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Reconstruction of Local Atomic Environments in the Disordered Hydrogen-Bonded Crystal Structures of Paraelectric Ammonium Dihydrogen Phosphate and Potassium Dihydrogen Phosphate

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In crystal structures in which one equivalent position is randomly occupied by different atomic species of different sizes the adjoining atoms must exhibit positional disorder. A special case is the statistical presence or absence of hydrogen atoms as observed in $NH_4H_2PO_4$ (ADP) and KH_2PO_4 (KDP), where the bond lengths in the phosphate group will vary locally depending on whether it is a P–O or a P–O–H [P–O(*h*)] bond. The ideal shape of an individual $PO_2(OH)_2$ group is predicted on the basis of the extended electrostatic valence rule and the O–P–O on P–O dependence in orthophosphate groups: P–O 1·501 Å, P–O(*h*) 1·573 Å, O(*h*)–P–O(*h*) 105·8°, O(*h*)–P–O 109·2° and O–P–O 113·9°. This calculated $PO_2(OH)_2$ group is fitted into unit cells of the same dimensions but lower symmetry than those of the paraelectric $I\bar{4}2d$ structures of ADP and KDP. These hypothetical local environments in C_{2v}^{19} (*I*-centered) and $P2_12_12_1$ are compatible with the observed averaged structure deduced from X-ray diffraction data for ADP. The hydrogen-atom positions as calculated for the least electrostatic energy in the local environments agree with their positions as determined from neutron-diffraction data. The local environments display interatomic distances which differ from the distances in the averaged structure individually as well as in their average values. Therefore, the bond lengths derived from the refinement of averaged disordered structures should be viewed with extreme caution. The distance between the averaged atomic positions can be different from the average of the individual distances. The situation resembles the case of the effects which thermal motion has on the estimation of bond distances. In these instances a valid correction is only possible if we have information on the nature of the thermal motion or on the type of disorder in the crystal structure. Such information is generally not available.

Introduction

In many crystal structures, and particularly in those of minerals, disorder is present. It can be evident in the random occupation of one equipoint by several atomic kinds. An example is the partial substitution of Al for Si in tetrahedral coordination in feldspars. Because the bond lengths Si–O, 1·61 Å, and Al–O, 1·75 Å (Smith & Bailey, 1963) differ by 0·14 Å the positions of the oxygen atoms must be affected by this substitution. At a given tetrahedral site occupied by Al the oxygen atoms will have a larger distance to the central cation than at a location where Si is the central atom. If the distribution of the Al and Si atoms is disordered then the X-ray data refinement will yield an averaged structure. The atomic positions of the averaged structure are the centroids of the atomic distributions in many asymmetric units. Therefore, the coordinates of the *averaged* positions are coordinates of *apparent* sites which most likely are not occupied in any single unit cell of the structure. In the averaged structure the atomic positions in the different unit cells superpose and cause a smearing out of the observed electron densities, which usually is not distinguishable from the effects of anisotropic thermal motion of the atoms. The thermal ellipsoid contains then the effects of both thermal motion and positional disorder. In any given asymmetric unit the local environment around an Al atom will be different from the environment in the averaged structure and from the local environment around an Si atom. The symmetry and geometry of such local environments generally cannot be deduced from an X-ray diffraction experiment. Certain conclusions about local environments can be drawn, however, from a variety of spectroscopic techniques, such as Mössbauer spectroscopy, e.s.r., *etc.*

In certain crystals a type of disorder occurs in which one equipoint is occupied by one atom in some locations but vacant in other locations. Formally this can be treated as random occupation of one equipoint by an atom and by a vacancy. An example of this is provided by $NH_4H_2PO_4$ (ADP) and KH_2PO_4 (KDP).

