

A Neutron Diffraction Study of the Crystal Structure of Calcium Bis(dihydrogen arsenate), $\text{Ca}(\text{H}_2\text{AsO}_4)_2$

BY G. FERRARIS

Istituto di Mineralogia e Geochimica dell'Università, via S. Massimo 24, 10123 Torino, Italy

AND D. W. JONES AND J. YERKES

School of Chemistry, University of Bradford, Bradford BD7 1DP, England

(Received 16 February 1972)

The crystal structure of $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ (triclinic, $P\bar{1}$, with two formula units per cell) has been refined by single-crystal neutron-diffraction analysis to give an R value of 0.025 over 930 independent neutron reflexions. For the non-hydrogen atoms, bond lengths, angles and thermal parameters agree very closely with the results of a recent X-ray analysis. Difference Fourier syntheses, before and after anisotropic least-squares refinement of all atomic parameters, enabled the four hydrogen atoms to be located unequivocally. In one anion, two half-hydrogens, located at centres of symmetry, are believed to be engaged in symmetrical hydrogen bonds, $\text{O}(5)\cdots\text{O}(5')=2.436 \text{ \AA}$, $\text{O}(8)\cdots\text{O}(8')=2.444 \text{ \AA}$. By contrast, another hydrogen bond is relatively long ($2.875 \pm 0.002 \text{ \AA}$) and non-linear [angle $\text{O}(7)\cdots\text{H}(3)\cdots\text{O}(3')=150.2 \pm 0.3^\circ$]. The As–O bonds carrying the half hydrogen atoms are $1.677 \pm 0.002 \text{ \AA}$ long, intermediate in length between As–O bonds with full hydrogens ($1.727 \pm 0.002 \text{ \AA}$) and those with no hydrogen atom attached ($1.651 \pm 0.002 \text{ \AA}$) (averaged values).

Introduction

The crystal structure of calcium bis(dihydrogen arsenate), $\text{Ca}(\text{H}_2\text{AsO}_4)_2$, determined recently in a single-crystal X-ray analysis by Chiari & Ferraris (1971) (referred to subsequently as CF) has triclinic symmetry with the calcium atom coordinated by eight oxygen atoms at the corners of distorted square-antiprisms. These polyhedra are linked along the z axis; the resulting chains, connected by hydrogen bonds, give rise to layers parallel to (100) (Fig. 1). A plausible interpretation of the X-ray analysis involves two symmetrical $\text{O}\cdots\text{O}$ hydrogen bonds; in view of the interest in such bonds, a neutron-diffraction analysis has been made as part of a series of such studies of acidic and/or hydrated inorganic compounds (Curry, Denne & Jones, 1968; Curry & Jones, 1971; Denne & Jones, 1971; Ferraris, Jones & Yerkess, 1971*a, b, c*; 1972*a, b*).

Experimental

Preliminary crystallographic and other physical data were taken to be as reported by CF: triclinic, space group $P\bar{1}$; $a_0=8.558$, $b_0=7.697$, $c_0=5.721 \text{ \AA}$, $\alpha=92^\circ 35'$, $\beta=109^\circ 52'$, $\gamma=109^\circ 59'$; $V=327.4 \text{ \AA}^3$, $M. W. 321.932$, $D_m=3.195$, $D_c=3.262 \text{ g.cm}^{-3}$, $Z=2$; no piezoelectric effect has been detected.

Suitable crystals for neutron-diffraction examination were obtained by the Guérin (1941) method for the synthesis of CaHAsO_4 (weilite) at 333 K. A single crystal, of dimensions 4.7 (z axis) \times 2.5 (across $\{100\}$) \times 1.8 (across $\{\bar{1}10\}$) mm, was mounted with its z axis

along the instrumental φ axis of a Ferranti automatic single-crystal diffractometer at the DIDO reactor, Atomic Energy Research Establishment, Harwell. Neutron intensity data for wavelength 1.178 \AA were collected for 1200 reflexions from half the reflexion sphere up to $2\theta=90^\circ$ ($\omega/2\theta$ scanning in 26 steps of 0.08° in ω for the peak, plus four more steps on each side for the background); the monitor count per step was 4×10^4 . 270 reflexions with an integrated intensity less than three times the estimated standard deviations were rejected. No absorption correction was made; the final value of an extinction factor, g (Larson, 1970), refined by least-squares methods, was $0.0086 \times 10^{24} \text{ cm}^{-2}$.

