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SHORT-FORMAT PAPERS

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Acta Cryst. (1991). C**47**, 2196–2198

Electrostatic Potential for O—H—O in Tetragonal Ammonium Dihydrogenphosphate

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Abstract. $NH_4H_2PO_4$, $M_r = 115·03$, tetragonal, $I\bar{4}2d$, $a = 7·500\,(1)$, $c = 7·550\,(2)$ Å, $V = 424·7$ Å^3, $Z = 4$, $D_x = 1·799$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 49·08$ cm^{-1}, $F(000) = 240$, $T = 298$ K, $R = 0·021$ for 99 independent reflections. The O—H—O system with O···O distance 2·493 (3) Å is described in terms of the H atom in a single site undergoing anisotropic thermal vibrations. Then the O···H distance is 1·31 (9) Å, the O—H—O angle is 145 (8)° and the maximum mean-square amplitude of vibration for H is 1·1 (7) Å^2. However, the probability distribution function for the proton could well have a double peak as reported in isomorphous KH_2PO_4 from high-resolution neutron diffraction. The electrostatic potential well in which the H occurs has a minimum of $-1·13$ e Å^{-1}.

Experimental. Colorless crystals were grown from water. Crystal size 0·13 × 0·13 × 0·66 mm. CAD-4 diffractometer, cell dimensions from 19 centered reflections ($16 < 2\theta < 76°$), Cu $K\alpha$ radiation, Ni-filtered, intensities measured to $2\theta = 120°$, ω–2θ scans, with ω-scan width $(0·7 + 0·15\tan\theta)°$, scan speed 0·91–2·50° min^{-1}, $-8 \le h \le 8$, $-8 < k \le 8$, $0 \le l \le 8$, $h + k + l =$ odd not collected, 680 reflections measured. Three standard reflections $(\bar{2}20, \bar{1}, \bar{1}\bar{1}2)$ were measured every 6000 s and varied in intensity by <3% during the data collection. An absorption correction was applied (Busing & Levy, 1957). Correction factors were in the range 0·412 to 0·580. Averaging ($R_{\rm int} = 0·027$) gave 99 independent reflections, all with $F_o > 3\sigma(F_o)$.

After placing the P and N atoms according to Ueda (1948) and refining isotropic temperature factors, the O atom was located in a difference map. The positional and anisotropic temperature factors of the O atom were refined by full-matrix least-squares refinement on F_o, including all 99 independent reflections, using the computer program *POP* (Craven, Weber & He, 1977). The H_N atom was located in a difference map. The H_O was placed in a special position (x, 0·25, 0·125), with $x = 0·146$ as starting value as assumed by Tenzer, Frazer & Pepinsky (1958). The positional parameters and isotropic temperature factor of the H_N atom and the x coordinate and the anisotropic temperature factors of the H_O atom were refined. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). A type I Lorentzian extinction correction was assumed (Becker & Coppens, 1974), giving $g = 0·082\,(14)$ rad^{-1} × 10^{-4}. Final $R = 0·021$, $wR =$

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Table 1. *Fractional positional parameters and thermal parameters for ammonium dihydrogenphosphate*

Positional parameters $\times 10^4$ for non-H atoms, $\times 10^3$ for H atoms. E.s.d.'s given in parentheses refer to the least significant digit. The temperature factor has the form $T = \exp[-2\pi^2\sum_i\sum_j h_i h_j a_i^* a_j^* U_{ij}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0	0	0	0·0198 (9)	0·0198	0·0272 (10)	0	0	0
O	1461 (3)	841 (3)	1150 (4)	0·0271 (13)	0·0250 (14)	0·0366 (14)	0·0058 (8)	−0·0079 (11)	−0·0046 (9)
N	0	0	5000	0·0340 (22)	0·0340	0·0254 (30)	0	0	0
H_N	26 (5)	79 (5)	438 (3)	0·029 (9)					
H_O	94 (12)	250	125	0·03 (4)	1·13 (73)	0·07 (4)	0	0	0·21 (16)

