetrahedra with and without shared edges. This illustrates how deceptive the results can be when populations which display different trends are mixed (compare 'all' with 'nsh' and 'sh' in Table 7).

An inspection of Table 7 and Fig. 11 reveals that the negative correlations between $d(\text{O-O})$ and $d(\text{P-O})_s$ (McDonald & Cruickshank, 1967) without exception are very weak. This is very pronounced for all the orthophosphates, but is also true of the condensed phosphates. The highest correlation coefficient (-0.68) between $d(\text{O-O})$ and $d(\text{P-O})_s$ was found for the polyphosphates. This defines a much weaker correlation than the polyphosphates show between $\log [\sin (\alpha / 2)]$ and $\log [d(\text{P-O})_s]$ (-0.94).

Few of the subpopulations conform to either the pure case II of Table 2 (equation (9) with the ideal values $a=\log [1.537 \sin (109.471 / 2)]=0.099$ and $b=-1.0$) or to the pure case IV (equation 10 with the ideal values $a=\log [\sin (109.471 / 2) / 1.255]=0.187$ and $b=1.0$). The closest match between these geometrically expected values and the coefficients of the regression equations is found for the orthophosphates proper without shared

edges. Taking into consideration both the values of the coefficients a and b and the correlation coefficients it appears that the orthophosphates proper agree best with equation (10). For most of the other populations the dependence of the angles on both $d(\text{P-O})_s$ [equation (9)] and $d(\text{O-O})$ [equation (10)] is pronounced. Some individual variations are apparent, such as the observation that the acid phosphates behave similarly to the orthophosphates proper, while the organic, the ring- and the polyphosphates conform better to equation (9). There is no contradiction in the observation that the same population can conform with high correlation coefficients to both equations (9) and (10). This can happen as long as the coefficients of the regression equations are clearly different from the geometrically ideal values expected for the pure cases II and IV of Table 2.

The observed dependence of the angle O-P-O on both $d(\text{P-O})_s$ and $d(\text{O-O})$ means that neither case II nor case IV completely describes the distortion behavior of the phosphate tetrahedron. Instead, the distortions follow a composite model of cases II and IV in which case II must be the dominating influence for most of the subpopulations, as is evidenced by the values of DI(TO) and DI(OO) in Table 4. In this composite distortion model $d(\text{O-O})$ tends to decrease as $d(\text{P-O})_s$ increases in length, and *vice versa*. Nevertheless, this tendency is not as pronounced as the relationships between $\angle(\text{O-P-O})$ and $d(\text{P-O})_s$ or $d(\text{O-O})$ are. Otherwise the correlation coefficients for $d(\text{O-O})$ versus $d(\text{P-O})_s$ would be larger than observed. The data for the different correlations when plotted in Figs. 9, 10 and 11 separately for the orthophosphates and the condensed phosphates (excluding the tetrahedra with shared edges) show an appreciable scatter, which is most pronounced for the $d(\text{O-O})$ versus $d(\text{P-O})_s$ relationship. The $\log[\sin(\alpha/2)]$ versus $\log[d(\text{O-O})/2]$ plots indicate a slight deviation from linearity.

Prediction of O-P-O bond angles

Of all the angle relationships only one is of practical value: the $\log[\sin(\alpha/2)]$ versus $[d(\text{P-O})_s]$ relation, because it allows the prediction of $\angle(\text{O-P-O})$ for a known $d(\text{P-O})_s$, which in turn can be calculated from the bond strength distribution within the tetrahedron. The coefficients of Table 7 and a modification of equation (9) can be used for such calculations:

$$\angle(\text{O-P-O}) = 2 \arcsin(10^{a+b \log[d(\text{O-P})_s]}), \quad (11)$$

where $d(\text{P-O})_s$ is the normalized average of the two sides of the angle. Angles calculated with equation 11 agree for the data of Fig. 9(a) on average within 1.6° with the observed values, for the data of Fig. 9(b) within 1.8° . A detailed example is given later.

The corresponding relation derived from equation (10) is:

$$\angle(\text{O-P-O}) = 2 \arcsin(10^{a+b \log[d(\text{O-O})/2]}), \quad (12)$$

where $d(\text{O-O})$ is the normalized edge length. However, since there is no simple way to predict individual $d(\text{O-O})$ values in a distorted tetrahedron, this relationship is of limited practical value.

Tetrahedral edge lengths

The length of an edge O-O in a regular tetrahedron is $d(\text{O-O}) = 2(\frac{2}{3})^{1/2}d(\text{P-O})$. Drits (1971) has investigated a number of tetrahedral groups (mostly silicates) and found that the mean $d(\text{O-O})$ length in a distorted tetrahedron is related to the mean $d(\text{T-O})$ length by the relation

$$d(\text{O-O})_m = 2(\frac{2}{3})^{1/2}d(\text{T-O})_m, \quad (13)$$

where T is a tetrahedrally coordinated cation. If this relationship holds true it means that any edge shortening is compensated by the lengthening of another edge

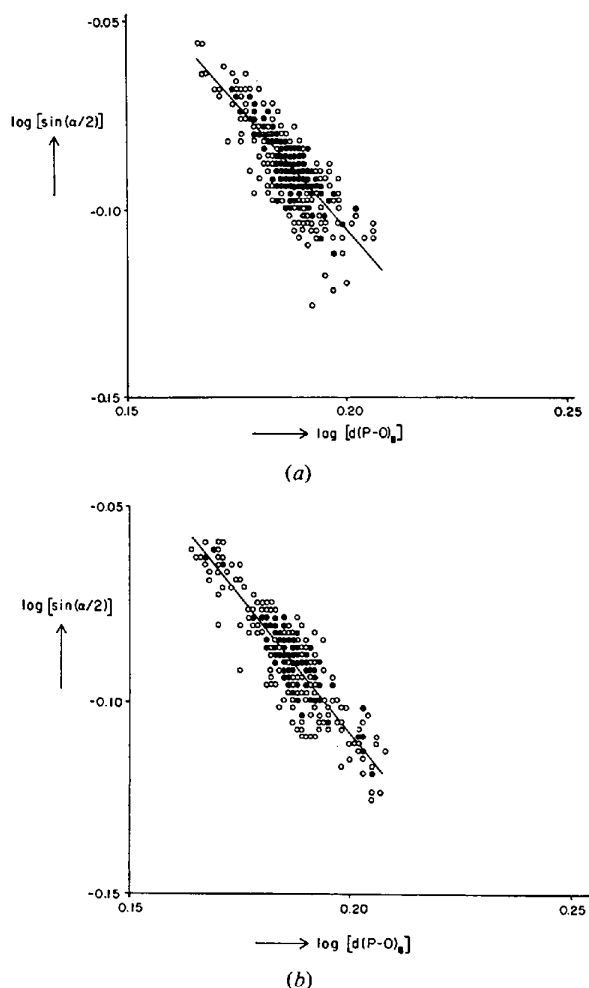


Fig. 9. Scatter diagram of $\log[\sin(\alpha/2)]$ versus $\log[d(\text{P-O})_s]$, phosphate groups without shared edges only [where $d(\text{P-O})_s$ is the normalized mean of the two sides of the angle, see Table 7]: (a) orthophosphates, including acid and organic phosphates; (b) condensed phosphates.