Disorder in room-temperature ADP and KDP

The hydrogen bond between the phosphate groups in room-temperature (RT) ADP and KDP is of the statistically symmetrical type $\text{P–O–}\tfrac{1}{2}\text{H–}\tfrac{1}{2}\text{H–O–P}$, with half a proton to either side of the twofold axis which is located between the two phosphate groups (double-well potential model). This is obvious from the neutron-diffraction studies of RT-ADP (Tenzer, Frazer & Pepinsky, 1958) and of RT-KDP (Bacon & Pease, 1955) and from the fact that single-well symmetrical hydrogen bonds have so far only been observed when the distance O–H–O is about 2·445 Å, *i.e.* significantly shorter than the 2·490 Å distance in the hydrogen bond in ADP (Speakman, 1972). In any individual location only one hydrogen atom will be situated between the oxygen atoms: $\text{P–O}(h)\text{–H}\cdots\text{O–P}$. The bond lengths P–O and P–O(*h*) must be different (Baur & Khan, 1970) but in ADP both types of oxygen atoms occupy statistically one set of equipoints and therefore the apparent symmetry of the phosphate group is $\bar{4}$. The distance from the P atom to the *averaged* (apparent) position of the oxygen atoms is 1·537 Å (Khan & Baur, 1973). Most of the phosphate groups in $NH_4H_2PO_4$ and KH_2PO_4 are $PO_2(OH)_2$ groups. The $PO_3(OH)$ and $PO(OH)_3$ groups discussed by Takagi (1948) are transient excited states representing a small part of the population of phosphate groups in ADP or KDP (see the work on RT–$NH_4H_2AsO_4$ by Lamotte, Gaillard & Constantinescu, 1972). The geometrical shape of *ordered* $PO_2(OH)_2$ groups is known from several precise crystal structure determinations: ferroelectric KH_2PO_4 (Bacon & Pease, 1955), $N_2H_6(H_2PO_4)_2$ (Liminga, 1966) and $N_2H_5(H_2PO_4)$ (Liminga, 1965). Here the average P–O distance is 1·506 Å, the mean distance P–O(*h*) from the P–atom to the hydroxyl oxygen atom is 1·572 Å, while the average P–O, O(*h*) over both types of distances is 1·539 Å, which means that it is almost identical with the mean P–O distance in RT–ADP and KDP. The individual $PO_2(OH)_2$ groups in RT–ADP or KDP must be similar to these ordered $PO_2(OH)_2$ groups. However, the X-ray data refinement gives a structure averaged over different orientations of the $PO_2(OH)_2$ groups. Therefore, the local environment at any given individual phosphate group must have a symmetry that is lower than the $\bar{4}$ symmetry at equipoint 4(*a*) in the space group $I\bar{4}2d$ of room temperature ADP or KDP.

In this paper an attempt is made to reconstruct these local environments in ADP and KDP, and to ascertain what lower symmetry distortions are possible that would not lead to unreasonable bond distances and bond angles. The structures of ADP and KDP lend themselves to such a procedure because they are simple, of high symmetry and NH_4 (or K) and the PO_4 groups are centered at special positions (Tenzer *et al.*, 1958; Bacon & Pease, 1953, 1955).

Shape of an individual $PO_2(OH)_2$ group

The bond lengths P–O and P–O(*h*) in the $PO_2(OH)_2$ tetrahedron can be predicted by using the extended electrostatic valence rule (Baur, 1970):

$$d(\text{P–O}) = d(\text{P–O})_{\text{mean}} + b\Delta p_{\text{O}}\,, \tag{1}$$

where Δp_{O} is the difference between the bond strength (Pauling, 1960) received by the individual oxygen atom and the mean bond strength of all oxygen atoms within the tetrahedron. In ADP the bond strengths received by O and by O(*h*) are 1·58 valence units and 2·25 v.u. respectively (in KDP the values are 1·67 and 2·33 v.u.). The value of $d(\text{P–O})_{\text{mean}}$, based on an average of 174 distances, is 1·537 Å. A determination of *b* by linear regression analysis of 174 pairs of data gave 0·109 Å/v.u. (Baur, 1970).

