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Hydrogen Bonding in the Crystalline State. The Crystal Structure of $NaH_2PO_4.2H_2O$ by X-ray and Neutron Diffraction*

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Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4.2H_2O$) is orthorhombic, space group $P2_12_12_1$, with $a=7{\cdot}275$ (9), $b=11{\cdot}384$ (6) and $c=6{\cdot}606$ (4) Å; $Z=4$. The structure was solved from X-ray measurements by direct methods and refined anisotropically with X-ray ($R=0{\cdot}032$ over 898 reflexions) and neutron data ($R=0{\cdot}059$ over 751 reflexions); both sets of intensities were collected on single-crystal diffractometers (Mo $K\alpha$ radiation and $\lambda=1{\cdot}035$ Å respectively). A correction for secondary extinction was applied to the neutron data. While the two acidic hydrogens form strong hydrogen bonds (2·577 and 2·536 Å), one of those of the water molecules is involved in a very weak O–H···O contact of 3·106 Å. The P tetrahedra are linked by hydrogen bonds in a distorted diamond-type framework. Six systems of pseudo-hexagonal channels are present; the largest of them, along [001], accommodates a chain of Na octahedra. The configuration of the hydrogen-bonded groups is described. Bond-strength/bond-length correlations are discussed and their weakness for the case of strongly hydrogen-bonded atoms is pointed out. A comparison of X-ray and neutron results by χ^2 tests and half-normal probability plots shows significant differences for the thermal parameters only.

Introduction

The title compound is the most hydrated member of the family of sodium dihydrogen phosphates which includes NaH_2PO_4 and $NaH_2PO_4.H_2O$ (Pascal, 1966).†

There are several reasons for undertaking the structural study of $NaH_2PO_4.2H_2O$: (1) the presence of fairly short hydrogen bonds in the related anhydrous compound (Catti & Ferraris, 1974), and the exclusion of symmetry-restricted bonds because of the space group ($P2_12_12_1$); (2) the interest in investigating the configurations of $(H_2PO_4)^-$ groups and of water molecules in a series of hydrated salts, in order to understand the reasons for structural stability; (3) the need for tests of bond-strength/bond-length correlations, particularly in highly hydrogenated compounds.

Preparation and crystal data

Colourless and transparent crystals of $NaH_2PO_4.2H_2O$ were obtained by recrystallization of the commercial product from water solutions, at room temperature. Although Joly & Dufet (1886) claim that the crystals are stable, in fact they lose water easily in the open air, and are stable in closed containers only. Small crystals look 'octahedral' because of the presence of {101} and {011} prisms (*cf.* Joly & Dufet, 1886); large crystals are (011) tabular and show several other forms.

Weissenberg photographs and single-crystal diffractometry confirmed the orthorhombic cell (Pascal, 1966) and showed that the space group is $P2_12_12_1$ (No. 19), on the basis of systematic absences. By least-squares refinement of 25 θ values ($17{\cdot}83° \le \theta \le 25{\cdot}54°$, $\lambda K\alpha = 0{\cdot}7107$ Å), measured on a single-crystal diffractometer, the following unit-cell parameters were obtained: $a=7{\cdot}275$ (9), $b=11{\cdot}384$ (6), $c=6{\cdot}606$ (4) Å. Other physical data are: M.W. 156·008, $V=547{\cdot}1$ Å^3, $Z=4$, $D_c=1{\cdot}894$ g cm^{-3}, $F(000)=384$, μ(Mo $K\alpha$) $=5{\cdot}4$ cm^{-1}.

Intensity measurements

X-rays

Intensities of two centrosymmetrical octants were measured (1922 reflexions, Mo $K\alpha$ radiation, graphite monochromator, $2\theta \le 60°$) from a bipyramidal crystal with body diagonals of 0·34 mm. An automatic Philips four-circle diffractometer was used, with the following measurement conditions: ω-scan, scanning speed 0·06° s^{-1}, scan width $\Delta\omega=1{\cdot}7°$, 5 s background time on both sides of each peak in the stationary positions.

Although the crystal was sealed in a Lindemann glass tube, a plot of the intensities of three reference reflexions (074, 454 and 364) against time showed that the diffracting power had started to decrease at about half the measurement time (24 h in total), and at the end had reached 93% of the initial value. The intensities were corrected for this effect. Equivalent reflex-

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† From the axial ratio of $a:b:c=0{\cdot}9147:1:1{\cdot}5687$, $NaH_2PO_4.2H_2O$ could be isostructural with $NaH_2AsO_4.2H_2O$ ($a:b:c=0{\cdot}9177:1:1{\cdot}6039$).

ions *hkl* and $\bar{h}\bar{k}\bar{l}$, not significantly different, were arithmetically averaged; after removal of the systematically absent reflexions and those with $|F_o| \leq 2\sigma(|F_o|)$, 898 independent reflexions were obtained.

A sample test showed a fairly constant transmission factor (0·94–0·96 for $|F_o|$) and therefore no absorption correction was applied. Atomic scattering factors were linear interpolations of the values reported for neutral atoms in *International Tables for X-ray Crystallography* (1962).

Neutrons

The measurements were performed with a four-circle automatic diffractometer at the Karlsruhe Research Reactor (FR2).