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

P—O	1·534 (2)	$O\cdots(H_O)\cdots O^{i}$	2·493 (3)
$O\cdots H_O$	1·31 (9)	$N\cdots O^{ii}$	2·913 (2)
$N—H_N$	0·78 (3)	$H_N\cdots O^{ii}$	2·29 (3)
$O—P—O^{iii}$	111·1 (1)	$H_N—N—H_N^{iii}$	106 (3)
$O—P—O^{iv}$	108·7 (1)	$H_N—N—H_N^{v}$	111 (3)
$P—O\cdots H_O$	102 (4)	$N—H_N\cdots O^{ii}$	137 (3)
$P—O\cdots O^{i}$	116·4 (1)		
$O\cdots H_O\cdots O^{i}$	145 (8)		

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{4}-z$; (ii) $-y, \frac{1}{2}-x, \frac{1}{4}+z$; (iii) $-x, -y, z$; (iv) $-y, x, -z$; (v) $-y, x, 1-z$.

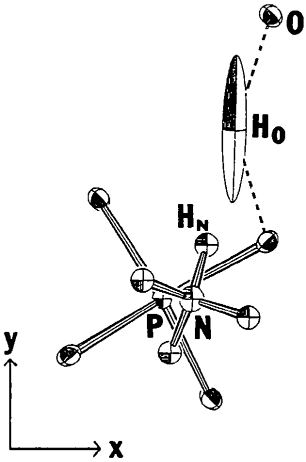

Fig. 1. Projection at 5° from the *c* axis. Thermal vibration ellipsoids drawn at the 10% probability level (*ORTEP*; Johnson, 1976).

0·031, $S = 1·736$, $w = 1/\sigma^2$, with $\sigma = [\sigma_{cs}^2 + (0·02 \times F_o)^2]^{1/2}$, last cycle gave $(\Delta/\sigma)_{max} = 0·03$. Atomic parameters are listed in Table 1,* distances and angles in Table 2. The crystal structure is shown in Fig. 1. A difference Fourier synthesis excluding H_O from F_{calc} is shown in Fig. 2(*a*).

An alternative model was refined in which the H_O was placed with a site factor of a half at 0·95 Å from O, with P—O—H angle 109° and with $O^{(iii)}$—P—O—H angle −84° (coordinates H_O: 0·110, 0·201, 0·147), in order to give the best fit to the observed residual electron density for the H_O atom (Fig. 2). Only U_{iso} for H_O was refined, the other atoms being treated as before. Final $R = 0·022$, $wR = 0·034$, $S = 1·821$, last cycle gave $(\Delta/\sigma)_{max} = 0·01$. U_{iso} of H_O is 0·09 (3) Å^2. None of the other parameters varied more than 1σ from the values obtained from the previous refinement. The two models are considered to be equally effective.

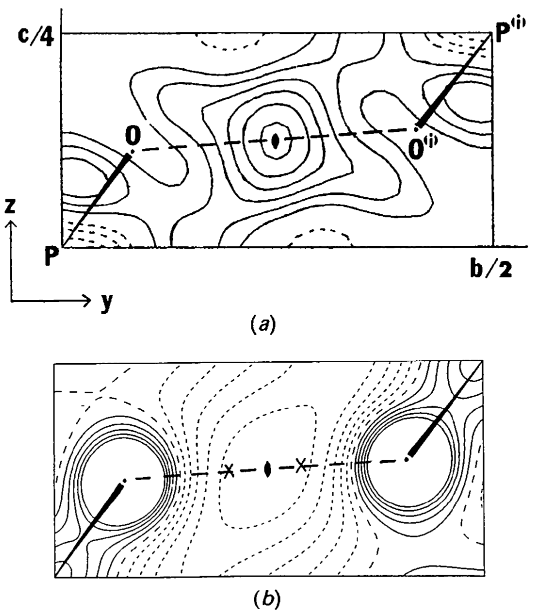

Fig. 2. Maps in the section $x = 0·094$ through the maximum electron density for H_O. (*a*) Final difference Fourier synthesis with H_O excluded from F_{calc}. Contours at intervals of 0·05 e Å^{-3}. The e.s.d. in electron density is 0·04 e Å^{-3}. (*b*) Electrostatic potential for the crystal structure with H_O removed. Contours are at intervals 0·2 e Å^{-1} with zero contour dashed and electronegative contours dotted. Contours are omitted for the strongly electropositive region near the O atoms. Crosses mark the sites 0·95 Å from the O atoms which might be occupied if H_O were bimodally distributed.