The oxygen-oxygen distances in the edges of a variety of acid phosphate groups (Baur & Khan, 1970) show a tendency to stay constant, while the angles O–P–O (α) vary inversely with the bond lengths in the sides of the angle. This relationship can be expressed as (Baur, 1970):

$$\log\,[\sin\,(\alpha/2)] = 0{\cdot}11 - 1{\cdot}08\,\log\,[d(\text{P–O})]\,, \tag{2}$$

where the numerical values have been empirically determined. The shape of an individual $PO_2(OH)_2$ group deduced from these equations differs clearly from the dimensions of the phosphate group observed in paraelectric ADP (Table 1) but it is similar to the phosphate groups in ferroelectric KH_2PO_4, in $N_2H_6(H_2PO_4)_2$ and in $N_2H_6(H_2PO_4)$.

Table 1. *Dimensions of the averaged phosphate group in room temperature ADP and shape of a* $PO_2(OH)_2$ *group as predicted from equations* (1) *and* (2)

	ADP, RT	Predicted $PO_2(OH)_2$
2 × P–O(*h*)	1·537 Å	1·573 Å
2 × P–O	1·537	1·501
1 × O(*h*)–O(*h*)	2·536	2·510
1 × O–O	2·536	2·501
4 × O–O(*h*)	2·497	2·506
1 × O(*h*)–P–O(*h*)	111·2°	105·8°
1 × O–P–O	111·2	113·9
4 × O–P–O(*h*)	108·6	109·2

Orientation of the $PO_2(OH)_2$ groups

The maximum point-group symmetry that can be exhibited by an ideal $PO_2(OH)_2$ group (Table 1) is *mm*. If a phosphate group of this shape is fitted into the unit cell of ADP or KDP the space-group symmetry must be lowered. It is only necessary to consider local symmetries fitting into the same unit cell as that of the $I\bar{4}2d$ structure of ADP or KDP because no indication is available for the occurrence of superstructures in the room-temperature phases. Possible space groups are the sub-groups of $I\bar{4}2d$: $I\bar{4}11$ ($=I\bar{4}$), $I21d$ ($Fdd2$) and $I221$($=I2_12_12_1$) (Neubüser & Wondratschek, 1969). Space group $I\bar{4}$ can be ruled out because the phosphate groups would have to retain $\bar{4}$ symmetry. In $Fdd2$ the twofold axis of the $PO_2(OH)_2$ groups must be aligned with the *c* axis of the (supergroup) $I\bar{4}2d$, so that all O(*h*) atoms of the phosphate group are pointing in one direction. This is the space group of the ferroelectric low-temperature modification of KH_2PO_4 (Bacon & Pease, 1955). The placing of both O(*h*) atoms in one direction of the *c* axis corresponds to the polar configuration of the $PO_2(OH)_2$ groups in Slater's (1941) theory of the transition in KH_2PO_4. The lateral configuration in which one O(*h*) atom is 'up' in the **c** direction, while the other is 'down' relative to the P-atom position, is not possible in space groups $Fdd2$ or $I2_12_12_1$. It can be achieved in $P2_12_12_1$, which is a subgroup of $I2_12_12_1$, and was found for the antiferroelectric low-temperature phase of ADP (Keeling & Pepinsky, 1955).

For easier comparison of the structure in space group $Fdd2$ with the structure in $I\bar{4}2d$ the body-centered setting has to be chosen. The coordinates of the general equivalent position of C_{2v}^{19} in the body-centered setting are: $(0,0,0\colon \frac{1}{2},\frac{1}{2},\frac{1}{2})+(\bar{x},\bar{y},z;\ x,y,z;\ \frac{1}{2}+y,x,\frac{1}{4}+z;\ \frac{1}{2}-y,\bar{x},\frac{1}{4}+z)$. The space group will be called here C_{2v}^{19} in *I* setting. It cannot be called '$Idd2$' because the glide planes are diagonal to the **a** and **b** directions. Given the shape of the $PO_2(OH)_2$ group as outlined above and assuming the orientation of the O(*h*1)–O(*h*1) edge to be the same as for the O(up)–O(up) edge in $I\bar{4}2d$ it is simple to calculate the coordinates of the oxygen atoms O(*h*1) and O(2) in C_{2v}^{19} [Table 2(*a*) and (*c*)].