Structure analysis and refinement

Location of the hydrogen atoms

A three-dimensional Fourier difference synthesis of the neutron data ($R=0.26$) with F_c 's computed from the CF non-hydrogen atomic coordinates, showed that two effectively half-hydrogen atoms were sited on two inversion centres; the other three hydrogen atoms in the formula unit were located at three general positions. Nuclear scattering lengths used here and subsequently were Ca, 4.9; As, 6.4; O, 5.77; H, $-3.72 \times 10^{-13} \text{ cm}$ (Bacon, 1969).

Structure refinement

Least-squares refinement with unitary weights was carried out by the full-matrix *ORFLS* program of the *X-ray 63* system (Stewart & High, 1963) (and its subsequent modifications) on the Chilton Atlas computer.

After a preliminary isotropic refinement over all atoms ($R=0.064$), anisotropic refinement led to $R=0.025$ with all shifts less than standard deviations. A final Fourier difference synthesis revealed only statistically distributed peaks.

Table 1 lists the final values of $|F_o|$ and F_c . Table 2 gives the final positional coordinates together with B_{ij} coefficients in the expression

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

and some useful quantities for comparison of the X-ray and neutron data (see below).

Discussion

Crystal structure and thermal motion

Tables 3 and 4 give motionally corrected [by the

Busing & Levy (1964) models] distances for As–O and O–H, but not for $\text{Ca} \cdots \text{O}$ since Ca and O have very similar r.m.s. amplitudes of thermal motion.

Fig. 1 shows an orthographic projection on (001) of the contents of one unit cell; the overall structure and hydrogen-bonding system are essentially as described by CF. In accordance with the theory (Kálmán, 1971) following Cruickshank's (1961) hypothesis and previous findings (Ferraris, 1970), the average As–O bond length is 1.686 Å; agreement between the four pairs of values in Table 3 for the two tetrahedra is independent of the treatment of thermal motion. For oxygen atoms carrying half-hydrogens, As–O bonds are intermediate in length (1.677 Å) between those with full hydrogens (1.727 Å) and those with no hydrogen (1.651 Å). While four of the five As–O–H angles are in the range 109.9–112.6°, the fifth, involving the longer symmetrical hydrogen bond, is significantly different at 116.8°; linearity of the $\text{O}(8) \cdots$

