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A precision neutron diffraction study of tetragonal RbH_2PO_4.

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A high-precision neutron study of the structure of paraelectric RbH_2PO_4 has been carried out. It is found that accurate neutron diffraction data can be used to distinguish between two closely related structural models, *i.e.* the centered-hydrogen and the disordered-hydrogen models, in this crystal. The final value of the conventional R factor based on 129 reflections is 1·7%. A significance test on the R-factor ratios suggests the rejection of the centered model in favor of the disordered model at a confidence interval of better than 99·5%.

Rubidium dihydrogenphosphate (RDP) is isostructural with potassium dihydrogenphosphate (KDP) and both are members of an isomorphous series of phosphates and arsenates which undergo low-temperature ferroelectric phase transitions. Room-temperature neutron diffraction investigations of KDP (Bacon & Pease, 1953; Peterson, Levy & Simonson, 1953) have demonstrated that the proton distribution is elongated along the O—H—O bond; but it was not possible to distinguish between a centered model with a strong anisotropic vibration of the proton about the bond center and a disordered model where the proton is displaced on either side of the bond center at positions closer to one or other of the two O atoms. However, the latter model was favored in both studies on the basis of the low-temperature ordering of the structure and other considerations. Similar conclusions have been outlined from the room-temperature neutron diffraction study of ammonium dihydrogenphosphate (ADP) (Tenzer, Frazer & Pepinsky, 1958).

A careful room-temperature neutron diffraction study of the structure of RbH_2PO_4 has been carried out in order to examine the feasibility of using accurate neutron diffraction data for choosing between the two closely related structural models described above. All previous attempts at choosing between the centered-hydrogen model characterizing a single-well potential and the alternative disordered-hydrogen model characterizing a symmetric double-well kind of potential in some symmetric hydrogen bonds (Hamilton & Ibers, 1968) have been unsuccessful, perhaps because the data used did not have the necessary high precision.

Experimental

The crystal used was a cuboid of size 7·70 × 5·00 × 3·54 mm (cut from a bigger crystal) with its longest and shortest edges being parallel to the a and c axes respectively. It was mounted on the diffractometer with its a axis parallel to the φ axis. Neutron diffraction data were recorded at room temperature on a paper-tape-controlled four-circle neutron diffractometer (Mitsubishi) at the NRI reactor in Baghdad. The reactor flux was $\sim 2 \times 10^{13}$ n cm^{-2} s^{-1} in the core. The cell parameters, refined on the basis of the optimized 2θ, χ and φ values for 25 random strong reflections with the program *REFINE* (Srikanta & Sequeira, 1968*a*), are: $a = b = 7{\cdot}622\ (7)$, $c = 7{\cdot}315\ (9)$ Å. The structure belongs to the tetragonal space group $I\bar{4}2d$.

The integrated intensities of 139 reflections within the limit $\sin\theta/\lambda = 0{\cdot}5$ Å^{-1} ($\lambda = 1{\cdot}031$ Å) were recorded in the bisecting position with the θ–2θ coupled step-scan technique. The typical counting time for a reflection was about 1 h. Two standard reflections were measured after every 20 reflections to provide a check on the experiment. During the course of data collection there was no systematic change in the intensities of the standard reflections.

The integrated intensities were then reduced to F_o^2 by applying the standard Lorentz and absorption corrections with the program *DATARED* (Srikanta & Sequeira, 1968*b*) which includes the absorption correction program *ORABS* (Wehe, Busing & Levy, 1962) as a subroutine. The linear absorption coefficient was calculated to be 1·04 cm^{-1}, with an effective incoherent scattering cross-section for hydrogen of 41 barns assumed, and the transmission coefficients ranged from 0·609 to 0·705.

Structure refinement

The starting parameters for the refinement were those given by Bacon & Pease (1953) for KH_2PO_4. The structure was refined on both the centered and disordered-hydrogen models by the method of full-matrix least squares with anisotropic temperature factors for all atoms and an isotropic extinction correction with the program *XFLS* (Busing, Martin & Levy, 1962). Neutron scattering lengths for Rb and P were also refined with the values for H and O held at $-0{\cdot}372$ and $0{\cdot}575$ ($\times 10^{-12}$ cm) respectively. The function minimized in the refinement was $\Sigma w|F_o^2 - |F_c|^2|^2$, where weights $w = 1/[0{\cdot}033 + 0{\cdot}028(F_o^2/\sin 2\theta)]$ based on an error analysis were used in the final stages of the refinement.