In $P2_12_12_1$ the phosphate group was arranged in the lateral position and then rotated about the vector connecting the midpoints of the edges O(*h*1)–O(*h*2) and O(3)–O(4) until the hydrogen bonds O(*h*1)–O(3) and O(*h*2)–O(4) were as nearly equal in length as the geometry of the arrangement would allow [Table 2(*b*) and (*d*)]. The coordinates of the general equivalent position in $P2_12_12_1$ have been shifted compared with the standard setting in order to correspond to the setting in $I\bar{4}2d$: $x,y,z;\ \frac{1}{2}+x,y,\frac{1}{4}-z;\ x,\frac{1}{2}+y,\frac{3}{4}-z;\ \frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z$ (Keeling & Pepinsky, 1955).

The individual deviations of the calculated atomic positions of the oxygen atoms in C_{2v}^{19} and in $P2_12_12_1$ from the oxygen-atom positions in the experimental averaged structures range from 0·05 to 0·09 Å. The deviations of the oxygen atom positions in C_{2v}^{19} and in $P2_12_12_1$ from each other (after transformation to the common oxygen atom position in $I\bar{4}2d$) range from 0·07 to 0·14 Å.

Table 2. $NH_4H_2PO_4$, *ADP and* KH_2PO_4, *KDP positional coordinates*

The parameters of the oxygen atoms are calculated as described in the text; those of the hydrogen atoms of the NH_4 groups, H(*n*), are taken from Tenzer *et al.* (1958); those of the hydrogen atoms of the O–H–O bond, H(*o*), are calculated to have positions of least electrostatic energy (see text). In the electrostatic calculations the positions of the H(*n*) atoms were fixed at the positions given here; the assumed point charges for the atoms are P, +2·0e; N and O, −1·0e; O(*h*), −0·5e; H(*n*) and H(*o*), +0·5e; K, +1·0e. The cell constants: $a=7·4997$ and $c=7·5493$ Å for ADP, $a=7·434$ and $c=6·945$ for KDP.

(*a*) ADP in space group C_{2v}^{19}, *I*-centered.

	x	*y*	*z*
P	0	0	0
N	0	0	½
O(*h*1)I	0·0834	0·1450	0·1258
O(2)I	0·8546	0·0836	0·8916
H(*n*1)	0·014	0·111	0·573
H(*n*2)	0·889	0·014	0·427
H(*o*)I	0·225	0·141	0·125

(*b*) ADP in space group $P2_12_12_1$

P	0	0	0
N	0	0	½
O(*h*1)P	0·0918	0·1471	0·1174
O(*h*2)P	0·1525	0·9181	0·8823
O(3)P	0·9253	0·8573	0·1182
O(4)P	0·8637	0·0863	0·8823
H(*n*1)	0·014	0·111	0·573
H(*n*2)	0·986	0·889	0·573
H(*n*3)	0·889	0·014	0·427
H(*n*4)	0·111	0·986	0·427
H(*o*1)P	0·233	0·148	0·130
H(*o*2)P	0·142	0·777	0·881

(*c*) KDP in space group C_{2v}^{19}, *I*-centered

P	0	0	0
K	0	0	½
O(*h*1)	0·0821	0·1474	0·1368
O(*h*2)	0·8522	0·0824	0·8821
H(*o*)	0·224	0·146	0·123

