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Hydrogen Bonding in the Crystalline State. Crystal Structure of $CaHAsO_4.3H_2O$[*]

By M. Catti and G. Ferraris

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

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Calcium hydrogen arsenate trihydrate ($CaHAsO_4.3H_2O$) crystallizes in the orthorhombic system, space group *Pbca*. Unit-cell parameters are: $a_0 = 11{\cdot}195$ (1), $b_0 = 10{\cdot}713$ (2), $c_0 = 11{\cdot}179$ (2) Å; $Z = 8$. The crystal structure was refined anisotropically to $R = 0{\cdot}034$, using 1321 non-zero reflexions measured on an automatic three-circle diffractometer (Cu $K\alpha$ radiation). Corrections for absorption, secondary extinction and anomalous scattering were applied. The hydrogen atoms were located from a difference map, and one of the three water molecules appears very weakly hydrogen bonded. $CaHAsO_4.3H_2O$ is isostructural with $MgHPO_4.3H_2O$ (newberyite) and with $MnHPO_4.3H_2O$; its crystal structure is built up from isolated Ca octahedra sandwiched between As tetrahedra. The resulting layers, parallel to (100), are connected by infinite zigzag chains of hydrogen bonds along [100]. Some common features of the related compounds $CaHAsO_4$ (weilite), $CaHAsO_4.H_2O$ (haidingerite), and $CaHAsO_4.2H_2O$ (pharmacolite) are discussed.

Introduction

Calcium hydrogen arsenate trihydrate, $CaHAsO_4.3H_2O$, is the most highly hydrated member of the group including $CaHAsO_4.2H_2O$ (pharmacolite), $CaHAsO_4.H_2O$ (haidingerite) and $CaHAsO_4$ (weilite), which have been studied both by X-ray (Ferraris, 1969; Calleri & Ferraris, 1967; Ferraris & Chiari, 1970) and neutron diffraction (Ferraris, Jones & Yerkess, 1971, 1972) with the aim of characterizing the hydrogen bond in the crystalline state (*cf.* Ferraris & Franchini-Angela, 1972). With the same aim, neutron, diffraction studies of the related compounds $CaHPO_4$, monetite (Denne & Jones, 1971), and $CaHPO_4.2H_2O$, brushite (Curry & Jones, 1971), have been recently carried out. The knowledge of the crystal structure of a series of hydrates is important for the understanding of both the role of the water molecule in the structures and the influence of the cation/oxygen stoichiometric

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ratio on the coordination polyhedron of the cation, especially when, as in the case of Ca, the coordination number can be variable.

Crystal data

$CaHAsO_4.3H_2O$ was synthesized for the first time by Guérin (1941), and again by Brasse, Guérin & Mattrat (1970); we are grateful to Professor H. Guérin for supplying the specimens used for the present work. The very small thin transparent crystals are orthorhombic, tabular on {100}, and rhomb-shaped by the presence of {011}.

Cu *Kα* X-ray diffraction analysis (Weissenberg and single-crystal diffractometry) showed orthorhombic symmetry with space group *Pbca* (D_{2h}^{15}, No. 61), according to the systematic absences. The reciprocal unit-cell parameters were refined by a least-squares procedure using 23 θ values, larger than 56°, which were measured at room temperature on a single-crystal diffractometer [$\lambda(\alpha_1) = 1{\cdot}54050$, $\lambda(\alpha_2) = 1{\cdot}54434$ Å]; the following values (standard deviations in parentheses) were obtained for the direct unit-cell parameters $a_0 = 11{\cdot}195$ (1), $b_0 = 10{\cdot}713$ (2), $c_0 = 11{\cdot}179$ (2) Å.

Owing to the close similarity between a_0 and c_0 values, the unit cell obtained from X-ray powder spectra by Brasse *et al.* (1970) was tetragonal.

Other physical data are: M.W.234·053, $V =$ 1340·6 Å^3, $D_m = 2{\cdot}317$ g cm^{-3} (Brasse *et al.*, 1970), $Z = 8$, $D_c = 2{\cdot}320$ g cm^{-3}, $F(000) = 928$, linear absorption coefficient for Cu *Kα* radiation $\mu = 139$ cm^{-1}.