The crystal (tabular 2·6 × 6·3 × 6·5 mm) was mounted with its x axis along the instrumental φ axis and was sealed in a vanadium container. 965 reflexions were collected for all reciprocal lattice points with $2\theta \leq 80°$ and for part of those with $80° < 2\theta \leq 110°$; $\lambda = 1·035$ Å from a Cu(111) monochromator, $\omega/2\theta$ scan in 14–20 steps with $\Delta\omega = 0·08–0·12°$. The background measurements were made by ω-scanning the background profiles with the detector held in the respective Bragg positions. Monitor counts per step were 10^5, both for peak and for background. The removal of weak [122 with $I \leq 3\sigma(I)$], of systematically absent and of duplicate reflexions left a final set of 751 independent observations. No absorption correction was applied. The following scattering lengths were used (Bacon, 1972): P 5·10, Na 3·60, O 5·80 and H $-3·74 \times 10^{-13}$ cm.

Structure analysis

The main calculations were performed with the aid of the X-RAY System programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and by *MULTAN* (Germain, Main & Woolfson, 1971).

X-rays

The crystal structure was solved by direct methods. The H atoms were located through difference maps; their positions and temperature parameters ($B = 2$ Å^2) were kept fixed in the refinement (Table 1).

During the last stage of the refinement by *ORFLS* the following weighting scheme was used ($0·044 \leq w \leq 1$):

$$w = 1/[16\sigma^2(F_o) + 0·12|F_o| + 0·003|F_o|^2] .$$

$\sigma(|F_o|)$ is referred to just the counting statistics. $w\Delta^2$ values averaged (*vs.* $|F_o|$ and sin θ) over groups of reflexions were within $\pm 2·5(w\Delta^2)_{\text{mean}}$, except for the group of about 100 reflexions with sin $\theta \leq 0·25$ and that of the eight strongest reflexions, with $|F_o| < |F_c|$; however, no secondary extinction correction was applied, since a graph of the function $I_c/I_o = k(1 + gI_c)$ appeared satisfactorily constant (0·97–1·03). The final fractional coordinates and the B_{ij} coefficients of the expression

$$\exp\left(-\tfrac{1}{4} \sum_{i=1}^{3} \sum_{j=1}^{3} B_{ij}h_i h_j a_i^* a_j^*\right)$$

are reported in Table 1; the corresponding R values were $R = 0·032$, $R_w = 0·043$ with a standard error of an

Table 1. *X-ray (first line) and neutron (second line) fractional coordinates* ($\times 10^4$) *and vibrational parameters* (Å$^2 \times 10^2$), *with the significant figures of the e.s.d.'s in parentheses*

	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	7135 (1)	6508 (1)	9560 (1)	107 (2)	104 (2)	123 (2)	−1 (2)	−4 (2)	−11 (2)
	7135 (4)	6508 (2)	9557 (3)	107 (10)	60 (6)	94 (6)	−13 (7)	1 (7)	−11 (5)
Na	3928 (2)	4204 (1)	7803 (2)	178 (4)	193 (5)	187 (5)	−17 (4)	−7 (4)	−26 (4)
	3918 (4)	4202 (4)	7805 (5)	154 (15)	138 (10)	151 (10)	−18 (12)	7 (12)	−28 (8)
O(1)	7261 (3)	7819 (2)	9452 (3)	179 (7)	138 (6)	211 (8)	−10 (7)	−61 (8)	−4 (7)
	7260 (4)	7824 (2)	9451 (3)	172 (10)	55 (5)	189 (6)	11 (7)	−36 (8)	−2 (5)
O(2)	8291 (3)	5853 (2)	8012 (3)	173 (8)	194 (8)	202 (8)	4 (7)	44 (7)	−53 (7)
	8288 (4)	5858 (2)	8017 (4)	166 (10)	121 (6)	162 (6)	24 (8)	37 (7)	−52 (5)
O(3)	5110 (3)	6038 (2)	9284 (3)	132 (7)	172 (7)	247 (9)	−10 (6)	−8 (7)	−58 (7)
	5107 (4)	6040 (2)	9298 (4)	94 (9)	116 (6)	229 (8)	−9 (8)	0 (8)	−61 (6)
O(4)	7765 (3)	6142 (2)	11756 (3)	193 (8)	200 (7)	154 (7)	−31 (7)	−28 (7)	34 (6)
	7764 (4)	6137 (2)	11756 (3)	189 (10)	136 (7)	124 (6)	−28 (8)	−38 (7)	37 (5)
W(1)	453 (4)	7229 (2)	5454 (4)	297 (10)	265 (9)	204 (8)	−9 (9)	51 (9)	−14 (9)
	455 (6)	7234 (2)	5459 (4)	304 (14)	183 (8)	194 (8)	−13 (10)	50 (11)	−15 (7)
W(2)	1229 (3)	4570 (2)	9732 (4)	204 (8)	202 (8)	268 (9)	20 (7)	14 (9)	10 (8)
	1227 (5)	4565 (2)	9737 (4)	183 (11)	152 (8)	228 (8)	29 (10)	21 (10)	−13 (7)
H(1)	4250	6450	9700	200					
	4031 (7)	6540 (4)	9827 (7)	234 (20)	173 (12)	245 (14)	13 (16)	16 (16)	−32 (11)
H(2)	7500	5350	12150	200					
	7346 (7)	5316 (4)	12192 (7)	269 (19)	202 (15)	215 (12)	−10 (16)	−29 (15)	29 (10)
H(3)	0	6900	6550	200					
	−304 (11)	6793 (5)	6411 (9)	410 (28)	279 (18)	288 (16)	−18 (20)	89 (22)	−11 (16)
H(4)	1550	7500	6050	200					
	1456 (12)	7508 (8)	6224 (12)	366 (26)	473 (29)	408 (25)	−29 (28)	−22 (25)	−22 (24)
H(5)	0	5000	9050	200					
	314 (10)	5039 (5)	9046 (9)	356 (26)	269 (18)	322 (18)	50 (23)	−31 (22)	25 (16)
H(6)	750	3900	9950	200					
	692 (10)	3802 (5)	9881 (12)	336 (27)	229 (18)	470 (27)	−24 (20)	−5 (22)	21 (17)