(*d*) KDP in space group $P2_12_12_1$

P	0	0	0
K	0	0	½
O(*h*1)	0·0897	0·1515	0·1256
O(*h*2)	0·1557	0·9181	0·8743
O(3)	0·9262	0·8568	0·1303
O(4)	0·8618	0·0831	0·8699
H(*o*1)	0·232	0·146	0·1280
H(*o*2)	0·146	0·776	0·8820

Electrostatic calculation of hydrogen-atom positions

The calculated oxygen-atom positions in C_{2v}^{19} and $P2_12_12_1$ show that the local details of the hydrogen-bond geometry must be slightly different from those observed in the averaged structure. A sensitive test for the reasonableness of the postulated lower-symmetry local environments in ADP and KDP is provided by a comparison of the hydrogen-atom positions as observed by Tenzer *et al.* (1958) and Bacon & Pease

(1955) by neutron diffraction with those which can be calculated employing the electrostatic model of the hydrogen bond (Baur, 1972*a*). The calculation was performed in the same manner as previously described (Baur, 1965) with an updated version of the computer program *MANIOC*. The distances O(*h*)-H(*o*) were held constant at 1·06 Å, the value to be expected for a hydrogen-bond length of 2·50 Å (see Hamilton & Ibers, 1968). The deviations of the individual calculated H-atom positions (Table 2) from the observed positions range from 0·05 to 0·07 Å, meaning that the agreement is as good as is usually found in such calculations.

Discussion of results

It has been assumed above that the local configurations which contribute to the observed averaged structure of room-temperature ADP and KDP (Fig. 1) in space group $I\bar{4}2d$ are phosphate groups $PO_2(OH)_2$ of point symmetry *mm*. This is a simplifying assumption, because it ignores PO_4, $PO_3(OH)$, $PO(OH)_3$ and $P(OH)_4$ groups and it excludes lower symmetries for $PO_2(OH)_2$ itself. Another simplification is the choice of space groups C_{2v}^{19} and $P2_12_12_1$, which are the subgroups of *highest* symmetry allowing the introduction of polar and lateral phosphate groups. In addition it was assumed that the relative positions of the P and the N (or K) atoms remain constant at the values of space group $I\bar{4}2d$. All three assumptions could be relaxed, by lowering the symmetry of the arrangements. However, the problem would become increasingly intractable if this were done. Nevertheless, the above-made assumptions are reasonable if we consider the symmetries and crystal structures of ferroelectric KDP (Bacon & Pease, 1955) and of antiferroelectric ADP (Keeling and Pepinsky, 1958) which are similar to the local environments in C_{2v}^{19} and $P2_12_12_1$ respectively. In the low-temperature phases the atoms P and N (or K) deviate only slightly from their special positions in the paraelectric phases. The rearrangements below the Curie point involve changes in the cell parameters. Since the local environments must occur within the unit-cell parameters of the room-temperature phases it is plausible to assume that the P and N (or K) atoms do not deviate significantly from their positions in space group $I\bar{4}2d$.