Intensity measurements

Intensities, all on the same relative scale, were measured by a General Electric automatic three-circle diffractometer, on a crystal (0·05 mm across {100} and 0·14 mm across the opposite faces of {011}) mounted with its *z* axis along the instrumental φ axis. Integrated intensities (θ–2θ scanning, 2°.min^{-1}, 0·5° background on both sides of each peak) were collected for two equivalent octants (*hkl* and $\bar{h}\bar{k}l$, $2\theta \le 163°$). A standard reflexion (442), checked every 50 reflexions, showed constant intensity and the two sets were identical within the counting statistics. A unique set of 1445 reflexions was therefore obtained from the arithmetic average; 124 of these were subsequently considered unobserved and rejected because very weak ($|F_c| < |F_o|$).

An absorption correction (transmission factor 0·50–0·73) was applied using the program *GONO*9 (Hamilton, 1966). A secondary extinction correction, introduced toward the end of the refinement, was performed by a least-squares procedure fitting the function:

$$I_c/I_o = k(1 + gI_c); \qquad (1)$$

$k = 0{\cdot}982$ and $g = 74{\cdot}10^{-8}$ e^{-2} were obtained. The atomic scattering factors, including the real and imaginary corrections for anomalous scattering, were linear interpolations of the values reported for neutral atoms in *International Tables for X-ray Crystallography* (1962).

Solution and refinement of the structure

From a three-dimensional Patterson function the As and Ca atoms were easily located; a subsequent difference synthesis ($R = 0{\cdot}34$) showed all the oxygen atoms ($R = 0{\cdot}13$). There are eight formula units in the unit cell and all the atoms are in general positions.

A least-squares refinement was then started with isotropic temperature factors; subsequent anisotropic cycles reduced *R* to 0·04. At this stage, a three-dimensional difference synthesis showed several maxima (0·4 to 1·0 e.A^{-3}), seven of which were assigned, on the basis of bond lengths and angles, to the independent hydrogen atoms. After one cycle with isotropic refinement of the hydrogen atoms, an extinction correction was introduced and the refinement completed ($R =$ 0·034) when all the shifts were less than the estimated standard deviations.* In the final stages, the positional parameters of the hydrogen atoms were kept fixed at the Fourier values, since the least-squares shifts seemed physically meaningless.

Table 1. *Fractional atomic coordinates and vibrational parameters* (Å^2) *with significant figures of the estimated standard deviations in parentheses*

(*a*) Heavy atoms (values for *x*, *y* and *z* are × 10^4)

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	1285·7 (3)	1516·7 (3)	5057·7 (3)	1·57 (2)	1·04 (2)	1·20 (1)	−0·10 (1)	−0·03 (1)	−0·11 (1)
Ca	2523·9 (7)	5841·8 (7)	2019·6 (6)	1·85 (3)	1·41 (3)	1·33 (2)	−0·26 (3)	−0·12 (3)	0·04 (2)
O(1)	1567 (3)	18 (3)	5375 (3)	2·34 (11)	1·34 (10)	1·87 (10)	−0·08 (9)	−0·37 (9)	0·32 (9)
O(2)	1452 (3)	1759 (3)	3591 (3)	2·28 (12)	1·59 (10)	1·74 (10)	0·26 (9)	0·06 (9)	0·03 (9)
O(3)	2058 (3)	2482 (3)	5896 (3)	2·94 (12)	2·05 (11)	2·59 (13)	−0·80 (11)	−0·40 (11)	−0·79 (10)
O(4)	−201 (3)	1812 (3)	5389 (3)	1·91 (11)	2·15 (12)	2·48 (12)	−0·23 (10)	0·32 (10)	−0·73 (10)
W(1)	738 (3)	6874 (4)	2565 (4)	2·25 (14)	3·95 (17)	2·62 (14)	0·47 (12)	−0·12 (12)	−1·22 (13)
W(2)	4133 (4)	4544 (4)	1398 (4)	2·60 (16)	2·65 (16)	6·46 (23)	0·36 (13)	0·19 (16)	−0·46 (16)
W(3)	1873 (3)	4312 (3)	3426 (3)	4·18 (16)	1·80 (13)	1·99 (12)	−0·64 (12)	−0·72 (11)	0·34 (10)

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* A list of $|F_o|$ and F_c is available either from the authors or as Supplementary Publication No. SUP 30022. Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (*cont.*)