(or edges), so that the sum of the lengths of the edges remains constant for a given $d(\text{T-O})_m$ value. For the type of distortion of a tetrahedron illustrated in Fig. 1(a), however, this relationship cannot be strictly obeyed. Any movement of the central cation out of the centroid of the tetrahedron will increase $d(\text{T-O})_m$, while the $d(\text{O-O})$ values stay constant (by definition in this type of distortion). Therefore $d(\text{O-O})_m$ as calculated from equation (13) will be greater than the actual $d(\text{O-O})_m$. Similarly it can be shown (by considering the limiting cases) that any distortion of the type illustrated in Fig. 1(c), must result in a decrease of the sum of the lengths of the edges. Again this means that $d(\text{O-O})_m$ resulting from equation (13) will be greater than the observed $d(\text{O-O})_m$. For the type of distortion in which the angles O-P-O stay constant [Fig. 1(b)] equation (13) likewise does not hold true. However, in this case the calculated value of $d(\text{O-O})$ is smaller than

the observed value. Since this latter type of distortion (case III of Table 2) does not occur among the phosphate tetrahedra studied here, $d(\text{O-O})_m$ as calculated from equation (13) is always larger than the observed $d(\text{O-O})_m$. The values of $\Delta d(\text{O-O}) [=d(\text{O-O})_{m,\text{calc}} - d(\text{O-O})_{m,\text{obs}}]$ range from 0 to 0.015 Å (Table 15). Therefore, for all practical purposes equation (13) does not give an exact value but instead defines an upper limit for the average $d(\text{O-O})$ in a phosphate tetrahedron. The more distorted a tetrahedron the larger the discrepancy between the calculated and observed values. The correlation coefficient between $\Delta d(\text{O-O})$ and $\text{DI}(\text{TO})$ is 0.87 (Fig. 12), between $\Delta d(\text{O-O})$ and $\text{DI}(\text{OTO})$ it is 0.85 and between $\Delta d(\text{O-O})$ and $\text{DI}(\text{OO})$ it is 0.48. Based on the result of the least-squares regression analysis equation (13) should be superseded for phosphates by

$$d(\text{O-O})_m = 2\left(\frac{2}{3}\right)^{1/2} d(\text{P-O})_m - 0.21 \text{DI}(\text{TO}) \quad (14)$$

For the 211 phosphate tetrahedra the mean deviation between $d(\text{O-O})_m$ as observed and calculated from equation (14) is 0.001 Å, while the mean deviation is 0.004 Å from equation (13). Since the distortions in most other tetrahedral ions are similar to those in the phosphate groups insofar as case III distortions seem to be rare, it is likely that equation (14) is applicable to various tetrahedral groups, including the silicate tetrahedron.

Shared tetrahedral edges

The lengths of edges shared between different polyhedra in an ionic or partly ionic crystal structure are usually shorter than the edges which are not shared (Pauling, 1960; Baur, 1972). The phosphate groups are no exception to this rule. Of the 211 phosphate tetrahedra 35 share one edge with neighboring polyhedra, 17 share two edges, 13 three edges and one shares four edges. These 66 tetrahedra have 112 shared edges of an average length of 2.472 Å and a corresponding mean angle O-P-O of 107.1°. The 284 unshared edges in these 66 tetrahedra have a mean length of 2.526 Å and a corresponding mean angle O-P-O of 110.3°. The difference between shared and unshared edges is even more pronounced in the orthophosphates proper. Of the 64 orthophosphate tetrahedra 29 contain 63 shared edges with a mean $d(\text{O-O}) = 2.469$ Å [$\angle(\text{O-P-O}) = 106.3^\circ$] and the 111 unshared edges have a mean $d(\text{O-O}) = 2.536$ Å [$\angle(\text{O-P-O}) = 111.2^\circ$]. The larger the bond strength contributed by the central cation in a polyhedron which shares an edge with the phosphate tetrahedron, the shorter the shared edge tends to be. However, the scatter is too large for the trend to be useful for predictive purposes. That the effect is small can be seen from a comparison of the shared edges in LiMnPO_4 (52), $\text{Li}(\text{Fe}, \text{Mn})\text{PO}_4$ (73) and NaMnPO_4 (99) where the common edges with the polyhedra around the monovalent cations (0.17 v.u.) are on the average 0.04 Å longer than the shared edges with the polyhedra around the divalent cations (0.33 v.u.).

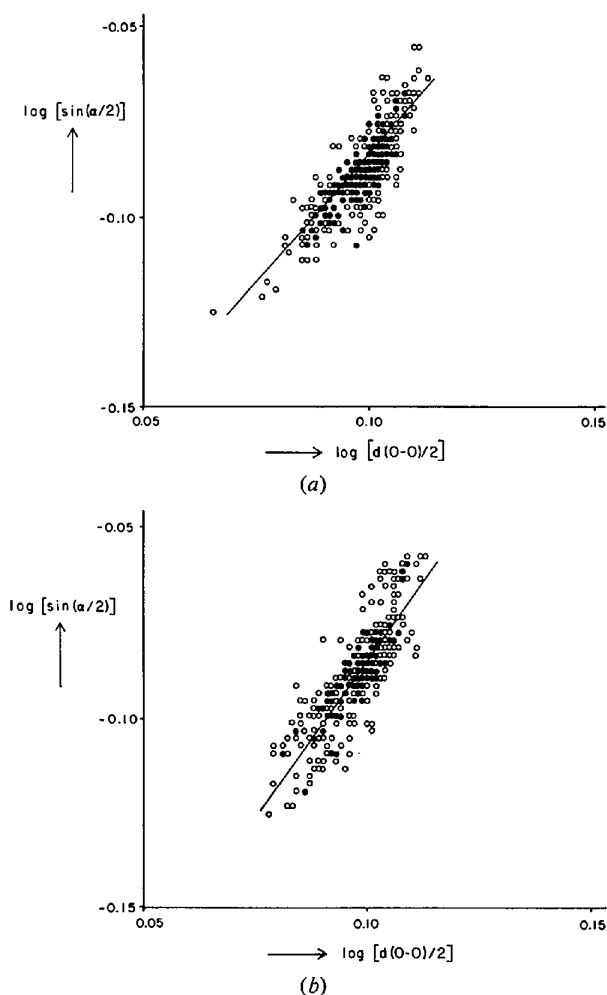


Fig. 10. Scatter diagram of $\log [\sin (\alpha / 2)]$ versus $\log [d(\text{O-O}) / 2]$, phosphate groups without shared edges only [where $d(\text{O-O})$ is the normalized length of the tetrahedral edge, see Table 7]: (a) orthophosphates, including acid and organic phosphates; (b) condensed phosphates.

Different tetrahedral groups show widely differing resistances to distortions caused by the shortening of shared edges. Comparisons of this kind are most reliable when isostructural compounds are compared because effects which are specific for a certain structure type remain constant in the series and cannot obscure the comparison. Of course the nature of the tetrahedral groups is not the only variable, since the sizes and charges of the other cations in an isostructural series can also vary. An inspection of Table 8 shows that the difference between the lengths of the shared and the unshared edges is about half as large for phosphate tetrahedra as it is for silicate tetrahedra. This means that phosphate groups are more rigid against distortions caused by shared edges than silicate groups. This greater flexibility of silicate tetrahedra is also evident from the large scatter of the $\log [\sin (\alpha/2)]$ versus $\log [d(\text{Si}-\text{O})]$ plots (Baur, 1970) in which the tetrahedra with shared edges were not separated from those without shared edges. For silicate tetrahedra one might expect an even greater difference in the bond-angle bond-length correlations for populations with and without shared edges than were found for the phosphates. Of the tetrahedral groups BeF_4 , BeO_4 , BO_4 , Cr^{5+}O_4 , AsO_4 and VO_4 , only BeF_4 is similar to PO_4 in its resistance to being distorted by the shortening of shared edges (Table 8). The differences in resistance seem to be related to differences in the cation-anion bond lengths and bond strengths.