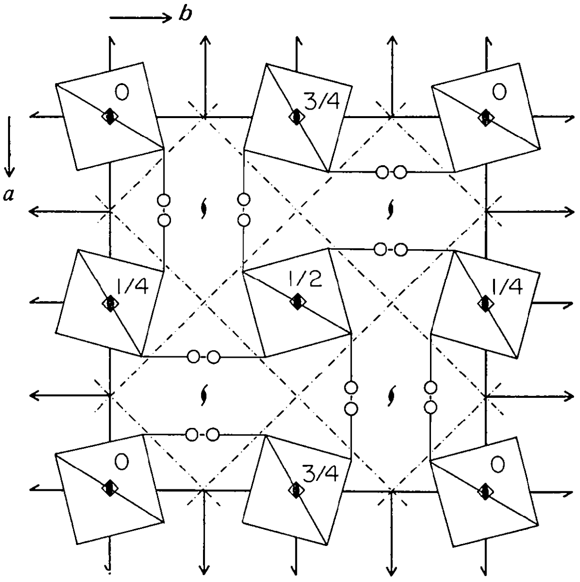

Fig. 1. Schematic representation in space group $I\bar{4}2d$ of the arrangement of phosphate groups, hydrogen bonds and symmetry elements in ADP and KDP viewed parallel to [001]. Phosphate groups are shown as tetrahedra, hydrogen atoms as small circles, the heights of the P atoms are indicated as fractions (*z*), hydrogen bonds as broken lines. The symbols of the symmetry elements are chosen in accordance with the *International Tables for X-ray Crystallography* (1952). In C_{2v}^{19} in *I* setting no 2 or 2_1 axes parallel to the (001) plane would be present and the $\bar{4}$ axes would be twofold axes. In $P2_12_12_1$ only the 2_1 axes would be present.

The distribution of the calculated oxygen-atom positions around the experimental position (Fig. 2) shows that the *major* axis of the 'thermal' ellipsoid would have to be approximately parallel to the **c** direction if all local environments were of C_{2v}^{19} symmetry. If the $P2_12_12_1$ local environments were dominant the *shortest* axis of the 'thermal' ellipsoid would have to be parallel to the **c** direction. However, the major axis of the experimentally observed ellipsoid is normal to the direction of the P–O bond and located in the plane defined by the **c** direction and the P–O vector (Table 5, Khan & Baur, 1973) and all calculated oxygen-atom positions of both local environments fall well within the extent of this ellipsoid. Therefore the proposed local environments are compatible with the observed structure, assuming that both of them occur with approximately equal frequency. Both lower-symmetry environments must occur in two different polarities relative to the averaged room-temperature structures, otherwise their paraelectric character would not be preserved. The coordinates averaged (by applying the $I\bar{4}2d$ transformations to the positional coordinates in C_{2v}^{19} and $P2_12_12_1$ and taking their mean value) for the C_{2v}^{19} and $P2_12_12_1$ environments agree well with the observed values (Table 3). In addition, both models are internally consistent because all interatomic distances are reasonable (Table 4).

The two local environments, as proposed here, are specific detailed examples of the short-range order domains postulated by Slater (1941) to exist in paraelectric KDP. Based on their neutron diffraction experiments, Bacon & Pease (1955) have concluded that the volumes of these domains in KDP should be 'small compared to the crystal volumes throughout which the neutron scattering is coherent'. That means that they should be smaller than the grain boundaries of the mosaic crystallites.

Conclusions

The approach used here to derive hypothetical local environments in a disordered structure is capable of

Table 3. *Comparison of observed averaged positional coordinates of* O(*obs*) [*ADP*: *Khan & Baur* (1973); *KDP*: *Bacon & Pease* (1953)] *and H*(*o*) [*ADP*: (*Tenzer et al.* (1958); *KDP*: *Bacon & Pease* (1955)] *with the averaged positions of the constructed local environments*

The value given for O(calc., mean) is the average of O(C_{2v}^{19}, mean) and O ($P2_12_12_1$, mean). The Δ value is the distance from O(obs) to O(mean).

(*a*) ADP

	x	y	z	Δ
O(obs)	0·0843	0·1466	0·1151	
O(calc., mean)	0·0836	0·1449	0·1174	0·02 Å
O(C_{2v}^{19}, mean)	0·0835	0·1452	0·1171	0·02
O($P2_12_12_1$, mean)	0·0837	0·1447	0·1178	0·03
H(obs)	0·227	0·146	0·122	
H(calc., mean)	0·226	0·143	0·125	0·03
H(C_{2v}^{19})	0·225	0·141	0·125	0·05
H($P2_12_12_1$, mean)	0·228	0·145	0·124	0·01