(*b*) Hydrogen atoms (values are $\times 10^3$)

	x	y	z	B
H(1)	−80 (7)	120 (7)	500 (7)	3·2 (1·9)
H(2)	60 (7)	735 (7)	310 (8)	0·8 (1·9)
H(3)	0 (8)	690 (7)	230 (7)	0·4 (1·8)
H(4)	500 (7)	465 (7)	165 (7)	4·4 (1·9)
H(5)	415 (7)	375 (8)	100 (7)	6·6 (1·8)
H(6)	230 (7)	440 (7)	410 (7)	3·4 (1·7)
H(7)	155 (7)	345 (7)	335 (7)	4·6 (1·7)

The full-matrix least-squares program by Busing, Martin & Levy (1962), with minor modifications, and in the later cycles with the following weighting scheme ($|F_o|$ on absolute scale) was used:

$$w=\frac{55}{0·01\,|F_o|^2+0·25\,|F_o|+36}\ \text{if}\ |F_o|\geq 18 \qquad (2)$$

$$w=0·0114\,|F_o|+0·6 \qquad \text{if}\ |F_o|<18\ . \qquad (3)$$

The final weighted R value and the standard error of an observation of unit weight were 0·04 and 1·44 respectively. The fractional coordinates and the B_{ij} coefficients of the expression:

$$\exp\,(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*) \qquad (4)$$

are listed in Table 1 with (in parentheses) the significant figures of the e.s.d.'s obtained, for all the atoms, from the least-squares refinement.

Discussion

Isostructurality between $MgHPO_4.3H_2O$ (newberyite) (Sutor, 1967) and $CaHAsO_4.3H_2O$ was realized only

