A Neutron and X-ray Refinement of the Crystal Structure of CaHAsO$_4$.H$_2$O (Haidingerite)

By G. Ferraris,* D. W. Jones and J. Yerkess

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

A neutron-diffraction analysis has been carried out on the crystal structure of the mineral haidingerite, CaHAsO$_4$.H$_2$O, based on space group *Pcnb* (D_{2h}^{14}), in accord with three recent X-ray analyses. Positions of the three independent hydrogen atoms have been located by a Fourier difference synthesis with neutron data collected at $\lambda = 1\cdot15$ Å. For positional and thermal parameters of all atoms, full-matrix least-squares refinement led to a final *R*-value of 0·057 over 518 independent neutron reflexions. Estimated standard deviations of the positional coordinates of the hydrogen atoms are 0·01 Å, and about 0·005 Å for the other atoms. Further full-matrix least-squares refinements of the X-ray data indicated that surprisingly large apparent discrepancies between the neutron and the original X-ray refinement could be attributed largely to differences in refinement procedure. The anionic hydrogen, H(1), is 1·00 (1) Å from O(1), which has the longest As–O bond of 1·729 (5) Å, and is engaged in a 2·63 Å long non-linear hydrogen bond to O(3). The water molecule has an unusually large H–O–H angle of 113 (1)° and forms markedly non-linear bonds of 2·80 and 2·82 Å to arsenate oxygen atoms. With the nearest calcium ion 0·41 Å out of the H–O–H plane and 10° off the line of the lone-pair bisector, the environment of the water molecule may be regarded as intermediate between one in which either one lone pair or the lone-pair bisector is directed towards the metal ion.

Introduction

Independent analyses [Calleri & Ferraris, 1967 (referred to subsequently as CF); Binas, 1966; Cassien, Herpin & Permingeat, 1966] from photographic X-ray data have shown that the crystal structure of the mineral haidingerite, CaHAsO$_4$.H$_2$O, involves double AsO$_4$ layers in the (010) plane. Calcium exhibits sevenfold coordination (to six arsenate oxygen atoms and one water oxygen), and the calcium polyhedra wind round the *x* axis so as to share edges in the *x* direction and vertices and edges in the *z* direction. From the most accurate of the X-ray analyses (CF), the anionic hydrogen can be assigned to the oxygen atom with the longest As–O bond and a hydrogen-bonding system can be inferred in which the arsenate ions of one double layer are linked through the acidic hydrogen atom, and water molecules are linked to arsenate ions of two adjacent double layers (Figs. 1 and 2). As part of a series of neutron-diffraction studies of acidic, mostly hydrated, arsenates (Ferraris, Jones & Yerkess, 1971*a*, *b*) and phosphates (Curry, Denne & Jones, 1968; Denne & Jones, 1969), aimed at surveying the stereochemistry of the (HXO$_4$)$^{2-}$ group (X = As, P) and the water molecules in these structures, we have undertaken a neutron-diffraction analysis of haidingerite in order to locate the hydrogen atoms more precisely.

Experimental

Long-exposure Weissenberg X-ray photographs from synthetic crystals failed to reveal the weak reflexions

from 0,10,1, 0,11,1, 0,12,1, and other 0*kl* planes with *l* odd which caused Martin, Durif & Averbuch-Pouchot (1970) to conclude that the space group is *Pmnb* (D_{2h}^{7})* instead of *Pcnb* (D_{2h}^{14}), as accepted independently by Binas (1966), Cassien *et al.* (1966), and CF. Earlier, Fischer (1960) had proposed *Pcmb* (D_{2h}^{11}). Significant degeneration to non-centrosymmetric space groups *Pcb* (C_{2v}^{5}) and *Pnb* (C_{2v}^{6}) is unlikely in view of the negative result from a careful piezo-electric test by Dr W. G. Perdok (private communication, 1970). Accordingly, preliminary crystallographic data are taken to be as reported by CF: Orthorhombic, space group *Pcnb* (No. 60, D_{2h}^{14}); $a = 6\cdot904$ (9), $b = 16\cdot161$ (9), $c = 7\cdot935$ (6) Å, $V = 885\cdot4$ Å^3; M.W. 198·01; $D_{meas} = 2\cdot96$, $D_{calc} = 2\cdot971$ g.cm^{-3}; $Z = 8$.