In Fig. 2(*b*) we show the electrostatic potential in the crystal in the O—H—O region. This was calculated according to Stewart (1982). We obtain the difference deformation potential including long-

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54092 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

range effects by means of a Fourier synthesis with coefficients $(F_o - F_H)\ \lambda^2/\sin^2\theta$ where F_H is the contribution of H_O to the structure factor. Potentials are then added for neutral spherical Hartree–Fock atoms (except for H_O). The electrostatic potential in the O—H—O region is a basin with a minimum of $-1{\cdot}13$ e Å^{-1} at the twofold axis. Alternative H_O sites are near the walls, but are located in a flattened region where there would not be a strong electrostatic force directed towards the central minimum.

Related literature. Ammonium dihydrogenphosphate and related isomorphous crystals have been extensively studied because of their piezoelectric properties. The X-ray structure has been determined for tetragonal $NH_4H_2PO_4$ at 153 K and for the antiferroelectric orthorhombic structure at 143 K (Keeling & Pepinsky, 1955). Following these studies of the structure in projection, the structure has been redetermined three-dimensionally at 152 K and 143 K by Fukami, Akahoshi, Hukuda & Yagi (1987) and at room temperature by Khan & Baur (1973). Because of interest in the O—H—O system, the structure was also determined in projection by neutron diffraction for the tetragonal form at ambient temperature (Tenzer, Frazer & Pepinsky, 1958). High-resolution neutron diffraction data for the isomorphous KH_2PO_4 have been used to show that the proton in the O—H—O system is distributed bimodally (Kuhs, Nelmes & Tibballs, 1983), although no details were given.

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Structure of Caesium Dicyanamide

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Abstract. $Cs[(CN)_2N]$, $M_r = 199{\cdot}0$, monoclinic, $C2/c$, $a = 9{\cdot}385\,(5)$, $b = 12{\cdot}702\,(9)$, $c = 8{\cdot}261\,(5)$ Å, $\beta = 110{\cdot}94\,(4)°$, $V = 920\,(2)$ Å^3, $Z = 8$, $D_m = 2{\cdot}86$, $D_x = 2{\cdot}873\,(3)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 8{\cdot}0$ mm^{-1}, $F(000) = 704$, $T = 299\,(1)$ K, $R = 0{\cdot}050$ for 1012 reflections.

Experimental. The crystals of the title compound were prepared as very thin plates by dropping a freshly obtained (through ion exchange) aqueous solution of dicyanamide $[NH(CN)_2]$ into an aqueous solution of Cs_2CO_3, and then allowing water to evaporate at ambient temperature. D_m by flotation in $C_2H_4Br_2/CH_2I_2$. Crystal $0{\cdot}55 \times 0{\cdot}40 \times 0{\cdot}04$ mm was cut from a larger one, and placed in a capillary. Syntex $P2_1$ diffractometer, lattice parameters from 15 reflections with 2θ between 18 and 28° (Mo $K\alpha$), variable $\omega/2\theta$ scan, $4 < 2\theta < 60°$, two standards every 50 reflections, mean relative e.s.d. of the control reflections 2·4%, index range $h\ 0 \rightarrow 13$, $k\ -17 \rightarrow 17$, $l\ -11 \rightarrow 10$. 2890 intensities measured of which 2034 had $I \geq 3\sigma(I)$ and of which 1012 were unique, R_{int} (after absorption corrections) = 0·0335. Absorption corrections with *DIFABS* (Walker & Stuart, 1983) between 0·620 and 1·396. Structure was solved with *SHELX*86 (Sheldrick, 1986) and refined with *SHELX*76 (Sheldrick, 1976). Neutral atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), real and imaginary components of anomalous dispersion included for all atoms. Final full-matrix least-squares refinement based on F with all atoms anisotropic, $R = 0{\cdot}0500$,

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