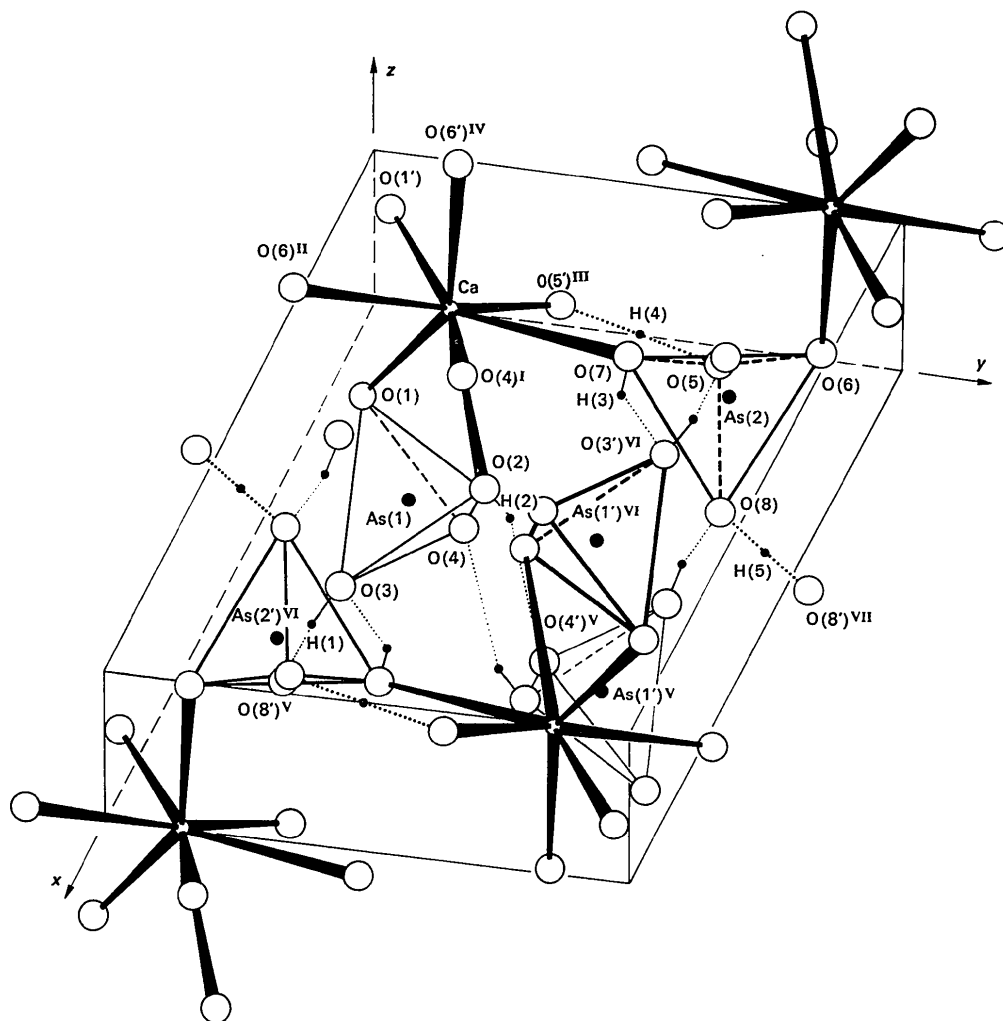


Fig. 1. Orthographic projection on (001) of the contents of the unit cell of calcium bis(dihydrogen arsenate); hydrogen atoms are shown as small closed circles and arsenic atoms as larger closed circles.

Table 2. Fractional coordinates and vibrational parameters (\AA^2)

The fractional coordinates have been multiplied by 10^5 for As(1) and As(2) and by 10^4 for Ca to H(3). The anisotropic temperature factors are $\times 10^2$. The estimated standard deviations of the least significant figures are in parentheses. The second line associated with each heavy atom contains the significant figures of Δ , defined as the X-ray parameter value minus the neutron value, and $|\Delta|/\sigma$; see text for discussion of this and of the H(4) and H(5) sites.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As(1)	34157 (13)	23990 (14)	-1476 (19)	67 (4)	83 (4)	84 (4)	17 (3)	33 (3)	20 (3)
	5 0.3	-13 0.7	55 2.3	37 7.4	26 5.2	15 3.0	15 3.5	19 4.5	16 4.4
As(2)	18712 (14)	76648 (14)	33085 (19)	73 (4)	79 (3)	88 (4)	26 (3)	29 (3)	7 (3)
	-16 0.9	-18 1.0	3 0.1	33 6.5	28 6.7	18 3.2	14 3.3	22 5.2	18 5.0
Ca	815 (2)	1866 (2)	3125 (3)	133 (6)	114 (5)	112 (5)	42 (4)	49 (4)	22 (4)
	1 0.4	-3 1.1	-9 2.1	-13 1.5	-7 1.0	-29 3.7	0 0	-5 0.8	11 1.9
O(1)	1741 (2)	617 (2)	32 (2)	101 (4)	98 (4)	117 (4)	10 (3)	46 (4)	17 (3)
	-2 0.3	-5 0.7	-3 0.3	3 0.1	34 1.7	-7 0.3	18 1.0	-5 0.3	25 1.4
O(2)	3785 (2)	4014 (2)	2368 (2)	138 (6)	136 (5)	130 (5)	18 (5)	58 (4)	-15 (4)
	-4 0.5	-1 0.1	-13 1.2	77 3.0	62 2.6	14 0.6	65 3.2	58 2.7	40 2.1
O(3)	5417 (2)	2082 (2)	734 (3)	106 (5)	181 (5)	153 (5)	65 (4)	41 (4)	32 (4)
	2 0.2	-2 0.2	25 2.4	20 0.9	44 1.8	83 3.8	7 0.4	-34 1.9	41 2.2
O(4)	3109 (2)	3252 (2)	-2793 (2)	132 (5)	109 (4)	100 (5)	16 (4)	32 (4)	31 (3)
	-12 1.5	-11 1.3	23 2.3	17 0.8	57 2.5	0 0	43 2.3	6 0.3	36 2.0
O(5)	454 (2)	6701 (2)	306 (2)	167 (5)	75 (5)	116 (5)	36 (4)	6 (4)	10 (3)
	19 2.3	15 2.1	15 1.5	1 0.0	10 0.5	-19 0.9	-6 0.4	8 0.5	20 1.3
O(6)	1255 (2)	9065 (2)	4759 (2)	136 (5)	110 (4)	129 (5)	58 (4)	67 (4)	16 (3)
	-3 0.4	-3 0.4	8 0.8	64 2.6	42 2.0	-11 0.5	52 2.7	34 1.8	17 1.0
O(7)	1701 (2)	5672 (2)	4665 (3)	155 (5)	123 (5)	137 (6)	56 (4)	39 (5)	49 (4)
	12 1.5	-1 0.1	14 1.2	22 0.9	21 1.0	15 0.6	3 0.2	16 0.8	41 2.1
O(8)	3971 (2)	8595 (2)	3405 (2)	93 (5)	164 (5)	165 (5)	26 (4)	64 (4)	-6 (4)
	-6 0.7	12 1.5	-39 3.5	16 0.7	2 0.1	-8 0.3	-24 1.3	-13 0.6	3 0.2
H(1)	5672 (3)	1760 (4)	-775 (5)	164 (9)	280 (10)	283 (12)	93 (7)	90 (8)	12 (8)
H(2)	4895 (3)	5151 (3)	2763 (5)	200 (10)	157 (9)	246 (10)	-7 (9)	47 (8)	-28 (7)
H(3)	2593 (4)	5993 (4)	6362 (6)	289 (12)	385 (12)	210 (12)	151 (10)	23 (10)	102 (9)
H(4)	0	$\frac{1}{2}$	0	227 (14)	300 (16)	185 (13)	97 (11)	40 (10)	51 (10)
H(5)	$\frac{1}{2}$	1	$\frac{1}{2}$	264 (15)	336 (16)	320 (16)	168 (14)	158 (13)	133 (14)