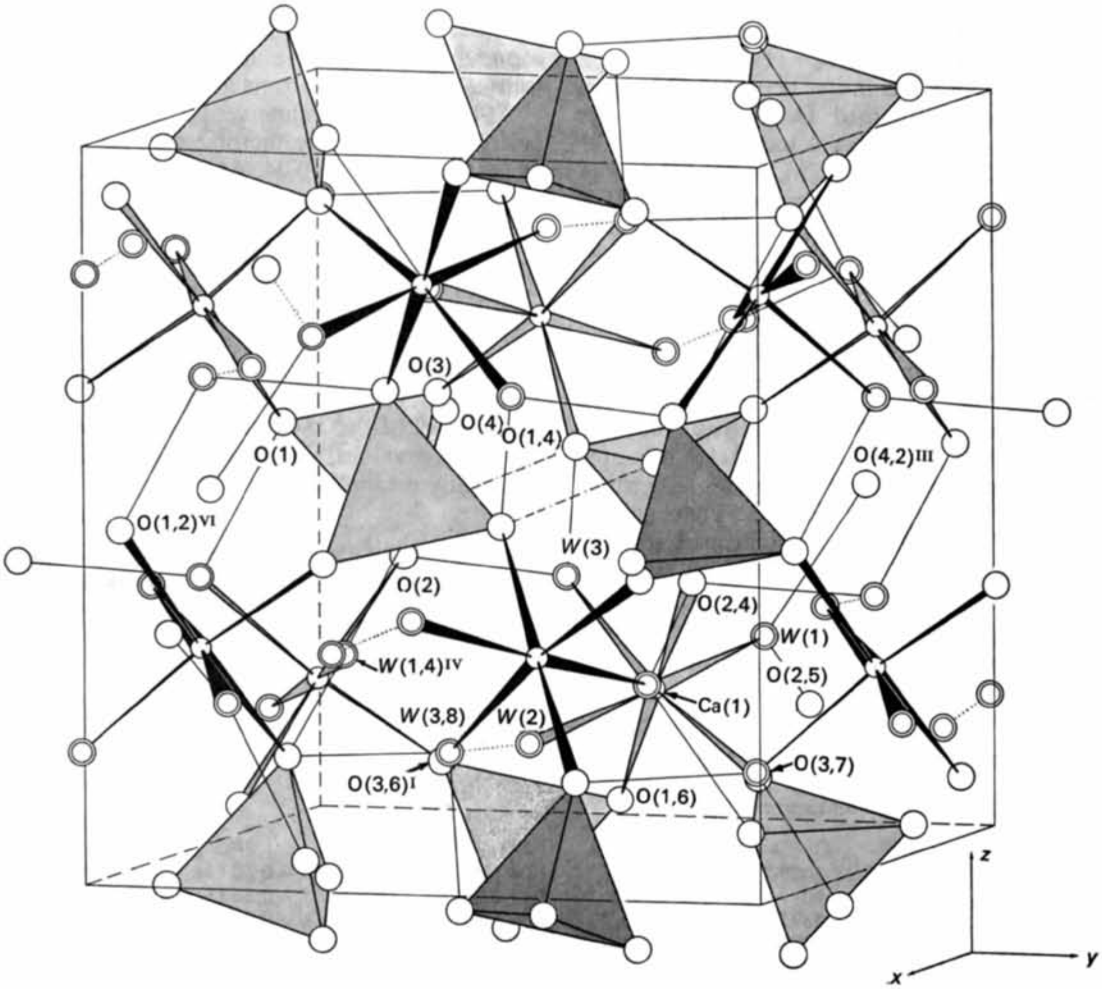

Fig. 1. Unit cell of $CaHAsO_4.3H_2O$ in clinographic projection down the x axis; water oxygen atoms are shown as double circles and calcium atoms as small circles. Hydrogen bonds donated by $W(1)$ and $W(3)$ (full lines), $W(2)$ (dotted lines) and O(4) (double dash and point) are shown.

after the present structure determination was completed; in fact it was masked by an interchange of axes of similar magnitude, implying the same Hermann–Mauguin symbol of the space group (x,y,z of the phosphate correspond to y,z,x of the arsenate). X-ray powder spectra also show isostructurality of the two compounds with $MnHPO_4.3H_2O$ (Durif, 1971).

The hydrogen bonding

The hydrogen bonding system is well defined, except for one bond involving the water molecule $W(2)$* which forms its three shortest contacts with $W(3,8)$ (3·084 Å), $W(1,4)^{IV}$ (3·174 Å) and $O(3,6)^{I}$ (3·228 Å). Since $H(4)\cdots W(3,8)=2{\cdot}13$ Å and angle $W(2)$–$H(4)\cdots W(3,8)=155°$, a weak hydrogen bond is evidently established between $W(2)$ and $W(3,8)$. H(5) is distant 2·69 Å both from $W(1,4)^{IV}$ and from $O(3,6)^{I}$, and the corresponding donor–hydrogen–acceptor angles are 112 and 116°, respectively; moreover, $W(1,4)^{IV}$ and $O(3,6)^{I}$ are 0·97 and 2·43 Å out of the water-molecule plane. On the basis of geometrical features of the hydrogen-bonded water molecule (Ferraris & Franchini-Angela, 1972), the existence of hydrogen bonds involving H(5) is improbable. However, since there is a 2·984 Å long hydrogen bond in newberyite between $W(2)$ and $W(1,4)^{IV}$, in agreement with Baur's (1970) electrostatic bond strength balance, we shall examine the present situation in the light of this theory.

Let T and Oc represent tetrahedral and octahedral central atoms, respectively. With respect to newberyite T–O(3) is, in $CaHAsO_4.3H_2O$, nearer the average As–O value and Oc–O(3) is no longer the shortest octahedral bond; moreover, $W(2)$ and $W(1)$ now have