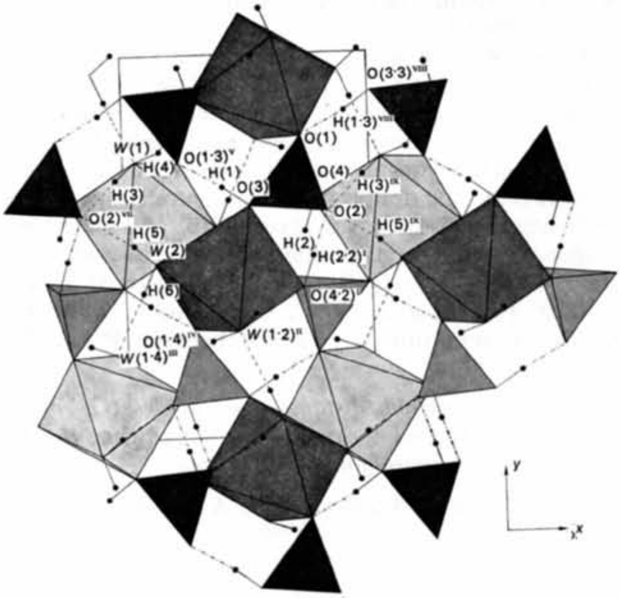

Fig. 1. Unit cell of $NaH_2PO_4.2H_2O$ in projection on to the (001) plane. O(2,2)$^{\mathrm{VI}}$ and O(4,3)$^{\mathrm{V}}$, which are hydrogen bonded to H(2) and to H(4), respectively, are not shown.

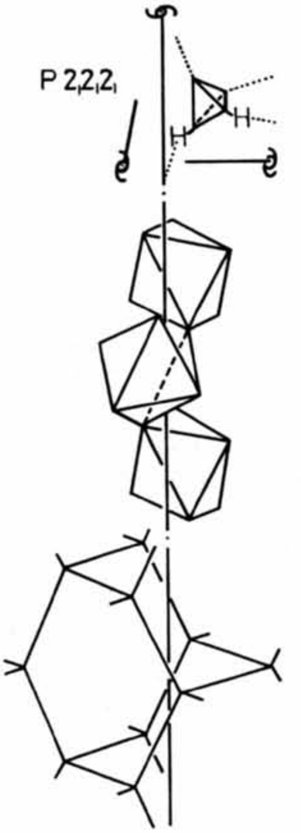

Fig. 2. Chain of Na octahedra within a channel of $\cdots$H–O–P–O$\cdots$H bonds along the z axis.

observation of unit weight of 1·89. In the last difference map the strongest ripples ($-0·4$ e Å^{-3}) were around the phosphorus atom.

Neutrons

Fourier difference maps against the isotropically refined X-ray solution were calculated; they finally showed all six independent H atoms. The anisotropic least-squares refinement led to the parameters reported in Table 1. In the final stage of the refinement a secondary extinction correction was applied, according to the above relationship; we obtained $g=5·2\times10^{21}$ cm^{-2} and $k=0·894$. The following weighting scheme was used ($0·031\le w\le 1$):

$$w=1/[0·2|F_o|+0·0015|F_o|^2-5\sin\theta]\,.$$

$w\Delta^2$ values averaged over groups of reflexions were within $\pm2·3$ $(w\Delta^2)_{\text{mean}}$. The following final R values were obtained:* $R=0·059$, $R_w=0·070$, standard error of an observation of unit weight$=1·10$; $0·032\le R\le 0·100$ for reflexions grouped with $|F_o|$ and $\sin\theta$. The last difference map showed randomly distributed ripples with a maximum height of $+10^{-13}$ cm Å^{-3} and a minimum of $-1·6\times10^{-13}$ cm Å^{-3} close to the phosphorus.

Description and discussion of the structure

Structure and hydrogen bonding

The dihydrogen phosphate group (Table 2) forms the asymmetric unit of a three-dimensional framework of hydrogen-bonded tilted P-tetrahedra, two corners of which are donors and the others acceptors of the framework bridges (Fig. 1). The arrangement follows the principle of a distorted diamond-type framework (Figs. 2 and 3), taking P for C and P–O–H$\cdots$O–P for the C–C bonds. Thus the hydrophosphate framework shows six systems of pseudo-hexagonal channels. The [001] channels, having the widest dimensions, accommodate chains of corner-sharing Na octahedra (Fig. 2). Four corners of every octahedron (Table 3) are contributed by the framework; the other two, including the common corners, are water molecules. Both of the hydrogen bonds of $W(1)$† and one of $W(2)$ contribute to the linkage of the Na polyhedra to the framework, whereas the other hydrogen bond of $W(2)$ interlinks contiguous chains.