Table 3. Interatomic distances and angles (O-As-O) in the AsO_4 group

Uncorrected values (A) and values corrected for thermal motion (B, C, D): lower (B) and upper (C) limits and 'riding' model (D). The estimated standard deviations are 0.002 \AA and 0.1° for distances and angles respectively.

	A	B	C	D		A	B	C	D
As(1)-O(1)	1.648 \AA	1.648 \AA	1.682 \AA	1.651 \AA	As(2)-O(5)	1.682 \AA	1.683 \AA	1.717 \AA	1.688 \AA
As(1)-O(2)	1.726	1.727	1.760	1.733	As(2)-O(6)	1.654	1.654	1.687	1.658
As(1)-O(3)	1.720	1.721	1.752	1.725	As(2)-O(7)	1.735	1.736	1.769	1.741
As(1)-O(4)	1.652	1.653	1.686	1.657	As(2)-O(8)	1.672	1.673	1.710	1.679
Average	1.686	1.687	1.720	1.692	Average	1.686	1.687	1.721	1.692
O(1)-O(2)	2.580 \AA	O(1)-As(1)-O(2)	99.7°	O(5)-O(6)	2.796 \AA	O(5)-As(2)-O(6)	113.9°		
O(1)-O(3)	2.831	O(1)-As(1)-O(3)	114.3	O(5)-O(7)	2.634	O(5)-As(2)-O(7)	100.9		
O(1)-O(4)	2.838	O(1)-As(1)-O(4)	118.7	O(5)-O(8)	2.733	O(5)-As(2)-O(8)	109.2		
O(2)-O(3)	2.687	O(2)-As(1)-O(3)	102.5	O(6)-O(7)	2.766	O(6)-As(2)-O(7)	109.5		
O(2)-O(4)	2.801	O(2)-As(1)-O(4)	112.1	O(6)-O(8)	2.813	O(6)-As(2)-O(8)	115.5		
O(3)-O(4)	2.731	O(3)-As(1)-O(4)	108.2	O(7)-O(8)	2.733	O(7)-As(2)-O(8)	106.7		
Average	2.745			Average	2.746				

Table 4. Interatomic distances and angles involving hydrogen atoms and hydrogen bonds

The estimated standard deviations are 0.003 \AA and 0.3° for distances and angles involving hydrogen atoms; the others are as in Table 3. $B-C$ are the O-H distances: uncorrected (1) and corrected for thermal motion (2,3,4): lower (2) and upper (3) limits and 'riding' model (4).

A	B	C	D	$B-C$	$B \cdots D$	$C \cdots D$	$A-B-C$	$B-C \cdots D$	$C-B \cdots D$
	1	2	3	4					
As(1)-O(2)-H(2) ... O(4') ^v	0.994 \AA	0.996 \AA	1.104 \AA	1.010 \AA	2.692 \AA	1.725 \AA	112.6°	163.4°	10.5°
As(1)-O(3)-H(1) ... O(8') ^v	1.001	1.003	1.096	1.014	2.659	1.663	111.2	173.9	3.8
As(2)-O(7)-H(3) ... O(3') ^{v1}	0.966	0.973	1.095	0.995	2.875	1.997	110.3	150.2	20.2
As(2)-O(5)-H(4)-O(5') ^{III}	1.218	-	-	-	2.436	1.218	109.9	180.0	0
As(2)-O(8)-H(5)-O(8') ^{vII}	1.222	-	-	-	2.444	1.222	116.8	180.0	0

Table 5. *Interatomic distances Ca...O and O...O and O...Ca...O angles, for the Ca coordination polyhedron*

Estimated standard deviations are as in Table 3.