(*b*) KDP

	x	y	z	Δ
O(obs)	0·0831	0·1486	0·1261	
O(calc., mean)	0·0822	0·1474	0·1276	0·02
O(C_{2v}^{19}, mean)	0·0823	0·1486	0·1274	0·01
O($P2_12_12_1$, mean)	0·0821	0·1472	0·1279	0·02
H(obs)	0·227	0·147	0·123	
H(calc., mean)	0·226	0·146	0·123	0·01
H(C_{2v}^{19})	0·224	0·146	0·123	0·02
H($P2_12_12_1$, mean)	0·228	0·146	0·123	0·01

wide application. It could be combined with spectroscopic methods which give evidence of local symmetries present at particular atomic positions. An example of the latter is the work of Lamotte *et al.* (1972) and of Dalal, Dickinson & McDowell (1972) who have discussed the identification of Slater configurations of AsO_4^{4-} in the room-temperature and low-temperature phases of KDP-type arsenates based on the measurement of e.s.r. spectra. The geometric reconstruction of local environments could be extended to cover and help to interpret such results. However, the problem is even more difficult in this case because the AsO_4^{4-} radical must be larger than the AsO_4^{3-} groups in these arsenates, thus introducing additional disorder. These more involved cases could possibly be treated by applying the method of computer simulation of crystal structures (Baur, 1972*b*).

Recently Hidaka (1972) has calculated the electron delocalization weight of the hydrogen bond in KH_2PO_4. He makes the assumption that the P–O and the P–O(*h*) interatomic distances are of identical length in RT-KDP, but have different lengths in the ferroelcetric

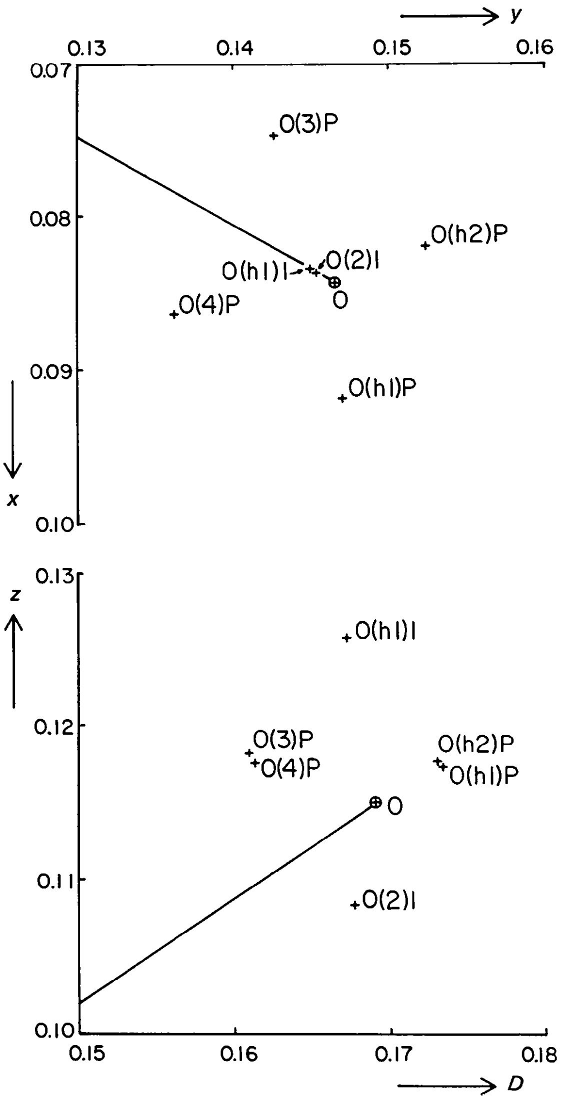

Fig. 2. Enlargement of the area around the oxygen atom in ADP. The solid line is the projection of the P–O bond direction. Atoms labeled as in Table 2. (*a*) View parallel to [001]. (*b*) View projected into the plane defined by the **c** direction and the P–O vector [$D=\sqrt{(x^2+y^2)}$].