The intensity data showed some moderate extinction effects and correction for secondary extinction was applied after the general theory of Becker & Coppens (1974). All possible forms, including the type I, type II and the general form, of extinction corrections were tried both with and without the primary extinction. The type I (mosaic-spread dominated) correction without primary extinction and with a Lorentzian distribution for the mosaic spread refined the best and was far superior to the others. The ten strongest reflections with extinction correction factor $Y < 0{\cdot}61$ were omitted from the refinement as some of them, particularly 200 and 020, indicated some anisotropy in extinction. 200 with $Y = 0{\cdot}395$ was the most severely affected by extinction.

In the disordered model 25 parameters were varied (including the y parameter of H) compared with 22 in the centered model. The z coordinate of H was constrained at 0·125 as the O(H)···O bond is normal to the z axis. y_H was

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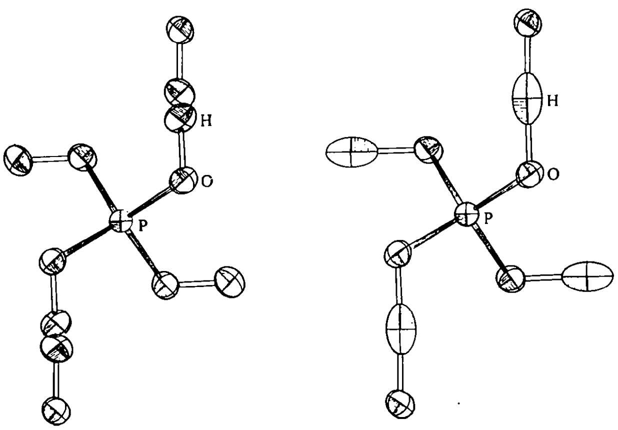
fixed at small discrete steps around 0·22 and the best weighted R factor corresponded to $y_H = 0·223$.

In the last cycle of refinement all parameters reached complete convergence. No systematic dependence of values of $w|F_o^2 - F_c^2|^2$ on F_o^2 was observed, which is correct for a proper weighting scheme. The final agreement factors for the two refined models are:

	R_F	R_F^2	R_w	S
Disordered	0·0175	0·0309	0·0457	1·048
Centered	0·0191	0·0338	0·0498	1·129

where $R_F = \Sigma|F_o - |F_c||/\Sigma F_o$, $R_F^2 = \Sigma|F_o^2 - F_c^2|/\Sigma|F_o^2|$, $R_w = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma wF_o^4]^{1/2}$ and S is the standard error of fit with all data included and is given by $[\Sigma w|F_o^2 - F_c^2|^2/(n_o - n_v)]^{1/2}$ where n_o and n_v are the number of observed reflections and number of variables respectively.



(a) (b)

Fig. 1. *ORTEP* drawing of the dihydrogenphosphate ion for (*a*) the disordered and (*b*) the centered-hydrogen models with thermal ellipsoids drawn on a 50% probability scale.

The refined atomic parameters for the two models are given in Table 1. The final neutron scattering lengths for Rb and P are 0·678 (9) and 0·493 (9) (× 10^{-12} cm) respectively. The final value of the extinction parameter g is 0·52 (4) × 10^4.*

Discussion

A view of the dihydrogenphosphate ion for both the disordered and the centered-hydrogen models, drawn with the program *ORTEP* (Johnson, 1965), is shown in Fig. 1. Interatomic distances and bond angles are listed in Table 2. The values listed are close to the corresponding values for KDP (Bacon & Pease, 1953) and ADP (Tenzer, Frazer & Pepinsky, 1958). Considering the high precision achieved in our work, it should be mentioned that some of the distances and angles involving the H atom in RDP are significantly different from the corresponding values in KDP and ADP. However, the basic structure of the $H_2PO_4^-$ ions is the same and each tetrahedral PO_4 group is connected to four neighbouring PO_4 tetrahedra by O—H···O hydrogen bonds.

The use of the R-factor ratio as a test of hypotheses concerning crystal structures has been discussed by Hamil-

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

The primed atoms are in an opposite **z** direction (relative to the central atom of the PO_4 tetrahedron) to those of the unprimed.