(a) Interatomic distances

Ca...O(1)	2.450 Å	O(1).....O(6) ^{II}	3.031 Å
Ca...O(2)	2.706	O(6) ^{II}O(6') ^{IV}	3.034
Ca...O(4) ^I	2.382	O(6) ^{II}O(4) ^I	3.076
Ca...O(6) ^{II}	2.483	O(6) ^{II}O(1')	3.140
Ca...O(7)	2.781	O(1').....O(5') ^{III}	2.866
Ca...O(1')	2.418	O(1').....O(6') ^{IV}	3.104
Ca...O(5') ^{III}	2.412	O(6') ^{IV}O(4)	3.287
Ca...O(6') ^{IV}	2.406	O(6') ^{IV}O(7)	3.765
Average	2.505	O(7).....O(5') ^{III}	2.914
O(1).....O(1')	2.787	O(7).....O(4) ^I	2.761
O(1).....O(2)	2.580	O(7).....O(2)	3.088
O(1).....O(5') ^{III}	3.204	O(2).....O(4) ^I	3.058
		O(2).....O(5') ^{III}	3.255

(b) Angles

O(1).....Ca...O(1')	69.9°
O(1).....Ca...O(2)	59.8
O(1).....Ca...O(5') ^{III}	82.5
O(1).....Ca...O(6) ^{II}	78.0
O(6) ^{II}Ca...O(6') ^{IV}	76.9
O(6) ^{II}Ca...O(4) ^I	78.4
O(6) ^{II}Ca...O(1')	79.7
O(1').....Ca...O(5') ^{III}	72.8
O(1').....Ca...O(6') ^{IV}	77.9
O(6') ^{IV}Ca...O(4)	86.7
O(6') ^{IV}Ca...O(7)	92.8
O(7).....Ca...O(5') ^{III}	67.9
O(7).....Ca...O(4) ^I	64.1
O(7).....Ca...O(2)	68.5
O(2).....Ca...O(4) ^I	73.6
O(2).....Ca...O(5') ^{III}	78.8

those of the oxygen atoms to which they are attached and to those of the other hydrogen atoms. The maximum vibrations of H(4) and H(5) are almost parallel to the respective O...O directions.

Secondly, it is well established experimentally [for X-ray and neutron data, see Hamilton & Ibers (1968) and, more specifically, Chidambaram (1968), Chidambaram & Sikka (1968), and Hamilton (1962)] and justified with the aid of a semi-empirical potential function [for infrared shift, see Bellamy & Pace (1969), and Bellamy & Owen (1969)] that, allowing for some scatter, as O...O (R in Fig. 4) in a hydrogen bond increases, the O-H bond length (r in Fig. 4) decreases monotonically (except for symmetrical hydrogen bonds), while the antisymmetric O-H stretching frequency, and the H-O...O and O-H...O angles (δ and α in Fig. 4) increase monotonically. Shallowness of gradient and the above-mentioned restriction about symmetrical bonds limit the utility here of O-H *versus* O...O graphs. However, if the five infrared absorption peaks in $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ at 3355, 2950, 2365, 1580, and 1475 cm^{-1} (Fig. 3) are tentatively ascribed to hydrogen bonds of lengths 2.875, 2.692, 2.659, 2.444, and 2.436 Å respectively, the experimental points conform to the ν (or $\Delta\nu$) *versus* O...O curve.

According to the Blinc, Hadži & Novak (1960) approach (see also Hamilton & Ibers, 1968), in terms of infrared absorption and presumed potential well of the the proton, two short hydrogen bonds should involve a single minimum in a symmetric potential well.