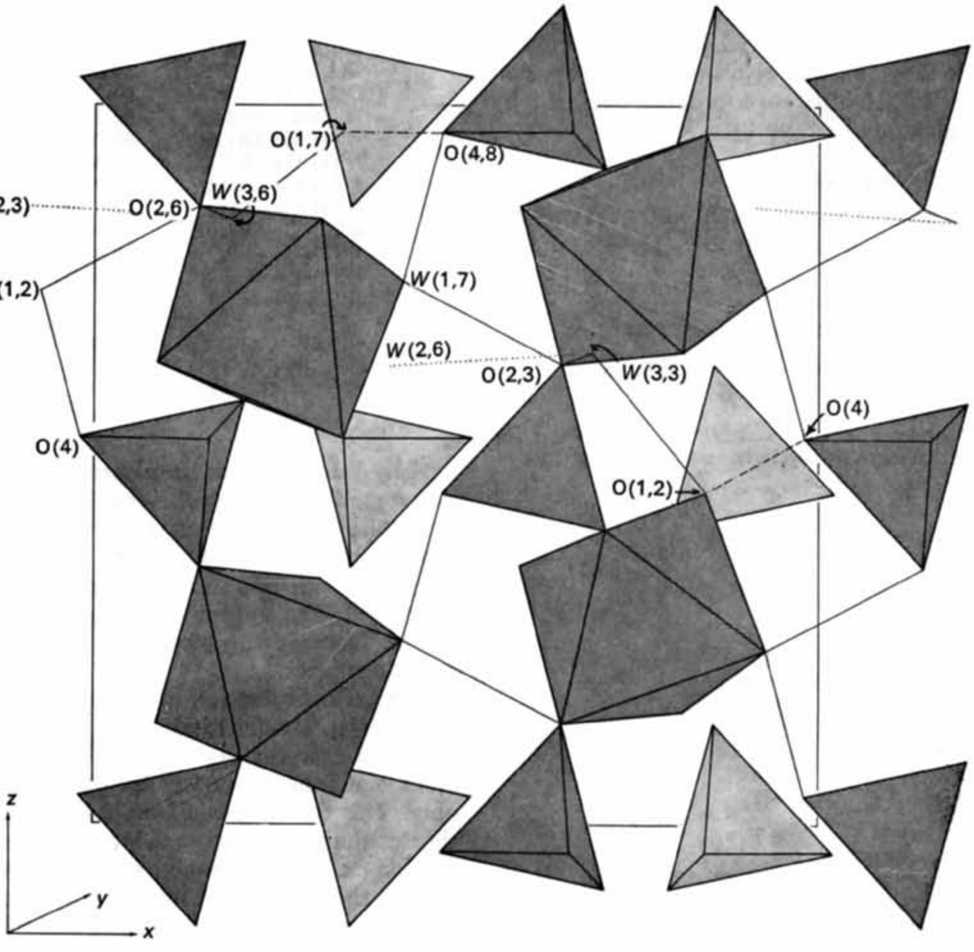

Fig. 2. About half the contents of one unit cell of $CaHAsO_4.3H_2O$ in projection onto the (010) plane. Atoms are labelled without indications for lattice translations; key for the hydrogen bonding as for Fig. 1.

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* The labelling of the atoms is as follows: a single figure (or no figure) in parentheses denotes an atom of the asymmetric unit; a second figure, ranging from 2 to 8, is included for atoms in the positions: $\bar{x},\bar{y},\bar{z}$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$; $\pm(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$ and $\pm(\frac{1}{2}-x,\bar{y},\frac{1}{2}+z)$. Roman numbers represent the following translations: I, $-\mathbf{c}$; II, $+\mathbf{b}$, $-\mathbf{c}$; III, $+\mathbf{b}$, $+\mathbf{c}$; IV, $-\mathbf{b}$; V, $+\mathbf{c}$; VI, $+\mathbf{a}$, $+\mathbf{c}$.

the longest and an intermediate *Oc*–oxygen distance, respectively. In terms of correlations between bond lengths and bond strengths *p*, this means that, with respect to newberyite, O(3) needs less *p* both from As and from Ca, and that *W*(2) and *W*(1) tend to receive less *p* and more *p*, respectively, from Ca. These features could be explained satisfactorily if the hydrogen bonding system is now changed so that H(5) is almost free from hydrogen bonds, in the sense that its influence on *W*(1,4)$^{\mathrm{IV}}$ is very weak and comparable with the influence exerted on O(3,6)$^{\mathrm{I}}$. The larger ionicity of the Ca compound requires, therefore, a rearrangement of bonds in favour of O(3) which is clearly underbonded, with its $p=1·58$ v.u. compared to 1·92 v.u. of O(1) and O(2), to 2·25 v.u. of O(4) and to a *p* not less than 2 v.u. of the *W* oxygens.

With respect to the lone-pair coordination (Chidambaram, Sequeira & Sikka, 1964; Ferraris & Franchini-Angela, 1972), *W*(1) and *W*(2) are of type *D* while *W*(3) is of type *H*.

In accordance with previous experience, the average O–H distance for hydrogen coordinates derived from maxima in difference-syntheses, while still short, is usually closer to the average value (0·96 Å) obtained from neutron studies (Ferraris & Franchini Angela, 1972) than the very short O–H distance (not reported in this work) from hydrogen coordinates refined by least-squares methods.