O–H	1·043 (2)	O–H···O	177·17 (15)
O–P	1·541 (1)	O–P–O′	108·91 (6)
O(H)···O	2·497 (2)	O–P–O	110·61 (6)
O···O′	2·508 (2)	P–O–H	115·25 (17)
O···O	2·534 (2)	P–O(H)···O	116·32 (7)

Table 1. *Final positional and thermal parameters*

The form of the anisotropic temperature factor is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β_{ij}'s are multiplied by 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Centered-hydrogen model									
O	0·1422 (1)	0·0866 (2)	0·1200 (1)	71 (3)	73 (5)	89 (4)	8 (1)	−26 (2)	−19 (2)
H	0·1387 (3)	0·25	0·125	89 (5)	257 (18)	129 (7)	0	0	49 (7)
Rb	0·0	0·0	0·5	79 (4)	79 (4)	58 (5)	0	0	0
P	0·0	0·0	0·0	51 (6)	51 (6)	70 (8)	0	0	0
Disordered-hydrogen model									
O	0·1421 (2)	0·0863 (2)	0·1199 (1)	71 (3)	72 (5)	89 (3)	6 (1)	−23 (2)	−22 (2)
H	0·1382 (6)	0·223	0·125	94 (5)	77 (17)	137 (7)	12 (8)	−49 (14)	46 (6)
Rb	0·0	0·0	0·5	79 (4)	79 (4)	58 (5)	0	0	0
P	0·0	0·0	0·0	51 (5)	51 (5)	71 (8)	0	0	0

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* A list of structure factors for the disordered model has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33137 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ton (1965). To decide between the disordered and the centered-hydrogen models for the structure of RDP, Hamilton's significance test was applied as follows: number of reflections = 129, number of variables = 25 (disordered model), number of variables = 22 (centered model); hypothesis: 'the hydrogen is centered on the O—H—O bond'.

The dimension of the hypothesis is 25 − 22 = 3 and the number of degrees of freedom for the refinement is 129 − 25 = 104. The value of $\mathscr{R}$ obtained by interpolating the appropriate table for testing the R-factor ratio (Hamilton, 1965) is $\mathscr{R}_{3,104,0\cdot005} = 1\cdot07$, while the observed R-factor ratio is

$$\mathscr{R}_{\rm obs} = \frac{R_w\,(\text{centered})}{R_w\,(\text{disordered})} = \frac{0\cdot0498}{0\cdot0457} = 1\cdot09.$$

This indicates that the above hypothesis can be rejected in favor of the disordered hydrogen model at a significance level of better than 0·5% (or at a confidence interval of higher than 99·5%). In other words, the results of our experiment favor the disordered-hydrogen model for the structure of paraelectric RbH_2PO_4 in which the proton is displaced on either side of the bond center at positions which are 0·41 Å apart.

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1-Phenyl-4,5-(D-glucofurano)imidazolidine-2-thione: erratum.

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A new table of torsion angles for the title compound [Jiménez-Garay, López-Castro & Márquez, *Acta Cryst.* (1976), B**32**, 2115–2118] is given.

In Fig. 1 of the paper on the title compound (Jiménez-Garay, López-Castro & Márquez, 1976) atoms C(10) and C(11) are interchanged with respect to their atomic parameters (Table 1); therefore, the selected torsion angles have been recalculated and are reported in the new Table 4.

Reference

JIMÉNEZ-GARAY, R., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1976). *Acta Cryst.* B**32**, 2115–2118.

Table 4. *Selected torsion angles* (°)

N(1)–C(1)–C(2)–C(6)	−176·6	O(3)–C(12)–C(11)–O(1)	−115·8
C(2)–C(1)–N(1)–C(9)	111·8	C(12)–C(11)–O(1)–C(9)	163·8
C(1)–N(1)–C(9)–C(7)	−175·1	C(11)–O(1)–C(9)–C(8)	−22·7
S–C(7)–N(1)–N(2)	179·3	N(1)–C(9)–C(8)–C(10)	−119·4
O(2)–C(10)–C(8)–C(11)	−116·8	O(4)–C(13)–C(12)–C(11)	−170·1
O(1)–C(9)–C(8)–C(10)	−1·1	O(3)–C(12)–C(11)–C(13)	−177·0
C(9)–C(8)–C(10)–C(11)	22·5	C(2)–C(1)–N(1)–C(7)	− 62·5
C(8)–C(10)–C(11)–O(1)	−36·3	C(1)–N(1)–C(9)–C(8)	−176·6
C(10)–C(11)–O(1)–C(9)	38·0	N(1)–C(9)–C(8)–O(1)	−118·3
C(13)–C(12)–C(11)–O(1)	61·2		