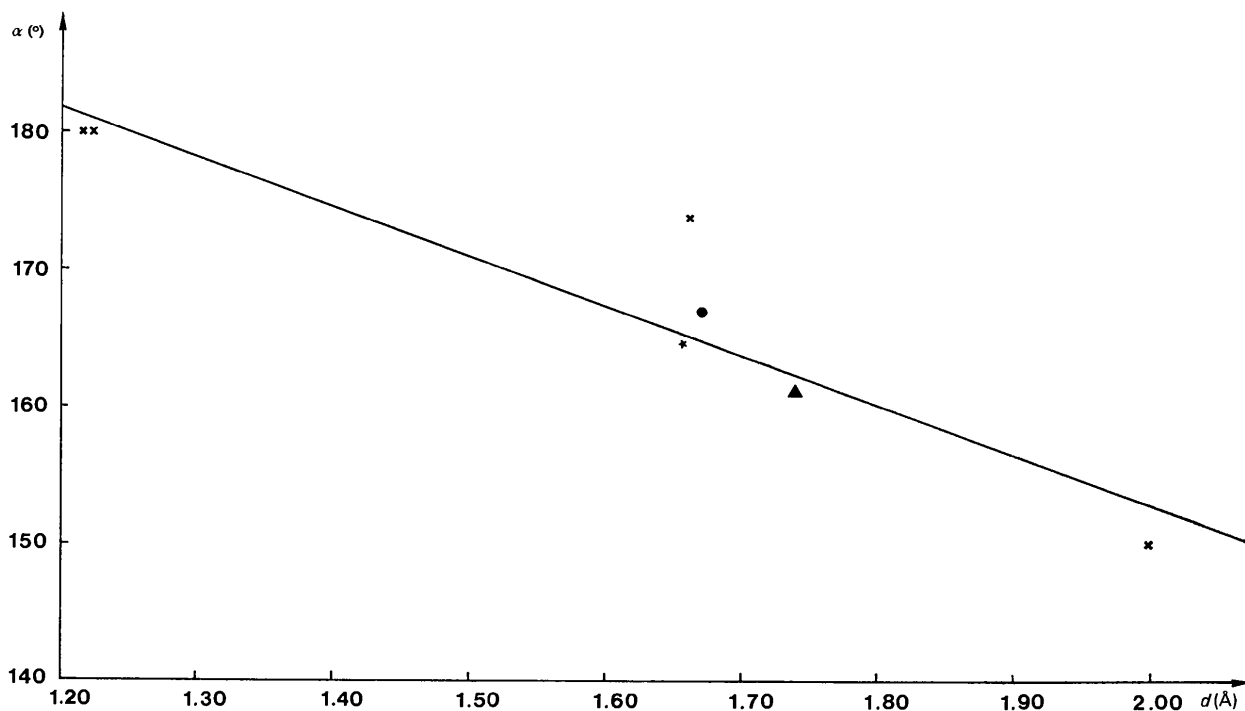


Fig. 2. Graph of experimental values of α (O-H...O) *versus* d (H...O) with the least-squares straight line drawn through the experimental points: ● $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ (Ferraris, Jones & Yerkess, 1971a); ★ $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Ferraris, Jones & Yerkess, 1971b); ▲ $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ (Ferraris, Jones & Yerkess, 1972a); × $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ (present paper).

Table 6. *Parameters characterizing the principal directions 1,2,3 of thermal vibration for all the atoms*

A is the root-mean-square displacement, and B , C and D are the angles which the principal directions make with the x , y and z axes respectively.

		A	B	C	D
As(1)	1	0.10 Å	76°	104°	34°
	2	0.11	127	25	70
	3	0.09	41	70	117
As(2)	1	0.10	127	34	60
	2	0.11	92	122	30
	3	0.10	37	80	90
Ca	1	0.12	91	36	71
	2	0.13	17	117	94
	3	0.12	107	111	20
O(1)	1	0.12	100	83	18
	2	0.14	142	35	90
	3	0.10	54	56	108
O(2)	1	0.13	34	81	131
	2	0.16	124	36	113
	3	0.11	92	55	50
O(3)	1	0.14	111	95	2
	2	0.15	93	20	88
	3	0.11	21	109	89
O(4)	1	0.11	69	71	57
	2	0.15	155	48	66
	3	0.10	103	132	43
O(5)	1	0.11	69	107	41
	2	0.17	21	101	131
	3	0.10	94	20	87
O(6)	1	0.12	68	48	128
	2	0.14	54	96	58
	3	0.10	136	43	54
O(7)	1	0.14	64	65	69
	2	0.15	150	67	43
	3	0.11	103	35	126
O(8)	1	0.13	98	53	47
	2	0.17	105	37	127
	3	0.10	17	93	114
H(1)	1	0.18	92	51	53
	2	0.20	91	135	42
	3	0.13	2	109	108
H(2)	1	0.19	126	91	18
	2	0.20	137	39	102
	3	0.12	71	51	77
H(3)	1	0.22	45	65	117
	2	0.23	125	35	58
	3	0.14	66	114	44
H(4)	1	0.19	37	77	128
	2	0.20	117	18	74
	3	0.14	68	103	42
H(5)	1	0.17	94	131	39
	2	0.22	83	53	59
	3	0.16	8	117	111