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* Two lists (neutron and X-ray data) of $|F_o|$ and $|F_c|$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31289 (12 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† Figures in parentheses denote atoms in the asymmetric unit; a second figure ranging from 2 to 4 is included for atoms in the positions: $\frac{1}{2}-x,\bar{y},\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$; $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$. Roman numerals represent the translations: (I) $\mathbf{a}+\mathbf{b}-\mathbf{c}$; (II) $+\mathbf{b}$; (III) $-\mathbf{b}+\mathbf{c}$; (IV) $+\mathbf{a}-\mathbf{b}+\mathbf{c}$; (V) $-\mathbf{a}+\mathbf{b}+2\mathbf{c}$: (VI) $+\mathbf{a}+\mathbf{b}$; (VII) $-\mathbf{a}$; (VIII) $+\mathbf{b}+2\mathbf{c}$; (IX) $+\mathbf{a}$.

Table 2. *Interatomic distances* [*uncorrected* (*A*) *and corrected* (*B*) *for thermal motion* (*riding model*)] *and angles* (O–P–O) *for neutron* (*N*) *and X-ray* (*X*) *results in the* PO_4H_2 *group*

The e.s.d.'s are 0·003 Å and 0·2°, 0·002 Å and 0·1° for *N* and *X* respectively; 0·4° for P–O–H angles, *N* only.

	N		*X*	
	A	*B*	*A*	*B*
P–O(1)	1·502 Å	1·509 Å	1·497 Å	1·504 Å
P–O(2)	1·512	1·520	1·520	1·529
P–O(3)	1·578	1·585	1·578	1·586
P–O(4)	1·581	1·589	1·577	1·585
Average	1·543	1·551	1·543	1·551
O(1)–O(2)	2·543 Å	115·0°	2·545 Å	115·1°
O(1)–O(3)	2·566	112·8	2·563	112·9
O(1)–O(4)	2·478	107·0	2·469	106·8
O(2)–O(3)	2·473	106·3	2·471	105·8
O(2)–O(4)	2·520	109·1	2·524	109·2
O(3)–O(4)	2·527	106·3	2·532	106·7
Average	2·518	109·4	2·517	109·4
P–O(3)–H(1)		119·2		118
P–O(4)–H(2)		114·6		116

Geometry of the groups with hydrogen bonds

The *W*(1) water molecule shows (Table 4) a very long (3·1 Å) and bent (151°) O···O contact with O(4,3)^{V} which, being also donor of an acidic hydrogen bridge, is outstandingly far from the H_2O plane (1·1 Å; the angle between H···O and the H_2O plane is 29°); this case lies probably at the boundaries of very weak hydrogen bonds.

The acceptors are situated in a *trans* arrangement with respect to the H_2O planes in both water molecules which, according to Ferraris & Franchini-Angela's (1972) classification, are of class 2; *W*(1) is of type *G* (Na and H directed towards the lone pairs), and *W*(2) is of type *A* (two Na atoms directed towards the lone pairs). The observed *W*–H and H···O distances agree with those predicted from linear relationships which were reported in the above paper. Similar correlations for O···H distances given by Falk & Knop (1973), however, would cause the present observations to be underestimated.

While O(1), O(3) and O(4) of the P tetrahedra are Na coordinated, O(2) is not. This oxygen is acceptor of three hydrogen bonds; one of them is acidic and the other two are donated by the water molecules. O(3) and O(1) are donors and acceptors of acidic framework bridges only; the donor and the acceptor properties of O(4) have been discussed above. O(3) and O(1) have 'trigonal' planar sp^2-type coordinations; in both cases the P–O–H or H···O–P angles have practically values of 120° (119·2° and 120·1°, respectively), while the maximum repulsion is observed between P and Na

Table 3. *Interatomic distances and angles* (O–Na–O) *for neutron* (*N*) *and X-ray* (*X*) *results involving the* Na *coordination polyhedron*

The e.s.d.'s are 0·005 Å and 0·2°, 0·003 Å and 0·1° for *N* and *X* respectively.

	N		*X*	
Na–O(1,4)^{IV}	2·328 Å		2·335 Å	
Na–*W*(1,2)^{II}	2·440		2·435	
Na–*W*(2,2)^{III}	2·468		2·464	
Na–*W*(2)	2·373		2·378	
Na–O(4,2)^{I}	2·541		2·534	
Na–O(3)	2·470		2·461	
Average	2·437		2·435	
W(1,2)^{II}–O(1,4)^{IV}	3·500 Å	94·4°	3·498 Å	94·3°
W(1,2)^{II}–*W*(2)	3·201	83·3	3·201	83·4
W(1,2)^{II}–O(4,2)^{I}	3·373	85·2	3·365	85·2
W(1,2)^{II}–O(3)	3·827	102·4	3·820	102·6
W(2,2)^{III}–O(1,4)^{IV}	3·114	80·9	3·112	80·8
W(2,2)^{III}–*W*(2)	3·915	107·9	3·910	107·7
W(2,2)^{III}–O(4,2)^{I}	3·366	84·4	3·367	84·7
W(2,2)^{III}–O(3)	3·239	82·0	3·236	82·2
O(1,4)^{IV}—*W*(2)	3·577	99·1	3·580	98·9
O(1,4)^{IV}—O(4,2)^{I}	3·569	94·2	3·568	94·2
O(3)——O(4,2)^{I}	3·370	84·5	3·368	84·8
O(3)——*W*(2)	3·297	85·8	3·294	85·8
Average	3·446	90·3	3·443	90·4
W(1,2)^{II}–*W*(2,2)^{III}	–	168·3	–	168·4
O(1,4)^{IV}—O(3)	–	162·9	–	162·9
W(2)——O(4,2)^{I}	–	163·1	–	163·3