Because the mean lengths $d(\text{O}-\text{O})$ in tetrahedra with a given constant $d(\text{P}-\text{O})$ tend to be approximately constant, the lengths of the shared and the unshared edges should depend on the number of the shared edges in the tetrahedra, provided that the amount of shortening of any shared edge relative to the unshared edges is more or less constant. This can be expressed as:

$$d(\text{O}-\text{O})_{m, \text{nsh}} = [6d(\text{O}-\text{O})_m + n_{\text{sh}}d]/6, \quad (15)$$

where $d(\text{O}-\text{O})_{m, \text{nsh}}$ is the mean length of the unshared edges, n_{sh} is the number of shared edges per tetra-

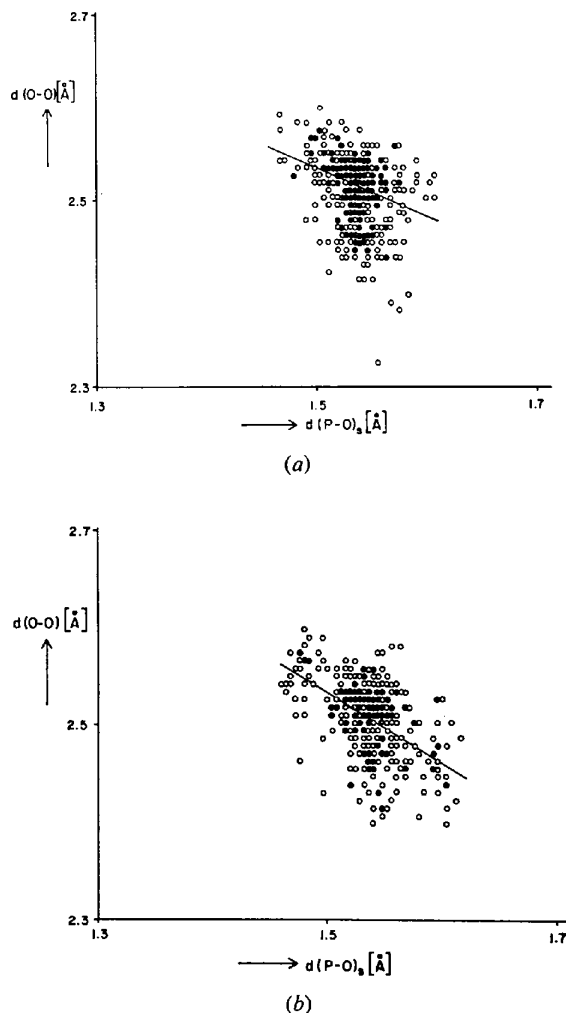


Fig. 11. Scatter diagram of $d(\text{O}-\text{O})$ versus $d(\text{P}-\text{O})_s$, phosphate groups without shared edges only (see Table 7): (a) orthophosphates, including acid and organic phosphates; (b) condensed phosphates.

Table 8. Difference (Δ) in the mean lengths of shared edges [$d(\text{O}-\text{O})_{\text{sh}}$] and unshared edges [$d(\text{O}-\text{O})_{\text{nsh}}$] for phosphates, silicates and several other tetrahedral groups of olivine, spodiosite and zircon types

The multiplicities are given in square brackets after the distances. The reference numbers refer to Table 16.

Compound	Structure type	Δ	Mean $d(\text{O}-\text{O})_{\text{sh}}$	Mean $d(\text{O}-\text{O})_{\text{nsh}}$	References
$\text{LiMn}[\text{PO}_4]$	olivine	0.105 Å	2.463 Å [3]	2.568 Å [3]	52
$\text{Li}(\text{Fe}, \text{Mn})[\text{PO}_4]$	olivine	0.105	2.466 [3]	2.571 [3]	73
$\text{NaMn}[\text{PO}_4]$	olivine	0.086	2.478 [3]	2.564 [3]	99
$\text{CaMg}[\text{SiO}_4]$	olivine	0.181	2.556 [3]	2.737 [3]	Onken (1965)
$(\text{Mg}, \text{Fe})_2[\text{SiO}_4]$	olivine	0.207	2.549 [3]	2.756 [3]	Hanke (1965)
$\text{Fe}_2[\text{SiO}_4]$	olivine	0.191	2.562 [3]	2.753 [3]	Hanke (1965)
$\text{Na}_2[\text{BeF}_4]$	olivine	0.080	2.490 [3]	2.570 [3]	Hanke (1965)
$\text{Al}_2[\text{BeO}_4]$	olivine	0.245	2.523 [3]	2.768 [3]	Farrell, Fang & Newnham (1963)
$\text{AlMg}[\text{BO}_4]$	olivine	0.144	2.349 [3]	2.493 [3]	Fang & Newnham (1965)
$\text{Ca}_2\text{Cl}[\text{PO}_4]$	spodiosite	0.096	2.484 [4]	2.580 [2]	128
$\text{Ca}_2\text{Cl}[\text{CrO}_4]$	spodiosite	0.236	2.693 [4]	2.929 [2]	128
$\text{Lu}[\text{PO}_4]$	zircon	0.166	2.391 [2]	2.557 [4]	129
$\text{Lu}[\text{AsO}_4]$	zircon	0.290	2.548 [2]	2.838 [4]	129
$\text{Y}[\text{VO}_4]$	zircon	0.247	2.637 [2]	2.884 [4]	129
$\text{Zr}[\text{SiO}_4]$	zircon	0.322	2.430 [2]	2.752 [4]	Robinson, Gibbs & Ribbe (1971)

hedron and Δ is the difference between the mean lengths of the unshared and the shared edges [$\Delta = d(\text{O-O})_{m, \text{nsh}} - d(\text{O-O})_{m, \text{sh}}$]. Because the influence of shared edges is dominant for the orthophosphates proper they have been selected for a test of equation (15) (see Table 9). It was assumed that $d(\text{O-O})_m$ is 2.512 Å, corresponding to the mean $d(\text{P-O})$ of 1.539 Å, and that Δ is 0.077 Å (2.536–2.469 Å, see above). The agreement is reasonable for $d(\text{O-O})_{m, \text{nsh}}$; however, the observed $d(\text{O-O})_{m, \text{sh}}$ display a smaller slope than the calculated values. This may mean that there is a lower limit for the shortening of shared edges in phosphate tetrahedra. As this limit is approached it becomes increasingly difficult to shorten the edges further, thus decreasing the rate at which $d(\text{O-O})_{m, \text{sh}}$ contracts with the diminishing number of shared edges.

Applications

The various correlations discussed above allow the prediction of all details of the shape of a phosphate tetrahedron based on the knowledge of the complete coordination and bond strength distribution of every individual oxygen atom within the PO_4 group. The example used here for a detailed calculation is the acid organic diphosphate group $-\text{CO}_3\text{P-O-PO}_3\text{H}_2$ in thiamine pyrophosphate hydrochloride (60). It contains a

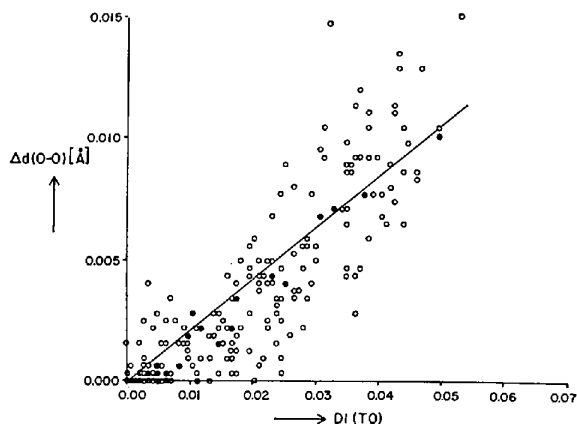


Fig. 12. Scatter diagram of $\Delta d(\text{O-O})$ versus $\text{DI}(\text{TO})$ (see text).

bridging oxygen atom bonded to two P atoms, as well as oxygen atoms bonded to carbon and to hydrogen. The estimated standard deviations of the P-O bond lengths are ± 0.002 Å. Therefore, the precision (and presumably the accuracy) of the crystal structure determination is so high that any deviations between observed and calculated distances and angles must be due to the shortcomings of the model used and cannot be blamed on errors in the observed data. All oxygen atoms in this $\text{CP}_2\text{O}_7\text{H}_2$ group are two-coordinated. The bond strengths contributed by the different neighbors vary from $\frac{1}{6}$ to $\frac{3}{4}$ and therefore the sums of the bond strengths, $p(\text{O})$, are as indicated in Table 10. These $p(\text{O})$ values are then used to calculate $\text{DI}(p\text{O})$ and to estimate the $\text{DI}(\text{TOSQ})$ values (see Table 6):

$$\text{DI}(\text{TOSQ}) = a + b\text{DI}(p\text{O}) \quad (16)$$

From the estimated $\text{DI}(\text{TOSQ})$ values and the mean coordination numbers, CN_m , the mean $d(\text{P-O})$ values can be calculated from equation (5). The predicted $d(\text{P-O})_m$ value for the tetrahedron around P(19) is 1.538 Å and for the tetrahedron around P(23) it is 1.529 Å. As can be seen both are in excellent agreement with the observed mean $d(\text{P-O})$ values (Tables 15 and 11). The bond strength variance $\Delta p(\text{O})$, derived from $p(\text{O})$ yields (equation (7), Table 6) the bond length variance, $\Delta d(\text{om})$. Using the calculated $d(\text{P-O})_m$, one arrives at the calculated individual $d(\text{P-O})$ values (Table 11). The calculated $d(\text{P-O})$ are then normalized

Table 10. Bond strength-calculation for the diphosphate group in thiamine pyrophosphate hydrochloride (60)

Covalently bonded hydrogen atoms are indicated under $\text{H}(d)$, hydrogen bonds accepted by the oxygen atoms are marked as $\text{H}(a)$. For P and C the donated bond strength is the formal charge divided by the coordination number. The bond strength of the hydrogen atom is divided in the ratio $\frac{1}{2}$ to $\frac{1}{2}$ between the donating oxygen atom and the hydrogen bond acceptor (Baur, 1970).