Description of the structure

Since the thermal motions of light and heavy atoms differ appreciably in magnitude, the As–O and Ca–oxygen distances have been corrected according to the riding model of Busing & Levy (1964) (Tables 2 and 3); along the bond direction, the thermal displacement is always small. The AsO_4 group appears to be normal as far as both bond lengths and O–As–O angles are concerned; the angles, as noted in general by Baur (1970), decrease with increase in the average of the two As–O distances.

Table 2. *Interatomic distances, uncorrected (A) and corrected (B) for the thermal motion, and angles* (O–As–O) *in the* AsO_4 *group*

The estimated standard deviations are 0·003 and 0·004 Å for As–O and O–O distances respectively and 0·1° for the angles.

	A	*B*
As–O(1)	1·675 Å	1·681 Å
As–O(2)	1·671	1·676
As–O(3)	1·642	1·656
As–O(4)	1·734	1·743
Average	1·681	1·689
O(1)–O(2)	2·735	
O(1)–O(3)	2·759	
O(1)–O(4)	2·759	
O(2)–O(3)	2·775	
O(2)–O(4)	2·733	
O(3)–O(4)	2·690	
Average	2·742	
O(1)–As–O(2)	109·7°	
O(1)–As–O(3)	112·6	
O(1)–As–O(4)	108·1	
O(2)–As–O(3)	113·8	
O(2)–As–O(4)	106·7	
O(3)–As–O(4)	105·6	
O(4)–H(1)	1·04 (8) Å	
As–O(4)–H(1)	115 (6)°	

Table 3. *Interatomic distances, uncorrected (A) and corrected (B) for the thermal motion, and angles* (O–Ca–O) *in the* Ca *coordination polyhedron*

The estimated standard deviations are 0·004 and 0·005 Å for Ca–O and O–O distances respectively and0·1° for the angles.

	A	*B*
Ca–O(1,6)$^{\mathrm{I}}$	2·319 Å	2·321 Å
Ca–O(3,7)$^{\mathrm{II}}$	2·241	2·250
Ca–O(2,4)	2·317	2·319
Ca–*W*(1)	2·352	2·363
Ca–*W*(2)	2·380	2·398
Ca–*W*(3)	2·386	2·394
Average	2·333	2·341
O(1,6)$^{\mathrm{I}}$–O(3,7)$^{\mathrm{II}}$	3·176	
O(3,7)$^{\mathrm{II}}$–O(2,4)	3·194	
O(2,4)—*W*(3)	3·230	
W(3)—O(1,6)$^{\mathrm{I}}$	3·502	
W(1)—O(1,6)$^{\mathrm{I}}$	3·294	
W(1)—O(3,7)$^{\mathrm{II}}$	3·176	
W(1)—O(2,4)	3·351	
W(1)—*W*(3)	3·150	
W(2)—O(1,6)$^{\mathrm{I}}$	3·127	
W(2)—O(3,7)$^{\mathrm{II}}$	3·500	
W(2)—O(2,4)	3·475	
W(2)—*W*(3)	3·407	
O(1,6)$^{\mathrm{I}}$–Ca–O(3,7)$^{\mathrm{II}}$	88·3°	
O(3,7)$^{\mathrm{II}}$–Ca–O(2,4)	89·0	
O(2,4)–Ca–*W*(3)	86·7	
W(3)–Ca–O(1,6)$^{\mathrm{I}}$	96·2	
W(1)–Ca–O(1,6)$^{\mathrm{I}}$	89·7	
W(1)–Ca–O(3,7)$^{\mathrm{II}}$	87·5	
W(1)–Ca–O(2,4)	91·7	
W(1)–Ca–*W*(3)	83·3	
W(2)–Ca–O(1,6)$^{\mathrm{I}}$	83·4	
W(2)–Ca–O(3,7)$^{\mathrm{II}}$	98·4	
W(2)–Ca–O(2,4)	95·4	
W(2)–Ca–*W*(3)	91·3	
O(1,6)$^{\mathrm{I}}$–Ca–O(2,4)	176·8	
O(3,7)$^{\mathrm{II}}$–Ca–*W*(3)	169·7	
W(1)—Ca–*W*(2)	170·8	

The Ca coordination polyhedron is a fairly regular octahedron, which includes all the oxygen atoms of the structure except O(4) (to which the acidic hydrogen atom is attached); vertices are shared by As tetrahedra only. The Ca–O bonds with tetrahedral oxygens are shorter than the average value, in agreement with the *p* value (<2 v.u.) of such oxygen atoms (*cf.* above).