Table 4. *Interatomic distances* (Å), *uncorrected* (*left*) *and corrected* (*right*) *for thermal motion* (*riding model*), *for* O–H *distances only, and angles* (°) *involving the hydrogen bonding for neutron* (*N*) *and X-ray* (*X*) *results with e.s.d.'s below*

A prime denotes an atom of a water molecule on the following line.

A *B* *C*	*AB*			*AC*		*BC*		*BB'*		*ABC*		*BAB'*		*CAC'*	
	N		*X*	*N*	*X*	*N*	*X*	*N*	*X*	*N*	*X*	*N*	*X*	*N*	*X*
O(3) –H(1)···O(1,3)^{V}	1·028	1·036	0·83	2·577	2·586	1·553	1·76			173·4	173				
	6			3	3	6				5					
O(4) –H(2)···O(2,2)^{VI}	1·023	1·033	0·96	2·536	2·537	1·515	1·59			175·1	169				
	5			3	3	5				4					
W(1)–H(3)···O(2)^{VII}	0·976	0·991	0·88	2·792	2·790	1·819	1·97			174·6	153				
	7			4	3	7		1·522	1·36	6		105·2	96	106·4	106·3
W(1)–H(4)···O(4,3)^{V}	0·939	0·973	0·94	3·106	3·109	2·251	2·30	11		151·0	144	7		1	1
	9			4	3	9				7					
W(2)–H(5)···O(2)^{VII}	0·970	0·991	0·90	2·834	2·827	1·872	1·94			170·8	169				
	7			4	3	7		1·537	1·41	7		105·9	107	97·9	97·9
W(2)–H(6)···*W*(1,4)^{III}	0·956	0·984	0·85	2·925	2·936	1·983	2·11	9		167·8	163	6		1	1
	7			4		7				7					

(P–O–Na = 131·0 and 132·8°, respectively), and the minimum one is between H and Na (Na–O–H = 109·7 and 100·8°, respectively). Because the bending angles O–H···O of the acidic hydrogen bonds are small, the acceptor oxygens lie approximately in the respective coordination planes. O(2) and O(4) show rather regular tetrahedral environments; the values of the P–O–H or H···O–P angles are larger than the tetrahedral value with the exception of P–O(4)···H(4,3)$^{\mathrm{VIII}}$ = 103·8°. The two acidic H atoms are in *trans* positions with respect to the P–O(3)–O(4) plane which forms angles of 60° and 35°, respectively, with the O(3)–H(1) and O(4)–H(2) bonds.

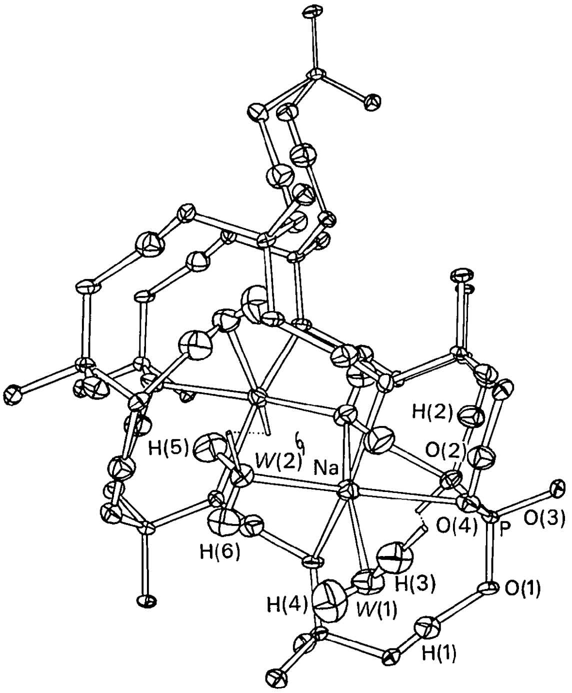

Fig. 3. One open cage $[\mathrm{H_2PO_4}]_{10}$ with cations and water molecules, 2_1 axis ∥ [001]; to be compared with Fig. 2.

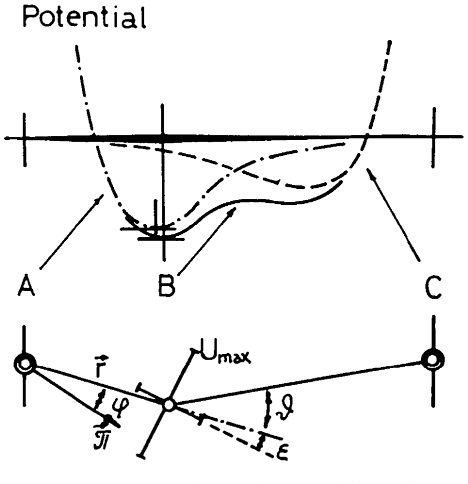

Fig. 4. Qualitative illustrations of potentials and geometrical parameters of a bent unsymmetrical hydrogen bond [from Zigan (1974)].