	P(19)	P(23)	C	H(d)	H(a)	$p(\text{O})$	
O(18)	4		$\frac{4}{4}$			2.250 v.u.	
O(20)						1.417	
O(21)					$\frac{1}{6}$	1.417	
O(22)					$\frac{1}{6}$	2.500	
O(24)		4		4		2.083	
O(25)						$\frac{1}{6}$	2.083
O(26)						$\frac{1}{6}$	1.417

Table 9. Orthophosphates proper, tetrahedra with shared edges: comparison of calculated and observed lengths of shared and unshared edges as a function of the number of shared edges according to equation (15) (see text)

The numbers in square brackets indicate how many tetrahedra were used in averaging.

n_{sh}	Calculated		Observed		#
	$d(\text{O-O})_{m, \text{sh}}$	n_{nsh}	$d(\text{O-O})_{m, \text{nsh}}$	$d(\text{O-O})_{m, \text{nsh}}$	
0	—	6	2.512 Å		
1	2.448 Å	5	2.525	2.458 Å	[8]
2	2.461	4	2.538	2.454	[9]
3	2.474	3	2.551	2.478	[11]
4	2.487	2	2.564	2.484	[11]
5	2.499	1	2.576		
6	2.512	0			

to a $d(\text{P-O})_m$ of 1.537 so that equation (11) can be applied, and the calculated $\angle(\text{O-P-O})$ are obtained with $a=0.180$ and $b=-1.44$ (Table 7, diphosphate, nsh). Now for every angle in the tetrahedron the lengths of both sides and the angles themselves are known, and the third sides of the triangles [the edges $d(\text{O-O})$] can

be calculated. The agreement between observed and calculated values is satisfactory (Table 11).

The input into such calculations consists only of the bond-strength distribution to the four oxygen atoms of the phosphate tetrahedron, which means that the $p(\text{O})$ values of the oxygen atoms must be known or

Table 11. *Diphosphate group in thiamine pyrophosphate hydrochloride (60), observed and predicted bond lengths $d(\text{P-O})$, bond angles $\angle(\text{O-P-O})$ and edges $d(\text{O-O})$*

Calculated = calc.; observed = obs.; normalized = norm.; the Δ_1 , Δ_2 and Δ_3 are the differences between the preceding observed and calculated values. For other explanations see text.

	$p(\text{O})$	$\Delta p(\text{O})$	Δd_{om} calc.	$d(\text{P-O})$ calc.	$d(\text{P-O})$ obs.	Δ_1
P(19)-O(20)	1.417 v.u.	-0.479 v.u.	-0.062 Å	1.476 Å	1.478 Å	0.002 Å
P(19)-O(21)	1.417	-0.479	-0.062	1.476	1.481	0.005
P(19)-O(18)	2.250	0.354	0.046	1.584	1.580	-0.004
P(19)-O(22)	2.500	0.604	0.079	1.617	1.602	-0.015
Mean	1.896			1.538	1.535	0.006
P(23)-O(26)	1.417	-0.604	-0.079	1.450	1.465	0.015
P(23)-O(25)	2.083	0.062	0.008	1.537	1.534	-0.003
P(23)-O(24)	2.083	0.062	0.008	1.537	1.537	0.000
P(23)-O(22)	2.500	0.479	0.062	1.591	1.584	-0.007
Mean	2.021			1.529	1.530	0.006

	$d(\text{P-O})_s$ norm.	$\angle(\text{O-P-O})$ calc.	$\angle(\text{O-P-O})$ obs.	Δ_2	$d(\text{O-O})$ calc.	$d(\text{O-O})$ obs.	Δ_3
O(20), O(21)	1.475 Å	119.7°	119.7°	0.0°	2.553 Å	2.559 Å	0.006 Å
O(20), O(18)	1.529	110.4	110.5	0.1	2.514	2.513	-0.001
O(20), O(22)	1.546	107.9	109.6	1.7	2.501	2.517	0.016
O(21), O(18)	1.529	110.4	107.2	-3.2	2.514	2.464	-0.050
O(21), O(22)	1.546	107.9	107.4	-0.5	2.501	2.485	-0.016
O(18), O(22)	1.600	100.6	100.8	0.2	2.462	2.452	-0.010
Mean	1.537	109.5	109.2	1.1	2.508	2.498	0.017
O(26), O(25)	1.502	114.8	113.5	-1.3	2.517	2.508	-0.009
O(26), O(24)	1.502	114.8	115.7	0.9	2.517	2.542	0.025
O(26), O(22)	1.529	110.4	112.0	1.6	2.499	2.529	0.030
O(25), O(24)	1.545	108.0	108.6	0.6	2.489	2.494	0.005
O(25), O(22)	1.572	104.2	103.0	-1.2	2.468	2.440	-0.028
O(24), O(22)	1.572	104.2	102.9	-1.3	2.468	2.442	-0.026
Mean	1.537	109.4	109.3	1.2	2.493	2.492	0.021

Table 12. *Average observed and calculated values for diphosphates (P_2O_7), ring-phosphates ($(\text{PO}_3)_n$) and chain-phosphates ($(\text{PO}_3)_\infty$)*

Only tetrahedra without shared edges were used. The number in square brackets in the heading shows how many tetrahedra were used in the averaging. The number in square brackets between the observed and calculated values indicates how many times the averaged values occur within a tetrahedron. Grand mean over tetrahedron = g.m.; bridging oxygen atom = O(b). Source of data is Table 15.

	P_2O_7 [30]		$(\text{PO}_3)_n$ [17]		$(\text{PO}_3)_\infty$ [11]	
	obs.	calc.	obs.	calc.	obs.	calc.
P-O(g.m.)	1.531 Å [4]	1.531 Å	1.544 Å [4]	1.543 Å	1.542 Å [4]	1.543 Å
O-O(g.m.)	2.497 [6]	2.487	2.512 [6]	2.519	2.510 [6]	2.519
O-P-O(g.m.)	109.4° [6]	108.7°	109.2° [6]	109.6°	109.2° [6]	109.6°
CN_m	2.43 [4]		2.79 [4]		2.75 [4]	
$p(\text{O})$ (g.m.)	2.050 v.u. [4]		2.118 v.u. [4]		2.134 v.u. [4]	
$p(\text{O})$	1.898 [3]		1.685 [2]		1.728 [2]	
$p[\text{O}(b)]$	2.506 [1]		2.551 [2]		2.540 [2]	
P-O	1.513 Å [3]	1.511 Å	1.480 Å [2]	1.487 Å	1.489 Å [2]	1.488 Å
P-O(b)	1.584 [1]	1.590	1.608 [2]	1.599	1.594 [2]	1.593
O-O	2.511 [3]	2.494	2.564 [1]	2.554	2.570 [1]	2.559
O-O(b)	2.483 [3]	2.480	2.508 [4]	2.521	2.509 [4]	2.517
O(b)-O(b)			2.477 [1]	2.475	2.455 [1]	2.475
O-P-O	112.2° [3]	111.2°	120.1° [1]	118.4°	119.4° [1]	118.6°
O-P-O(b)	106.6 [3]	106.2	108.5 [4]	109.5	108.8 [4]	109.5
O(b)-P-O(b)			100.9 [1]	101.4	100.6 [1]	101.9

Table 13. Averaged observed and calculated values for acid phosphate groups

Oxygen atoms to which a hydrogen atom is covalently bonded = O(h); oxygen atom participating in a symmetrical hydrogen bond = O(h/2); for other explanations see Table 12. Source of data see Table 15: HPO₄ (151, 191, 192, 193, 351, 461, 531, 801, 841); H₂PO₄ (171, 181, 591, 592, 632, 701, 751, 811, 821, 1071, 1221); H_{2.5}PO₄ (401, 402, 781); H₃PO₄ (11, 161, 162, 611, 612).