Even though alternating As and Ca strata parallel to (001) (Fig. 1) are an outstanding feature of the crystal structure, a description in term of layers parallel to (100) (Fig. 2) has a better crystallochemical meaning. The Ca octahedra appear to be sandwiched between two

Table 4. *Interatomic distances* (Å) *and angles* (°) *in hydrogen bonds*

The estimated standard deviations are 0·005 Å and 0·2° for bond distances and angles involving oxygen atoms only, and 0·09 Å and 8° for bond distances and angles also involving hydrogen atoms. For *W*(2) see discussion in the text.

A	*B*	*C*	*D*	*E*	*AB*	*BC*	*AC*	*CD*	*CE*	*DE*	*BD*	*BCD*	*ACE*	*ABC*	*CDE*
O(2,5)···	H(3)—	*W*(1)—	H(2)···	$O(4,2)^{III}$	1·91	0·88	2·773	0·82	2·768	1·97	1·22	92	102·2	166	166
$O(3,6)^{I}$··					2·69		3·228						132·3	116	
	:H(5)—	*W*(2)—	H(4)···	*W*(3,8)		0·96		1·02	3·084	2·13	1·54	102			155
$W(1,4)^{IV}$··					2·69		3·174						81·7	112	
O(2)···	H(7)—	*W*(3)—	H(6)···	O(1,4)	1·84	1·00	2·781	0·90	2·893	2·02	1·56	111	108·0	158	164
		O(4)—	H(1)···	$O(1,2)^{V}$				1·04	2·630	1·62					

layers of As tetrahedra oriented with their OH groups towards the next layer; the other three oxygens are shared by different octahedra, two of which belong to the same row of octahedra parallel to [010]. Bent infinite chains of hydrogen bonds, not involving *W*(2), run along [100] (Fig. 2, Table 4). O(4)···$O(1,2)^{V}$ is the strongest term of these chains, and it ties the As tetrahedra in pairs across two layers. While *W*(1) and *W*(3) form intra- and inter-layer hydrogen bonds (Fig. 1) respectively, clearly *W*(2) has a secondary function, and the loose contacts involving its hydrogen atoms tend to bridge a bend of the infinite chain (Fig. 2).

Comparison with related structures

The structure described would appear to favour a {100} cleavage, corresponding to the {010} cleavage in newberyite; the crowding of atoms between the layers is, however, nearly the same as elsewhere. This is in contrast to the related structures $CaHAsO_4.2H_2O$ (pharmacolite) and $CaHAsO_4.H_2O$ (haidingerite), which are characterized by strongly individualized layers built up from chains (pharmacolite) or from a two-dimensional network (haidingerite) of Ca–O polyhedra; such layers are linked by hydrogen bonds, but there is no hydrogen bonding within the layers. In $CaHAsO_4.3H_2O$, on the other hand, the layers contain isolated Ca–O octahedra, so that the hydrogen bonding is extended throughout all the structure to ensure the necessary stability. The overall crowding of atoms in $CaHAsO_4.3H_2O$ is, however, less than that found in the three related minerals (including weilite, $CaHAsO_4$), and the density of the four compounds decreases (*cf.* Ferraris & Chiari, 1970) as the oxygen/calcium stoichiometric ratio increases.

$CaHAsO_4.3H_2O$ too, as noted for the less hydrated pharmacolite and haidingerite (Pierrot, 1964), tends to change into a lower hydrate (Guérin, 1941; Brasse *et al.*, 1970). So, favoured by the similarity of the crystal structures, a continuous solid-state transition (*cf.* Ferraris, 1969; Abbona & Ferraris, 1970) is possible, even at room temperature, from the most highly hydrated compound to the anhydrous one; this would imply the passage, *via* small rearrangements, from isolated Ca polyhedra to a three-dimensional framework sharing vertices and edges.