Table 5. *Experimental values for* $\mathrm{NaH_2PO_4.2H_2O}$ (*see Fig.* 4)

A–C (Å)	A–$B+\Delta$*(Å)	θ	ε	$U_{\max}$(Å)	Bond
2·536	1·023 + 0·010	5°	15°	0·191	O(4)–H(2)···O(2)
2·577	1·028 + 0·008	7	37	0·182	O(3)–H(1)···O(1)
2·792	0·976 + 0·015	6	35	0·241	O(2)–H(3)···*W*(1)
2·834	0·970 + 0·021	9	13	0·221	O(2)–H(5)···*W*(2)
2·925	0·956 + 0·028	12	4	0·245	W(1)–H(6)···*W*(2)
3·106	0·939 + 0·034	29	6	0·248	O(4)–H(4)···*W*(1)

* Thermal motion correction for O–H.

With respect to some characteristic geometrical parameters of asymmetrical bent hydrogen bonds, $\mathrm{NaH_2PO_4.2H_2O}$ provides a monotonic series of six different cases, which are listed in Table 5. The observations match the theoretical model which Zigan (1974) has given for the correlations between these quantities in hydrogen bonds of medium strength. The orientation angle ε of the hydrogen's thermal ellipsoid against the donor bond, which results from superposing the convex acceptor potential function over the concave donor potential, can be considered as an indicator for the bridging function of the involved hydrogen. For short bonds ε is very strongly dependent on φ and θ, so that considerable angles may result, yet the qualitative principle of orientation, as indicated in Fig. 4, is observed. For weaker bonds, however, an observed ε angle indicates divergence between the orbital direction (π) and the interatomic vector ($\mathbf{r}$); this may be taken as proof for the presence of a bond.

Attention has often been drawn to the correlation between O–H··· and O···O. The function, as interpolated in a revised form by Bartl (1970), is shown in Fig. 5. The bond lengths from this paper as well as some recent neutron diffraction results are added as full and open circles respectively. There is good agreement for entries without corrections for thermal motion, but there is a systematic deviation between these neutron diffraction results and Lundgren's (1974) comprehensive survey: this interpolated graph of numerous other observations predicts shorter O–H bonds for bridge lengths of over 2·55 Å, perhaps because of the admixture of X-ray results.

Phosphate group

The P tetrahedron shows distortion indices (Baur, 1974) of 0·023, 0·018 and 0·011 for the P–O and O–O bond lengths and the O–P–O angles, respectively; such values are in the order, greater, smaller and equal to the average values reported by Baur for acidic phosphates (0·017, 0·025 and 0·011). The geometrical correlations proposed by the same author led to values of 1·540 and 2·515 Å for the $(\mathrm{P{-}O})_{\mathrm{mean}}$ and the $(\mathrm{O{-}O})_{\mathrm{mean}}$ distances respectively.

Bond-length/bond-strength relationships

Introducing bond strengths, s, dependent on bond distances, R, has been certainly the most useful way to account for the deviations from Pauling's second rule in most crystal structures, and inverse power curves of s *vs.* R (Brown & Shannon, 1973) represent at the moment the highest generalization of the problem. However, things are less clear as far as the H–O bond is concerned, since data on H atom positions to check the correlations are often missing.

Table 6. *Calculated individual and total* ($\sum s_i$) *bond strengths for each atom in the structure*

	O(1)	O(2)	O(3)	O(4)	W(1)	W(2)	$\sum s_i$
P	1·398	1·336	1·125	1·122			4·981
Na	0·211		0·166	0·147	0·174	0·166 0·195	1·059
H(1)	0·277		0·679				0·956
H(2)		0·293		0·686			0·979
H(3)		0·197			0·760		0·957
H(4)				0·124	0·826		0·950
H(5)		0·185				0·770	0·955
H(6)					0·163	0·795	0·958
$\sum s_i$	1·886	2·011	1·970	2·079	1·923	1·926	

The bond strengths calculated by means of Brown & Shannon's (1973) universal curves are reported in Table 6 (individual curves gave very similar results). The maximum deviations from 2 v.u. are −6% for O(1) and 4% for O(4); they just concern the two O atoms which are more under-bonded (1·59 v.u.) and over-bonded (2·42 v.u.), respectively, according to Pauling's second rule: O(1) is acceptor and O(4) is donor of a strong hydrogen bond. A similar situation is found for the compound NaH_2PO_4 (Catti & Ferraris, 1974), where, moreover, a Na atom shows a very distorted coordination. Probably, in the case of strong asymmetric hydrogen bonds the 'universal' dependence of s on R used is inadequate; the two bonds donor–H and H···acceptor seem to be too different for the use of only one single correlation.

By the use of s *vs.* O···O (strong acidic hydrogen bonds) or s *vs.* H···O curves (water molecules) the H···acceptor bonds (Brown, 1975, private communication) would have the following s values: 0·33, 0·39, 0·18, 0·09, 0·16, 0·13 for H(1)–H(6) respectively; if $s_{\text{donor}} = 1 - s_{\text{acceptor}}$, $\sum s_i$ for the corresponding six O atoms is: 1·94, 2·07, 1·96, 1·97, 1·93, 2·07 v.u. respectively, W(1)–H(4)···O(4,3)$^{\text{V}}$ would then be a weak but definite hydrogen bond.