	HPO ₄ [9]		H ₂ PO ₄ [12]		H _{2.5} PO ₄ [3]		H ₃ PO ₄ [5]	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
P-O(g.m.)	1-539 Å	1-541 Å	1-536 Å	1-540 Å	1-531 Å	1-538 Å	1-533 Å	1-530 Å
O-O(g.m.)	2-511	2-518	2-506	2-517	2-499	2-513	2-501	2-501
O-P-O(g.m.)	109-4°	109-6°	109-4°	109-7°	109-4°	109-6°	109-4°	109-7°
CN _m	3-42		2-94		3-17		2-40	
P(O) (g.m.)	1-879v.u.		1-919v.u.		1-986v.u.		1-984v.u.	
P(O)	1-769		1-639		1-713		1-583	
P(O)(h)	2-208		2-198		2-157		2-117	
P(O)(h/2)					1-917			
P-O	1-522 Å	1-527 Å	1-503 Å	1-504 Å	1-500 Å	1-503 Å	1-491 Å	1-478 Å
P-O(h)	1-590	1-584	1-569	1-576	1-555	1-560	1-547	1-547
P-O(h/2)					1-516	1-529		
O-O	2-523	2-527	2-539	2-539	2-504	2-516	2-519	2-511
O-O(h)	2-500	2-509	2-497	2-517	2-528	2-527	2-483	2-490
O-O(h/2)					2-503	2-500		
O(h)-O(h)			2-506	2-495	2-477	2-508		
O(h)-O(h/2)								
O-P-O	111-9°	111-7°	115-3°	115-1°	110-2°	110-5°	111-9°	112-2°
O-P-O(h)	106-9	107-5	108-7	109-6	113-9	112-9	106-8	107-2
O-P-O(h/2)					107-2	106-5		
O(h)-P-O(h)			106-1	104-7	107-6	108-6		
O(h)-P-O(h/2)								

Table 14. Averaged observed and calculated values for organic phosphate groups

Oxygen atom to which a carbon atom is bonded = O(c); for other explanations see Tables 12 and 13. Source of data Table 15: CPO₄H (621, 631, 861, 901, 951, 1091, 1131, 1141, 1181, 1211, 1212); CPO₄ (741, 761, 891, 911); C₂PO₄ (871, 1041, 1042, 1061, 1062, 1101, 1121); C₃PO₄ (381, 961, 981, 1031).

	CPO ₄ H[11]		CPO ₄ [4]		C ₂ PO ₄ [7]		C ₃ PO ₄ [4]	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
P-O(g.m.)	1-540 Å	1-538 Å	1-532 Å	1-545 Å	1-541 Å	1-536 Å	1-536 Å	1-533 Å
O-O(g.m.)	2-510	2-505	2-498	2-517	2-509	2-503	2-498	2-498
O-P-O(g.m.)	109-3°	109-1°	109-4°	109-2°	109-3°	109-2°	109-2°	109-4°
CN _m	2-71		3-56		2-29		1-75	
P(O) (g.m.)	1-935v.u.		1-928v.u.		1-921v.u.		2-125v.u.	
P(O)	1-628		1-774		1-544		1-250	
P(O)(c)	2-326		2-390		2-298		2-417	
P(O)(h)	2-159							
P-O	1-496 Å	1-498 Å	1-508 Å	1-525 Å	1-482 Å	1-487 Å	1-437 Å	1-419 Å
P-O(c)	1-603	1-589	1-606	1-605	1-599	1-585	1-570	1-571
P-O(h)	1-564	1-567						
O-O	2-549	2-528	2-512	2-528	2-568	2-530	2-540	2-520
O-O(c)	2-510	2-502	2-484	2-506	2-495	2-503		
O-O(h)	2-503	2-507			2-503	2-476		
O(c)-O(c)								
O(c)-O(h)	2-504	2-483						
O-P-O	116-9°	115-1°	112-9°	112-0	120-0°	116-6°		
O-P-O(c)	107-3	108-2	105-8	106-4	108-1	109-1	115-3°	114-8°
O-P-O(h)	109-7	109-8						
O(c)-P-O(c)								
O(c)-P-O(h)	104-5	103-8	103-0	102-7	103-0	102-7	103-1	104-0

assumed. This information necessarily includes the knowledge of the coordination numbers of these oxygen atoms. The result is a complete geometrical description of the tetrahedral shape, which includes all distances and angles within the phosphate group.

Analogous predictions of the shapes of tetrahedral groups are presented in Tables 12, 13 and 14 but in these cases the calculations refer to averaged groups. The bond strengths $p(O)$, $p(O(b))$, $p(O(c))$ etc. and the CN_m values have been averaged for every kind of the 11 different phosphate tetrahedra and used as input for the calculations. Mean deviations between observed and calculated values are 0.006 Å for $d(P-O)$, 0.013 Å for $d(O-O)$ and 0.9° for $\angle(O-P-O)$, 0.004 Å for $d(P-O)$ (g.m.), 0.008 Å for $d(O-O)$ (g.m.) and 0.3° for $\angle(O-P-O)$ (g.m.). The greatest discrepancy was ob-

tained for the CPO₄ group where the calculated mean P-O distance is 0.013 Å longer than the observed $d(P-O)$ (g.m.). Tables 12, 13 and 14 are also useful because of the mean observed values listed there for the different phosphate groups. These values can be employed for comparative purposes: for instance when a new structure is determined and it has to be decided whether or not a particular phosphate tetrahedron has OH groups.

The calculated tetrahedral shapes can be of value as input to the computer simulation of crystal structures. A case in point is the solution of the superstructure of cubic SiP₂O₇. The substructure of this compound ($a=7.47$ Å) had been known for a long time (Levi & Peyronel, 1935). The superstructure ($a=22.42$ Å) has a volume 27 times as large as the substructure

Table 15. Phosphate tetrahedra: interatomic distances, bond angles, bond strengths, coordination numbers, distortion indices and e.s.d.'s

i (a) Orthophosphates proper

21	Y-01	T-02	O-T-0	O-O-SH	PH01	H	261	T-01	T-02	O-T-0	O-O-SH	PH01	H	422	T-01	T-02	O-T-0	O-O-SH	PH01	H	563	T-01	T-02	O-T-0	O-O-SH	PH01	H	941	T-01	T-02	O-T-0	O-O-SH	PH01	H	
1.518	1.526	113.2	2.530	0.1913	1.2	1.517	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.518	1.528	110.7	2.480	0.1917	1.2	1.518	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.518	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.518	1.528	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.478	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.531	109.6	2.487	0.1750	3.1	1.533	1.534	109.9	2.511	0.1917	1.2	1.526	1.529	110.6	2.512	0.1783	0.3	1.536	1.536	110.6	2.517	0.2083	0.3	1.522	1.526	110.6	2.508	0.1917	1.2
1.528	1.531	108.6	2.480	0.1917	1.2	1.512	1.																												