Table 4. *Comparison of selected bond lengths and angles in the observed averaged ADP structure* (*in* $I\bar{4}2d$) *and in the local environments provided by space groups* C_{2v}^{19} *and* $P2_12_12_1$

The positional parameters are taken from Table 3(*a*). Since Tenzer *et al.* (1958) did not provide e.s.d.'s for the hydrogen-atom positions given by them, no errors can be quoted here. It is estimated that the error in the H-atom position is not larger than ± 0·01 Å.

	$I\bar{4}2d$	C_{2v}^{19}	$P2_12_12_1$
N–O(I)	2·909 (1) Å	2·89, 2·93 Å	2·86, 2·91, 2·91, 2·98 Å
N–O(II)	3·170 (1)	3·09, 3·21	3·13, 3·13, 3·17, 3·17
O···H(*n*)	1·950	1·94, 1·97	1·90, 1·95, 1·96, 2·02
O–O(H-bond)	2·490 (1)	2·500	2·494, 2·504
O–H(*o*)	1·071	1·06	1·06, 1·06
H(*o*)···O	1·418	1·44	1·44, 1·45
O–H···O	178·8°	174°	175, 176°

phase. However, the equality of the P–O and P–O(h) distances can be interpreted as a result of the disorder in KDP and the $\bar{4}$ symmetry of the phosphate group is only apparent. This interpretation removes the premise of his argument.

The comparison of corresponding interatomic distances in the averaged structure and in the two lower-symmetry local environments (Table 4) points to a principal difficulty in the interpretation of the results of refinements of disordered structures. We can expect the real individual bond distances to be easily outside the confidence limits of the distances observed between averaged atomic sites [see N–O(I), N–O(II) and O–O in Table 4]. It can also occur that the average of the individual bond distances in the local environments is different from the distance between the observed averaged positions. The average N–O(II) distances in C_{2v}^{19} and $P2_12_12_1$ are shorter (3·15 Å) than the experimentally observed N–O(II) distance. For the hydrogen bond the situation is reversed since in both local environments the O–O distance is longer than in the experimental structure. This is the case because the atomic displacements in the local environments are coupled to each other.

The distances involving atoms for which we have only averaged experimental positions do not have to agree with the average of the individual distances in the local environment, or, more pointedly: the distance between the averaged atomic positions can be different from the average of the individual distances. A similar situation results when the effects of thermal motion on the estimation of bond lengths are considered. The distances between the centroids of the electron-density distributions can be corrected for thermal-vibration effects only if we know the joint distribution which describes the motion of the atoms in question (Busing & Levy, 1964). The corresponding difficulty in the case of averaged structures is that generally we do not know the symmetry and geometry of the local environments in the individual unit cells of an averaged structure. Therefore, the bond distances derived from averaged disordered structures should be viewed with extreme caution. It may be possible to compare bond distances and bond angles of two isostructural averaged structures, as is being done for ADP and ADA in the preceding paper because the local environments are likely to be similar. However, when we compare the bond distances and bond angles of an experimentally determined averaged structure with data from different structures we should remember that the real accuracy which we can obtain is much less than the apparent precision of the results would make us believe.

In the interpretation of the bond lengths involving statistically occupied sites it is usually tacitly assumed that the observed bond lengths are a simple average of the individual bond lengths, weighted according to the relative proportions of the occupants of the sites. This assumption is the basis of the procedure used to calculate the occupancy of a particular site from the observed distances between the apparent averaged distances. Since, however, the observed distances between averaged positions are not simple averages of the individual distances we should expect deviations from the simple law. Such effects may be responsible for some of the deviations observed by Smith & Bailey (1963) in their calibration of (Al,Si)–O distance *versus* Al content in framework aluminosilicates. This shows that the averaging accomplished by a diffraction experiment can obscure the details of interatomic distances, both in the case of time-averaging (thermal motion) and in the case of space-averaging (disorder) as discussed above.

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