Reliability of bond lengths and angles involving hydrogen bonds

The O···O distances of the two acidic hydrogen bonds increased by about 0·02 Å after inclusion of the H atoms in the X-ray refinement. This effect, which was also found for NaH_2PO_4 (Catti & Ferraris, 1974), could be systematic and increasing with the shortening of the O···O length. A possible model would be the following: if the electron of the H atom is not accounted for, its absence is compensated, by the least-squares refinement, by moving the donor (and perhaps the acceptor as well) towards the H position; the more linear the bond, the shorter should be the apparent O···O distance.

Another effect was observed in the present and in two other similar crystal structures which had been anisotropically refined by neutron data, $Ca(H_2AsO_4)_2$ and $MgSO_4.7H_2O$ (Ferraris, Jones & Yerkess, 1972, 1973): the correction for the thermal motion according to the riding model increases systematically with the increase of the O···O distance (Table 5).

Comparison of the X-ray and neutron parameters

The significance of the parameter differences of the two refinements (heavy atoms only) was tested statistically by means of half-normal probability plots (Abrahams & Keve, 1971) (not reported) and by χ^2 tests (Abrahams, 1974; Hamilton, 1969) (Table 7). The half-normal probability plot for all the coordinates ($\delta p_{\max} = 2·8\sigma$) is linear, except for the extremes, with a slope of 1 and intercept of 0. The χ^2 tests on the coordinates x, y and z show, however, a possible significant difference between the two sets of y parameters as do the

Table 7. χ^2 *analysis for sets of parameters with* ν *degrees of freedom*; $\delta p_{\max}$ *is the maximum value of the weighted* $p_X - p_N$ *difference for the set*

	ν	$\delta p_{\max}$	χ^2	$\chi^2_{\nu,\,0·05}$
x	8	1·40	3·4	15·5
y	8	1·77	16·4	
z	8	2·80	11·0	
B_{11}	8	3·16	15·7	
B_{22}	8	10·63	393	
B_{33}	8	9·80	176	
B_{12}	8	2·12	11·6	
B_{13}	8	2·21	8·7	
B_{23}	8	2·16	5·0	
All coord.	24	2·80	30·8	36·4
All B_{ij}	48	10·63	610	65
All par.	72	10·63	641	92

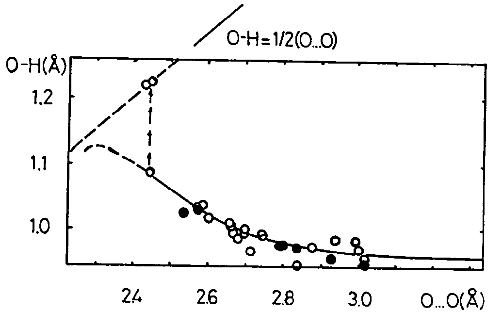

Fig. 5. Correlation of O–H *vs.* O···O. Full circles, this work; open circles, other neutron diffraction investigations as referenced; full line after Pimentel & McClellan (1959) and Bartl (1970). $CaHPO_4$ (Denne & Jones, 1971). $CaHAsO_4.2H_2O$ (Ferraris, Jones & Yerkess, 1971). $CaHPO_4.2H_2O$ (Curry & Jones, 1971). $Ca(H_2AsO_4)_2$ (Ferraris, Jones & Yerkess, 1972). $NaH_2AsO_4.H_2O$ (Ferraris, Jones & Sowden, 1974).

relative χ^2 tests for the P–O and Na–O bond lengths. Considering, however, that least-squares calculations generally underestimate the e.s.d.'s, it can be concluded that the positional parameters and the bond distances from the two refinements are not significantly different.

Both χ^2 tests and half-normal probability plots were performed for the coefficients of the thermal ellipsoids in order to achieve homogeneity with reported data; however, analysing the principal axis lengths (normal probability plot in this case) and direction cosines of the ellipsoids would perhaps be a better method from a physical point of view. The χ^2 tests of B_{ij} values (i and j fixed) (Table 7) cannot be given a direct interpretation, but the systematically bigger thermal motion of the electron density with respect to the nuclear one (Table 8) should be clearly related to the inadequacy of the spherical approximation of the scattering factors (*cf.* Hamilton, 1969). With the lack of appropriate values, the hypothesis of constant e.s.d.'s for the δp_i of the direction cosines is accepted, and then a half-normal probability plot should be valid, except for a scale factor. Such a plot is linear with slope about 1 for the first 50 smallest δp_i (out of 72), and then it assumes a slope of about 2. Furthermore, in all the P–O bonds the orientation of thermal motion is such that the longest ellipsoid semi-axis of the O atom always has an angle with the bond close to 90° (86–93° for X-rays, 86–97° for neutrons) and the shortest semi-axis is nearly parallel to the same bond; it should then be concluded that, while the dimensions of the X-ray thermal ellipsoids are systematically greater than the neutron ones (Table 8), the orientations of the ellipsoids are not significantly different in the two cases.