Table 15 (cont.)

i (b) Acid orthophosphates

Table with multiple columns of numerical data, organized into groups labeled 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.

i (c) Organic phosphates

Table with multiple columns of numerical data, organized into groups labeled 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.

and was solved by first predicting all 173 individual P-O, Si-O and O-O distances by employing, *inter alia*, relations as outlined in a paper. Then the predicted distances were treated as observations in a distance least-squares refinement in which the 134 positional coordinates of the 50 atoms in the asymmetric unit were varied until the calculated distances fitted the predicted distances. A conventional structure-factor calculation gave an R value of 0.18 (1382 F_obs) for the predicted superstructure and was refined subsequently to 0.06 after three least-squares cycles (Tillmanns, Gebert & Baur, 1973).

phosphate tetrahedra in the other populations and because the various correlations are best displayed for large distortions. The best opportunity for the calculation of orthophosphate tetrahedra is given for those that have shared edges with other polyhedra in the crystal structure, in this case equatorial (14) and (15) can be used to calculate the lengths of the edges. The angles O-P-O can then be deduced from the triangle P-O(1), P-O(2) and O(1)-O(2). However, it has to be kept in mind that the lengths of the shared and unshared edges in coordination polyhedra depend also on packing considerations within a crystal structure. Many distortions can be viewed as a consequence of the geometric adjustments of the polyhedra to each other. The distances and angles are strained in response

Table 15 (cont.)

ii (a) Diphosphates

Table of crystallographic data for diphosphates, including columns for unit cell parameters (a, b, c, alpha, beta, gamma), space group, and various distortion indices (T-01 to T-102).

ii (b) Ring phosphates

Table of crystallographic data for ring phosphates, including columns for unit cell parameters (a, b, c, alpha, beta, gamma), space group, and various distortion indices (T-01 to T-102).

ii (c) Polyphosphates

Table of crystallographic data for polyphosphates, including columns for unit cell parameters (a, b, c, alpha, beta, gamma), space group, and various distortion indices (T-01 to T-102).

to adjustment stresses. Such phenomena have been discussed at some length previously for the case of the Mg_2SiO_4 polymorphs (Baur, 1972).

Conclusion

The approach outlined above is strictly empirical. It describes the various populations of phosphate tetrahedra and relates the variations in shape and size to (1) variations in bond strengths received by the individual oxygen atoms, (2) the shortening of shared edges, (3) the distortion indices, (4) the mean coordination numbers, and (5) geometrical relationships between angles and interatomic distances. The correlations between many of the variables are strong enough to be useful for predictive purposes.

It is possible to calculate the mean P–O distance in the phosphate group from a knowledge of the coordination numbers and the distortion indices [equations (5) and (16)]. The individual P–O distances are obtained from the bond strength distribution [equation (7)]. Then the bond angles O–P–O are estimated from the normalized bond lengths [equation (11)]. The O–O distances opposite the angles O–P–O are herewith determined because three parts of the triangle OPO are known. In addition the mean O–O distance in a phosphate tetrahedron can be obtained as a function of the mean P–O distance and a distortion index [equation (14)]. Furthermore, the lengths of the shared and the unshared edges can be estimated because they depend on the number of shared edges per tetrahedron [equation (15)].

The calculated shapes of the phosphate tetrahedra can be of value for the computer simulation of crystal structures. Another possible application is in the interpretation of known structures. When observed and predicted values disagree this could be a starting point for further fruitful investigations. It should be of interest to extend analogous studies to other tetrahedral anions as well as to other types of polyhedra (octahedra, etc.).

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APPENDIX

The dimensions of the 211 phosphate tetrahedra used in this study are listed in Table 15, subdivided into

the six populations described above. The number at the top left of every small table (which contains information on one tetrahedron) refers within its first three places to the literature listed in Table 16. The last digit is a consecutive numbering of the tetrahedra within each crystal structure. Each line contains the lengths (Å) of the two sides T–O1 and T–O2 of an angle, the angle O–T–O (°), the corresponding edge length O–O (Å) and in column SH a '0' if the edge is not shared, or a '1' if it is shared with neighboring polyhedra. The mean $d(\text{P–O})$, $\angle(\text{O–P–O})$ and $d(\text{O–O})$ values are listed in columns 1, 3 and 4 of line 7. The bond strengths [$p(\text{O})$] and coordination numbers (H and C) are given in a sequence corresponding to the oxygen atoms of T–O1 (line 1), T–O2 (line 1), T–O2 (line 2) and T–O2 (line 3). The average $p(\text{O})$ is listed in column 2 of line 7. The 9 two digit numbers in the lower right hand corner are, line 5: DI(TO), DI(OTO), DI(OO) (all $\times 10^3$); line 6: mean estimated standard deviation of $d(\text{P–O})$ (Å, $\times 10^3$), mean e.s.d. $\angle(\text{O–P–O})$ (°, $\times 10$), mean e.s.d. $d(\text{O–O})$ (Å, $\times 10^3$); line 7: $\Delta d(\text{O–O})$ (difference between observed $d(\text{O–O})$ and calculated according to equation (13), in Å, $\times 10^3$), DI($p(\text{O})$) ($\times 10^2$), DI(TOSQ) ($\times 10^3$). Any values used above for the various correlations can be easily calculated from these numbers. Table 16 contains the chemical formulas and the references to the structural data in a highly abbreviated form. The abbreviations used for the journal names are explained at the bottom of Table 16. In case of multiple authorship only the first author is listed.

All calculations were performed on an IBM 370/155 using the computer program *PEANUTS* written by the author. The program processes the tetrahedral data, calculates a variety of statistical information, computes the coefficients of the regressions and displays scatter diagrams as printer plots. In all linear regressions calculated here the data were weighted with the inverse squares of the estimated standard deviations of the dependent variable. Since it is unlikely that the accuracy of modern crystal structure determinations matches their precision, the weighting was modified by increasing the estimated standard deviations of $d(\text{P–O})$ to 0.005 Å and of $\angle(\text{O–P–O})$ to 0.3° if the reported values were smaller.

For the calculation of correlation coefficients (r) and coefficients of the regression equation (a, b) it is necessary to evaluate the sum of the squares of the deviation from the mean for both the independent variable (x) and the dependent variable (y). This can be calculated either as $\sum(x_i - x_m)^2$ or as $\sum x_i^2 - (\sum x_i)^2/n$ (Brownlee, 1965). The first formula has the disadvantage that the mean value of x (and y) has to be calculated beforehand. The second formula requires only one pass, but has a disadvantage in that the difference of two numbers must be taken. In some case these numbers may be numerically almost equal and considerable loss in accuracy can result for r , a and b . This is particularly true when the calculation is performed in single precision on a computer which has

only 24 bits in the mantissa of its floating-point word. The use of double precision arithmetic lessens the problem although it does not eliminate it. The subroutine used in *PEANUTS* therefore employs the first formula. Special care has to be taken when canned programs are used. Some of the original regression calculations

for this work used the 'Statistical Package for the Social Sciences' (Nie, Bent & Dale, 1970). This program is designed throughout for a one-pass calculation. Since the current version computes the Pearson correlation in single precision, inaccurate results were originally obtained.