When correlations between the geometrical features of the hydrogen bond are sought, the perturbing influence of environment may be minimized by restricting consideration to the acidic hydrogen bonds of a coherent group of arsenates for which reliable neutron-diffraction data (Ferraris *et al.*, 1971*a, b*; 1972*a*) are available. In an effort to find less equivocal linear correlations, linear least-squares fits of α , s , and δ against R or d (Fig. 4) were tested with the values $\alpha=180^\circ$, $s=0$, and $\delta=0^\circ$ for the supposed symmetrical hydrogen bond to see if the fitted straight line requires $\text{O}-\text{H}=\text{H}\cdots\text{O}=\frac{1}{2}(\text{O}\cdots\text{O})$. The six possible graphs showed that these values of α , s , and δ are indeed characteristic

of a symmetrical hydrogen bond; the best fit (' R value' for deviations: 0.015) was obtained for the graph of α against d ; Fig. 2 shows experimental points for this graph [with H(4) and H(5) in $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ plotted as for symmetrical hydrogen bonds], together with the least squares line

$$\alpha = -36(6)d + 225(9) \quad (1)$$

(estimated standard deviations are given in parentheses). While other anionic $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds established by neutron diffraction conform approximately to equation (1), those from water molecules (which typically have rather longer $\text{O}\cdots\text{O}$ distances at about 2.8 Å) tend to lie randomly above the line in Fig. 2; hydrogen-bond properties appear to be less predictable in the region of $R=2.8$ Å.

Comparison of neutron and X-ray parameters

While comparison of neutron and X-ray refinements can yield information about bonding effects on electron distributions (Coppens, 1970) in some organic crystals, in which chemical significance can be attached to parameter shifts as low as 0.01 Å, this would be premature for inorganic structures like $\text{Ca}(\text{H}_2\text{AsO}_4)_2$, with largely ionic bonds and comparatively large X-ray e.s.d.'s for the light atoms. In the few examples available of separate refinements of X-ray and neutron data to give comparable sets of results (*cf.* Baur, 1964; Brown & Chidambaram, 1969; El Saffar & Brown, 1971; Ferraris *et al.*, 1972*a*; Sikka & Chidambaram, 1969; Torrie, Brown & Petch, 1964), neutron and X-ray results are generally found to be the same within the limits of the e.s.d.'s.

In addition to the neutron parameters, Table 2 lists the significant figures of Δ (X-ray parameter minus neutron parameter) and the ratio of Δ to its standard error, $\sigma = [\sigma_{\text{neutron}}^2 + \sigma_{\text{X-ray}}^2]^{1/2}$; average values for $|\Delta|/\sigma$ of 1.1 and 1.9 for positional and thermal parameters respectively indicate substantial agreement between the two sets, but some systematic discrepancies may possibly have physical (experimental errors, errors in atomic model) or chemical significance. Firstly, relatively large Δ 's for the B_{ij} of the arsenic atoms (average $|\Delta|/\sigma=4.8$, Δ always positive) could be the consequence of a slightly erroneous As scattering length (or, less probably, atomic scattering factor). Causes of the consistently larger B_{ij} 's for neutrons than for X-rays could be a combination of errors in scattering lengths and scattering factors, uncorrected effects such as thermal diffuse scattering, or extinction anisotropy or absorption effects, as well as bonding effects. Secondly, occurrence of the largest Δ 's of positional parameters in the z direction may be a residual absorption effect (the X-ray crystal was elongated in this direction). Finally, the shifts of O(5) and O(8), which are engaged in symmetrical hydrogen bonds, could be due in part to omission of hydrogen atoms in the X-ray refinement and to deformation of the electron cloud.