Table 8. *Neutron* (N) *and X-ray* (X) *parameters characterizing the principal directions of thermal vibrations for the atoms in the structure: root-mean-square amplitudes* (A) *and angles which the principal directions make with the crystallographic* $x(B)$, $y(C)$ *and* $z(D)$ *axes*

	A		*B*		*C*		*D*	
	N	*X*	*N*	*X*	*N*	*X*	*N*	*X*
P	0·111 Å	0·117 Å	107°	163°	101°	73°	20°	91°
	0·119	0·128	21	98	107	114	77	25
	0·083	0·111	77	106	20	150	75	115
Na	0·136	0·154	35	37	84	102	124	124
	0·152	0·166	60	103	126	40	51	127
	0·120	0·139	75	56	37	53	57	55
O(1)	0·135	0·136	39	117	86	36	51	112
	0·166	0·181	129	128	93	88	39	38
	0·083	0·125	95	50	5	54	90	61
O(2)	0·148	0·154	40	43	53	49	104	81
	0·162	0·182	59	70	109	124	38	41
	0·093	0·124	113	126	43	60	56	50
O(3)	0·113	0·137	37	126	123	44	105	68
	0·180	0·188	89	91	114	118	24	28
	0·103	0·125	53	36	42	59	72	73
O(4)	0·129	0·145	53	40	46	50	67	88
	0·169	0·177	38	127	116	47	116	65
	0·107	0·130	82	76	125	110	36	25
W(1)	0·154	0·182	72	75	36	15	120	90
	0·203	0·202	23	28	97	104	68	66
	0·146	0·151	104	113	55	84	38	24
W(2)	0·158	0·166	40	48	55	48	107	108
	0·173	0·186	69	76	91	78	21	18
	0·128	0·152	122	135	35	44	77	88
H(1)	0·172		27		70		107	
	0·182		67		105		28	
	0·141		103		26		69	
H(2)	0·168		60		51		54	
	0·191		31		105		117	
	0·150		98		43		132	
H(3)	0·187		83		7		89	
	0·241		28		96		62	
	0·175		118		88		28	
H(4)	0·230		117		83		28	
	0·248		101		17		103	
	0·210		30		74		66	
H(5)	0·205		82		62		29	
	0·221		27		71		108	
	0·171		115		34		112	
H(6)	0·208		12		101		86	
	0·245		93		85		6	
	0·168		79		12		94	

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Studies in Molecular Structure, Symmetry and Conformation. XIII. Crystal and Molecular Structure of D-Alloisoleucine Hydrochloride Monohydrate*

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D-Alloisoleucine hydrochloride monohydrate is orthorhombic, space group $P2_12_12_1$, with $a=6{\cdot}13$, $b=24{\cdot}03$, $c=6{\cdot}80$ Å, $Z=4$. The structure was solved by the heavy-atom method and refined to an R of 0·075 with 1054 visual reflexions. The structure is not isomorphous with D-isoleucine hydrochloride monohydrate but has many common structural features.

Introduction

An X-ray crystallographic investigation of D-alloisoleucine.HCl.H_2O was undertaken as part of a series of analyses of stereoisomeric forms of amino acids with more than one asymmetric carbon. The present study forms a parallel with the structure of D-isoleucine.HCl.H_2O (Trommel & Bijvoet, 1954). Results for D-alloisoleucine are reported separately (Varughese & Srinivasan, 1976). Investigation of a number of such crystalline forms leads to information on configurational and conformational variations (Srinivasan, Varughese & Swaminathan, 1973, 1974).

Experimental

D-Alloisoleucine was dissolved in dilute hydrochloric acid and crystals were obtained by slow evaporation of the solution. The crystals were elongated along **a** with well developed {010} faces and exhibited a tendency to cleave perpendicular to **b**. Cell dimensions were measured on $hk0$ and $h0l$ precession photographs. The density was measured by flotation in benzene/bromoform.

Crystal data‡

Orthorhombic, $a=6{\cdot}13$ (1) [6·13], $b=24{\cdot}03$ (2) [25·01], $c=6{\cdot}80$ (1) [6·79] Å. Systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd; space group $P2_12_12_1$, $C_6H_{13}O_2N.HCl.H_2O$, $M=185{\cdot}6$, $D_m=1{\cdot}258$, $D_x=1{\cdot}23$ g cm^{-3}, μ for Cu $K\alpha=33$ cm^{-1}.

Intensities were collected with Ni-filtered Cu $K\alpha$ (1·5418 Å) radiation for layers hkl, $l=1$ to 5 and hkl, $h=1$ to 3 by the equi-inclination Weissenberg technique. The specimen had a cross-section of about 0·15 × 0·15 mm for the c and about 0·15 × 0·25 mm for the a axis data. The intensities were estimated visually and corrected for Lorentz, polarization and spot shape factors (Phillips, 1954). No absorption correction was applied. The two sets were correlated (Rollett & Sparks, 1960) through 521 common reflexions. The discrepancy index was 0·10. 1054 independent reflexions were observed which is about 77% of the reflexions accessible.

Structural determination and refinement

This structure has the same space group and very nearly the same cell dimensions as D-isoleucine.HCl–H_2O, suggesting that the two structures could be isomorphous. A test for isomorphism (Srinivasan & Ramachandran, 1965*a*, *b*) was performed and found to be

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‡ Values given in brackets are for D-isoleucine.HCl.H_2O (Trommel & Bijvoet, 1954).