Table 16. *Chemical formulas and references to phosphate crystal structures*

1 H_3PO_4	Cole, ACAAS, 66 (1964) and UD, PC	66 $Na_4P_4O_{12} \cdot 4H_2O$ (tricl)	Ondik, AC, 17, 1159 (1964)
2 $Al_3(P_3O_4)_2(OH)_3 \cdot 5H_2O$	Araki, ZK, 127, 21 (1968)	67 Li_3PO_4	Keffler, IC, 6, 119 (1967)
3 $Al_2PO_4(OH)_3$	Araki, AM, 53, 1096 (1968)	68 $B-Cu_2P_2O_7$	Robertson, CJC, 46, 605 (1968)
4 $\alpha-Ca_2P_2O_7$	Calvo, IC, 2, 1345 (1968)	69 $\alpha-Cu_2P_2O_7$	Robertson, AC, 22, 665 (1967)
5 $\alpha-Mg_2P_2O_7$	Calvo, AC, 23, 289 (1967)	70 $Ca(H_2PO_4)_2 \cdot H_2O$	Dickens, AC, B27, 2247 (1971)
6 $(NH_4)_4P_4O_{12}$	Koster, JCSA, 435 (1970)	71 $Li_3P_3O_9 \cdot 3H_2O$	Masse, CSC, 1, 259 (1972)
7 $B-Ca_2P_2O_7$	Webb, AC, 21, 942 (1966)	72 P_4O_8	Begley, TFS, 65, 1219 (1969)
8 $(Mn, Fe)_2PO_4OH$	Waldrop, ZK, 131, 1 (1970)	73 $Li(Fe, Mn)PO_4$	Finger, CIY, 68, 290 (1970) and UD, PC
9 $Zn_3(P_3O_4)_2 \cdot 4H_2O$	Chao, ZK, 130, 261 (1969)	74 $C_{10}H_{12}N_2O_4PO_4 \cdot Na \cdot 8H_2O$	Rao, JACS, 21, 1210 (1969)
10 $Na_3H_3(PO_4)_4$	Jost, AC, B24, 992 (1968)	75 $C_6H_9N_3O_7 \cdot H_3PO_4 \cdot H_2O$	Freeman, AC, B28, 2906 (1972)
11 $(Ca, Sr, Ba)_2PO_4(OH)$	Calleri, AC, 17, 1097 (1964)	76 $(NH_4)_2CH_3PO_4 \cdot 2H_2O$	Garbassi, AC, B28, 1665 (1972)
12 $LiK_2P_3O_9 \cdot H_2O$	Eanes, AC, 15, 1280 (1962)	77 $(Fe, Mn)_3(PO_4)_2$	Moore, AM, 57, 24 (1972)
13 $Na_4P_2O_7 \cdot 10H_2O$	McDonald, AC, 22, 43 (1967)	78 $(NH_4)_2CO_3 \cdot H_3PO_4$	Kostansek, AC, B28, 2454 (1972)
14 $Na_4P_2O_7 \cdot 4H_2O$ (monoc)	Ondik, AC, 14, 555 (1961)	79 $C_6H_5PO_4$	Boer, AC, B28, 1201 (1972)
15 $MgHPO_4 \cdot 3H_2O$	Sutor, AC, 23, 418 (1967)	80 $Mn_6(H_2O)_4(PO_4OH)_2(PO_4)_2$	Moore, AM, 58, 302 (1973)
16 $H_3PO_4 \cdot 1/2H_2O$	Nighell, AC, B25, 776 (1969)	81 $C_6H_5O_2N_4 \cdot H_2PO_4 \cdot H_2O$	Saenger, AC, B28, 2237 (1972)
17 $N_4H_5H_2PO_4$	Liminga, ACS, 19, 1629 (1965)	82 KH_2PO_4 , LT	Bacon, PRSLA, 230, 359 (1955)
18 $N_2H_6(H_2PO_4)_2$	Liminga, ACS, 20, 2483 (1966)	83 $AlPO_4$	Schwarzenbach, ZK, 123, 161 (1966)
19 $C_7H_9N_3 \cdot 3/2H_3PO_4 \cdot 5H_2O$	Huse, AC, B25, 498 (1969)	84 $C_{10}H_{30}N_4 \cdot 2(HPO_4) \cdot 6H_2O$	Iitaka, AC, 18, 110 (1965)
20 $Mg_3(PO_4)_2$	Nord, ACS, 22, 1466 (1968)	85 $KAlP_2O_7$	Ng, UD, PC (1975)
21 $Fe^{3+}Fe^{2+}(OH)_5(PO_4)_4 \cdot 6H_2O$	Fanfani, AC, 22, 173 (1967)	86 $C_7H_5NO_7PO_4$	Sundaralingam, AC, B26, 790 (1970)
22 $K_2Fe_2(PO_4)_3$	Sljukic, ZK, 130, 148 (1969)	87 $AgPO_4(OC_2H_5)_2$	Hazel, AC, B28, 2951 (1972)
23 $(Mn, Fe)_2PO_4F$	Waldrop, ZK, 130, 1 (1969)	88 $KTi_2(PO_4)_3$	Masse, BSFMC, 95, 47 (1972)
24 $Al_2PO_4F \cdot OH \cdot 7H_2O$	Guy, AM, 51, 1579 (1966)	89 $C_9H_{11}N_2O_5PO_4 \cdot 2Na \cdot 4H_2O$	Viswanitra, AC, B28, 1108 (1972)
25 $\alpha-2n_2P_2O_7$	Robertson, JSSC, 1, 120 (1970)	90 $C_{10}H_{12}N_2O_5PO_4 \cdot 2H_2O$	Sundaralingam, AC, 21, 495 (1966)
26 $Na_3PO_4 \cdot (NaOH)_x \cdot 12H_2O$	Tillmanns, AC, B27, 2124 (1971)	91 $C_{10}H_{13}N_2O_5PO_4 \cdot Ca \cdot 6H_2O$	Trueblood, AC, 14, 965 (1961)
27 $SiP_2O_7 \cdot Al$	Tillmanns, JSSC, 2, (1975)	92 $Mn_3(OH)_2B(OH)_2PO_4$	Moore, AM, 56, 1527 (1971)
28 $SiP_2O_7 \cdot AlIII$	Bissert, AC, B26, 233 (1970)	93 $K_2Fe_4(OH)_2(H_2O)_2(PO_4)_4 \cdot 2H_2O$	Moore, AM, 57, 397 (1972)
29 $Fe_3(PO_4)_2 \cdot 4H_2O$, RT	Abrahams, JCP, 44, 2223 (1966)	94 $NaMnFe_2(PO_4)_3$	Moore, AM, 56, 1955 (1971)
30 $Fe_3(PO_4)_2 \cdot 4H_2O$, LT	Abrahams, JCP, 44, 2230 (1966)	95 $C_7H_5NPO_4$	Kraut, AC, 14, 1146 (1961)
31 $(NH_4)_3PO_4 \cdot 3H_2O$	Mootz, AC, B26, 1826 (1970)	96 $C_8H_{15}O_3PO$	Svetich, AC, 19, 645 (1965)
32 Mn_2PO_4F	Rea, AC, B28, 2525 (1972)	97 $C_8H_9NPO_4 \cdot H_2O$	Putkey, AC, B26, 782 (1970)
33 Mn_2PO_4Cl	Rea, AC, B28, 2505 (1972)	98 $C_7H_7PO_4$	Newton, JACS, 88, 1503 (1966)
34 $CuH_2(PO_3)_4$	Laügt, AC, B28, 2721 (1972)	99 Na_2NPO_4	Moore, AM, 57, 1353 (1972)
35 $(NH_4)_2H_2PO_4$	Khan, AC, B28, 2065 (1972)	100 $Na_3P_3O_9$	Ondik, AC, 18, 226 (1965)
36 $MgNH_4PO_4 \cdot 6H_2O$	Whitaker, AC, B26, 1429 (1970)	101 $Na_3P_3O_9 \cdot H_2O$	Ondik, AC, 18, 226 (1965)
37 $Ca_2Mn(PO_4)_2 \cdot 2H_2O$	Fanfani, AC, B26, 640 (1970)	102 $\alpha-Sr_2P_2O_7$	Grenier, BSFMC, 92, 91 (1969)
38 $(C_6H_5N_2O_3)_3PO_4$	Mazar-ul-Haque, AC, B26, 1528 (1970)	103 $C_7H_5PO_4$	Steitz, JACS, 87, 2488 (1965)
39 $Na_2H_2P_2O_7 \cdot 6H_2O$	Collin, AC, B27, 291 (1971)	104 $N(C_2H_5)_3 \cdot C_9H_{10}N_2O_4PO_4$	Coulter, AC, B25, 2055 (1969)
40 $KH_2(PO_4)_2$	Philippot, ACS, 25, 512 (1971)	105 $Cu_2P_4O_{12}$	Laügt, AC, B28, 201 (1972)
41 Mg_2PO_4F	Coda, AANLR, 43, 212 (1967)	106 $C_8H_{20}NO_2PO_4$	Abrahamson, AC, 21, 79 (1966)
42 $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$	Cid - Dresdner, ZK, 121, 87 (1965)	107 $Ca(H_2PO_4)_2$	Dickens, UD, PC (1973)
43 $Na_4NH_3P_5O_{15}$	Joet, AC, B28, 732 (1972)	108 $Mn_2(PO_4)_3Cl$	Engel, UD (1973)
44 $Na_6P_4O_{18} \cdot 6H_2O$	McAdam, AC, B28, 2740 (1972)	109 $C_{10}H_{14}N_2O_5PO_4 \cdot H_2O$	Kraut, AC, 16, 79 (1963)
45 $Ca_2(PO_4)_3Cl$	Mackie, AC, B28, 1840 (1972)	110 $C_{10}H_{12}N_2O_5PO_4 \cdot 8H_2O$	Sheffer, AC, B25, 895 (1969)
46 $CaHPO_4$	Dickens, AC, B28, 797 (1971)	111 $Na_6F(OH)_2 \cdot 18NaH_2O \cdot (PO_4)_2$	Tillmanns, NW, 57, 242 (1970) and UD
47 $FePO_4 \cdot 2H_2O$	Fanfani, AANLR, 40, 880 (1966)	112 $C_{25}H_{29}N_4O_6PO_4$	Sax, AC, B26, 114 (1970)
48 $(AlPO_4OH)_2 \cdot 2Fe(OH)_2$	Baur, NW, 54, 561 (1967) and UD	113 $C_{10}H_{14}N_2O_5PO_4 \cdot 3H_2O$	Murayama, AC, B25, 2236 (1969)
49 $FeAl_2(PO_4)_2(OH)_2 \cdot 6H_2O$	Baur, AM, 53, 1025 (1968) and UD	114 $C_9H_{14}N_3O_4PO_4$	Bugg, JMB, 25, 67 (1967)
50 $MnFe_2(PO_4)_2(OH)_2 \cdot 8H_2O$	Baur, AM, 54, 1312 (1969)	115 $MoOPO_4$	Kierkegaard, ACS, 24, 427 (1970)
51 $FeAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$	Baur, NJMM, 430 (1969)	116 $\beta-Na_2P_2O_7$	Calvo, CJC, 43, 1147 (1965)
52 $LiMnPO_4$	Geller, AC, 13, 325 (1960)	117 $Na_4P_2O_7$	Leung, CJC, 50, 2519 (1972)
53 $Na_2HPO_4 \cdot 7H_2O$	Baur, AC, B26, 1584 (1970)	118 $C_{10}H_{13}N_2O_5PO_4 \cdot Na \cdot 6H_2O$	Reddy, CSC, 2, 9 (1973)
54 $Ca_4Mg_5(PO_4)_6$	Dickens, TMPM, 16, 79 (1971)	119 $\alpha-2n_3(PO_4)_2$	Calvo, UD, PC (1973)
55 $Ba_2K(PO_3)_5$	Martin, CSC, 1, 349 (1972)	120 $(C_6H_5CH_2)_2PO_4H$	Dunitz, AC, 9, 327 (1956)
56 $CuLi(PO_3)_3$	Laügt, AC, B28, 2352 (1972)	121 $Ca(C_{10}H_7HPO_4)_2 \cdot 3H_2O$	Li, AC, 19, 637 (1965)
57 $BaNaP_3O_9$	Martin, AC, B28, 2348 (1972)	122 $C_6H_4N_4O_2 \cdot H_3PO_4 \cdot H_2O$	Aoki, AC, B27, 11 (1971)
58 $Cd_2P_2O_7$	Calvo, CJC, 47, 3409 (1969)	123 $Sr_5(PO_4)_3OH$	Sundarsanan, AC, B28, 3688 (1972)
59 $C_5H_{11}N_3(H_2PO_4)_2 \cdot H_2O$	Veidis, JCSA, 2660 (1969)	124 $Ge_2O(PO_4)_6$	Mayer, MC, 103, 1560 (1972)
60 $C_{12}H_{19}Cl_4N_4P_2O_7S$	Pietgher, JACS, 94, 3998 (1972)	125 $Mg_2(PO_4)Cl$	Rea, AC, B28, 3461 (1972)
61 $CH_3COOH \cdot H_3PO_4$	Jönsson, ACS, 26, 1599 (1972)	126 $\beta-Mg_2P_2O_7$	Calvo, CJC, 43, 1139 (1965)
62 $CaH_4N_8O_7PO_4$	Sundaralingam, JMB, 13, 914 (1965)	127 $\alpha-Co_2P_2O_7$	Krishnamachari, AC, B28, 2883 (1972)
63 $C_2H_4N_4SPO_4H \cdot H_2PO_4 \cdot 3H_2O$	Karle, AC, 20, 118 (1966)	128 Ca_2PO_4Cl	Greenblatt, AC, 23, 166 (1967)
64 $NaPO_3$	McAdam, AC, B24, 1621 (1968)	129 $LuPO_4$	Lohmüller, AC, B29, 141 (1973)
65 $RbPO_3$	Cruickshank, AC, 17, 681 (1964)		