The weakly hydrogen-bonded water molecule *W*(2) should play a central role in the dehydration process of $CaHAsO_4.3H_2O$; in fact, although the overall crystalline structure is stable, a small activation energy seems sufficient to loosen *W*(2) [*cf.* its high and strongly anisotropic thermal motion (Table 5)]. An intermediate formation of $CaHAsO_4.3H_2O$ during the preparation of related compounds is described by Guérin (1941). From the study of this series of compounds it seems clear that a weakly hydrogen-bonded water molecule, even if strongly Ca coordinated, is easily lost. This would explain the otherwise puzzling observation that the natural dehydration process leads ultimately to the compound (weilite) in which the coordination polyhedra share most of their vertices and edges.

Table 5. *Parameters characterizing the principal directions* 1, 2, 3 *of thermal vibration for* As, Ca *and oxygen atoms*: *root-mean-square displacements* (*A*) *and angles which the principal directions make with the x* (*B*), *y* (*C*) *and z* (*D*) *axes*

		A	*B*	*C*	*D*
As	1	0·126 Å	93°	115°	26°
	2	0·142	10	100	91
	3	0·111	81	27	64
Ca	1	0·129	92	118	28
	2	0·159	27	114	101
	3	0·127	63	39	64
O(1)	1	0·15	57	65	43
	2	0·18	33	101	121
	3	0·12	95	27	117
O(2)	1	0·15	96	90	6
	2	0·17	20	71	84
	3	0·14	109	19	92
O(3)	1	0·20	112	111	31
	2	0·21	35	124	83
	3	0·12	65	41	60
O(4)	1	0·15	18	75	100
	2	0·20	73	126	42
	3	0·14	96	41	50
W(1)	1	0·17	25	87	65
	2	0·25	79	32	120
	3	0·15	113	58	41
W(2)	1	0·19	45	45	87
	2	0·29	88	97	7
	3	0·17	45	134	96
W(3)	1	0·15	67	59	40
	2	0·24	23	105	107
	3	0·14	87	35	125

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Crystal Structure of 2,4,6-Triphenylverdazyl

By Donald E. Williams

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, *U.S.A.*

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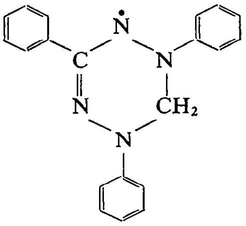
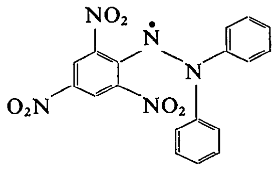
The stable free radical 2,4,6-triphenylverdazyl ($C_{20}N_4H_{17}$) crystallizes in space group $P2_12_12_1$ with four molecules per cell. The lattice constants are $a = 18.467(2)$, $b = 9.854(1)$, and $c = 8{\cdot}965(1)$ Å. X-ray intensity data were collected on a quarter-circle diffractometer with scintillation-counter detection. The crystal structure was solved by molecular packing analysis, and was refined by structure-factor least-squares calculations using individual anisotropic temperature factors and calculated hydrogen positions. The final discrepancy index was 0·076 for 1309 reflections which were more than one standard deviation above background. The verdazyl ring is nonplanar, with the methylene carbon atom displaced 0·59 Å from the plane of the four nitrogen atoms. The phenyl groups attached to N(2) and N(4) are also warped out of the plane of the nitrogen atoms; in addition, these phenyl groups are twisted by 23 and 13° respectively, about the phenyl–nitrogen bonds.

The class of stable free radicals called the verdazyls Kuhn & Trischmann, 1963) is based on the 3,4-dihydro-*s*-tetrazin-1(2*H*)-yl ring system. A very stable and crystalline member of this series is the 2,4,6-triphenyl substituted compound (Kuhn & Trischmann, 1964), TPV:



TPV is geometrically similar to 1,3,5-triphenylbenzene, except that a preliminary X-ray diffraction study (Williams, 1969*b*) showed that the methylene carbon atom is significantly out of the plane of the central ring. The e.s.r. spectrum (Kuhn & Trischmann, 1964) indicates approximately equal sharing of the unpaired electron among the four nitrogen atoms. The radical is even more stable than 2,2-diphenyl-1-picrylhydrazyl (DPPH), where the unpaired electron is shared primarily by only two nitrogen atoms, and is further shielded and stabilized by *o*-nitro groups (Williams, 1967):



Experimental

Crystals of TPV suitable for X-ray diffraction measurements were kindly supplied by Dr F. A. Neuge-