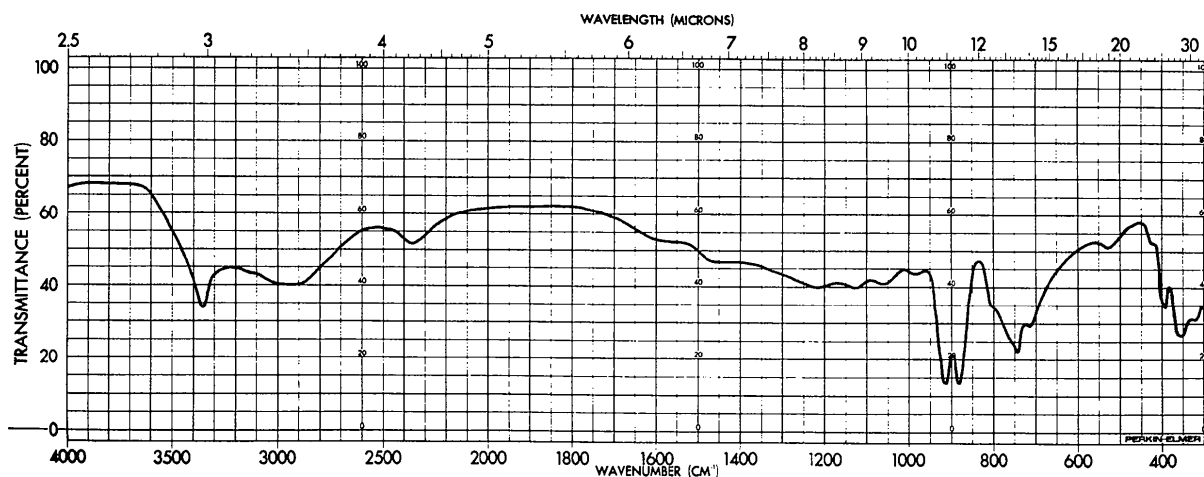


Fig. 3. Infrared spectrum of $\text{Ca}(\text{H}_2\text{AsO}_4)_2$, recorded as KBr disc on a Perkin-Elmer 621 spectrometer.

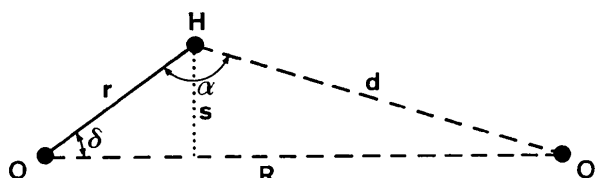


Fig. 4. Configuration and symbols for a non-linear $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond.

References

- BACON, G. E. (1969). *Acta Cryst.* **A25**, 391.
 BAUR, W. H. (1964). *Acta Cryst.* **17**, 863.
 BELLAMY, L. J. & OWEN, A. J. (1969). *Spectrochim. Acta*, **25A**, 319.
 BELLAMY, L. J. & PACE, R. J. (1969). *Spectrochim. Acta*, **25A**, 329.
 BLINC, R., HADŽI, D. & NOVAK, A. (1960). *Z. Elektrochem.* **64**, 567.
 BROWN, G. M. & CHIDAMBARAM, R. (1969). *Acta Cryst.* **B25**, 676.
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
 CHIARI, G. & FERRARIS, G. (1971). *Atti Accad. Sci. Torino*, **105**, 725.
 CHIDAMBARAM, R. (1968). *Proc. Nucl. Phys. Solid State Phys. Symp.* Dept. Atomic Energy, Bombay (India).
 CHIDAMBARAM, R. & SIKKA, S. K. (1968). *Chem. Phys. Letters*, **2**, 162.
 COPPENS, P. (1970). Chapter 6 in *Thermal Neutron Diffraction*. Edited by B. T. M. WILLIS. Oxford Univ. Press.
 CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* p. 5486.
 CURRIE, M. & SPEAKMAN, J. C. (1970). *J. Chem. Soc. (A)*, p. 1923.
 CURRY, N. A., DENNE, W. A. & JONES, D. W. (1968). *Bull. Soc. Chim. Fr.* p. 1748.
 CURRY, N. A. & JONES, D. W. (1971). *J. Chem. Soc. (A)* p. 3725.
 DENNE, W. A. & JONES, D. W. (1971). *J. Cryst. Mol. Struct.* **1**, 347.
 EL SAFFAR, Z. M. & BROWN, G. M. (1971). *Acta Cryst.* **B27**, 66.
 FERRARIS, G. (1970). *Rend. Soc. Ital. Miner. Petrol.* **26**, 589.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1971a). *Acta Cryst.* **B27**, 349.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1971b). *Acta Cryst.* **B27**, 354.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1971c). *J. Chem. Soc. (D), Chem. Commun.* p. 1566.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1972a). *Acta Cryst.* **B28**, 209.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1972b). *Z. Kristallogr.* In the press.
 GUÉRIN, H. (1941). *Ann. Chim.* **16**, 101.
 HAMILTON, W. C. (1962). *Ann. Rev. Phys. Chem.* **13**, 19.
 HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
 KÁLMÁN, A. (1971). *J. Chem. Soc. (A)*, p. 1857.
 LARSON, A. C. (1970). *Crystallographic Computing: Proceedings of the International Summer School, Ottawa*, p. 291. Edited by F. R. AHMED, S. R. HALL and C. P. HUBER. Copenhagen: Munksgaard.
 SCHLEMPER, E. O., HAMILTON, W. C. & LA PLACA, S. J. (1971). *J. Chem. Phys.* **54**, 3990.
 SIKKA, S. K. & CHIDAMBARAM, R. (1969). *Acta Cryst.* **B25**, 310.
 STEWART, J. M. & HIGH, D. (1963). *X-ray 63: Program System for X-ray Crystallography*. Depts. of Chemistry, Univ. of Washington, Seattle and Univ. of Maryland, College Park, Maryland.
 TORRIE, B. H., BROWN, I. D. & PETCH, H. E. (1964). *Canad. J. Phys.* **42**, 229.