AANLR Atti Acc. Naz. Lincei, Rend.
AC Acta Crystallographica
ACAAS American Crystallographic Association Abstracts
ACS Acta Chemica Scandinavica
AM American Mineralogist
BSFMC Bulletin Societe Franc. Min. Crist.
CIY Carnegie Institution Yearbook
CJC Canadian Journal Chemistry
CSC Crystal Structure Communications
IC Inorganic Chemistry
JACS Journal American Chemical Society
JCP Journal Chemical Physics

JCSA Journal Chemical Society (A)
JMB Journal Molecular Biology
JSSC Journal Solid State Chemistry
NJMM Neues Jahrbuch Mineralogie, Monatshefte
NW Naturwissenschaften
MC Monatshefte für Chemie
PC Private Communication
PRSLA Proceedings Royal Society London (A)
TFS Transactions Faraday Society
TMPM Tschermarks Mineralogisch Petrographische Mitteilungen
UD Unpublished Data
ZK Zeitschrift für Kristallographie

Glossary

$p(X), p(O)$	Sum of bond strengths received by an anion X (or oxygen atom O) according to the electrostatic valence rule (Pauling, 1960; Baur, 1970). The bond strength given by a cation to an anion is the formal charge of the cation divided by its coordination number. It corresponds approximately (with a change in sign) to the formal charge of the anion (Pauling's postulate).	α	Distorted, nonideal angles $\angle(X-A-X)$ or $\angle(O-T-O)$.
$p(X)_m, p(O)_m$	Mean $p(X)$ or $p(O)$ of all anions in a given coordination polyhedron around a cation.	β	Ideal angles $\angle(X-A-X)$ or $\angle(O-T-O)$ in undistorted regular or idealized polyhedra.
$\Delta p(X), \Delta p(O)$	Bond strength variation: difference between the $p(X)$ or $p(O)$ of one individual anion in a coordination polyhedron around a cation and the mean value [$=p(X)-p(X)_m$].	a	Intercept of the linear regression equation.
m (as lower index)	Denotes the mean taken over all values in a given coordination polyhedron.	b	Slope of the regression equation.
v.u.	Valence units, measure of $p(X)$ in units of the formal charge.	r	Correlation coefficient.
$d(T-O)$	Distance from a cation T to an oxygen atom in a tetrahedral coordination TO_4 (where T can be P, Si, etc.).	CN	Coordination number.
$d(A-X)$	Distance from a cation A to an anion X in any coordination AX_n .	DI(TO), DI(OTO) DI(OO), DI(ρ O) DI(TOSQ)	Distortion indices of bond lengths, bond angles, tetrahedral edges and bond strengths [see equations (1), (2), (3), (8) and (4)].
$\Delta d(\text{om})$	Bond-length variation: difference between the $d(T-O)$ or $d(A-X)$ of one individual anion in a coordination polyhedron around a cation and the mean value [$=d(A-X)-d(A-X)_m$].		
$d(X-X), d(O-O)$	Distances within the edges of coordination polyhedra.		
$\Delta d(X-X), \Delta d(O-O)$	Difference between the observed mean values of $d(X-X)$ or $d(O-O)$ for a given polyhedron and the values calculated according to equation (13).		
$\angle(X-A-X), \angle(O-T-O)$	Angles subtended at the central cations of coordination polyhedra.		
$d(A-X)_s, d(T-O)_s$	Mean values of the two sides $d(A-X)$ or $d(T-O)$ of the an-		

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