A single crystal, 6·0 (*c* axis) $\times 3\cdot7 \times 1\cdot7$ mm, tabular on (120), was prepared by the method of Guérin (1941). With the crystal *c* axis mounted along the instrumental *φ*-rotation axis, neutron intensity data for wavelength 1·148 Å were collected for the positive octant on a Ferranti automatic single-crystal diffractometer at the PLUTO reactor, Atomic Energy Research Establishment, Harwell. For each reflexion, counts were recorded with an $\omega/2\theta$ step scan in 20 steps of 0·08° in ω for the peak (highest step count of 4000 for the strongest reflexion 020) and four further steps on each side (typical background counts were from 5 to 30 per step); the monitor count per step was 4×10^4. An Atlas program by N. A. Curry converted diffractometer output punched tapes to relative structure amplitudes and their estimated standard deviations. Of the 1290 reflexions with $2\theta \leq 100°$

---

accessible in the *hkl* octant, 518 had non-zero integrated intensity. With $\mu = 0.03$ cm^{-1}, absorption was neglected; extinction is discussed later.

Structure analysis and refinement

Location of hydrogen atoms

A three-dimensional Fourier difference synthesis ($R = 0.31$) with the neutron data, with F_c values computed from the non-hydrogen atom coordinates from the CF X-ray analysis, showed all hydrogen atoms in the approximate locations expected from the hydrogen-bonding scheme proposed by CF. Nuclear scattering lengths (Bacon, 1969) used here and subsequently were: Ca, 0.49×10^{-12} cm; As, 0.64×10^{-12} cm; O, 0.577×10^{-12} cm; and H, -0.372×10^{-12} cm.

Refinement with neutron data

In the course of the least-squares refinement with unitary weights by the full-matrix *ORFLS* program of the *X-ray* 63 *System* on the Chilton Atlas computer, weak reflexions ($|F_o| \leq 1.5 \times 10^{-12}$ cm) were rejected for which the corresponding F_c's were near zero. After a preliminary isotropic refinement over all atoms to an R value of 0.18, anisotropic refinement was satis-

Fig. 1. Unit cell of haidingerite projected down the *x* axis. Hydrogen atoms are shown as closed black circles, water oxygens as bold open circles, calcium ions as small bold circles and arsenic atoms as small circles; lines of alternating dashes and dots represent hydrogen bonds.

Table 1. *Observed and calculated structure factors*

factory for all atoms except As, for which the temperature factor remained not positive-definite even when only half shifts were applied. With As restricted to isotropic refinement and all other atoms treated anisotropically, the refinement converged to give an R of 0·057, with all shifts less than standard deviations. Examination of the structure-factor listing revealed no evidence of serious extinction except for 020; with this reflexion omitted, the final R value was 0·055. Further cycles of least-squares refinement neither produced significant shifts nor reduced R; consequently, the discussion is based on the parameters derived from the

final cycle with 020 included. A Fourier difference synthesis revealed only statistically distributed peaks with maximum heights $\pm 0·03 \times 10^{-12}$ cm Å^{-3}. Table 1 lists the final $|F_o|$ and F_c values, and the upper entries in Table 2 give the final positional coordinates for all atoms (with e.s.d.'s in parentheses), together with B_{ij}

Fig. 2. Projection down the y axis of a characteristic double layer of the crystal structure of haidingerite; key as for Fig. 1.

Table 3. *Parameters from the neutron refinement characterizing the principal directions 1,2,3 of thermal vibration for the atoms: root-mean-square displacement (r.m.s.d.) (Å), and angles which the principal directions make with the x, y and z axes (B, C and D)*

		A	B	C	D
	1	0·14 Å	87°	90°	3°
Ca	2	0·14	90	0	90
	3	0·08	3	90	93
	1	–	–	–	–
As	2	–	–	–	–
	3	–	–	–	–
	1	0·12	130	41	97
O(1)	2	0·16	107	95	17
	3	0·10	45	49	74
	1	0·13	80	104	17
O(2)	2	0·16	94	15	75
	3	0·06	11	84	99
	1	0·12	116	104	30
O(3)	2	0·15	95	14	77
	3	0·10	26	91	64
	1	0·12	82	24	68
O(4)	2	0·15	98	111	23
	3	0·06	12	101	86
	1	0·14	78	22	109
W	2	0·19	130	68	48
	3	0·12	43	86	48
	1	0·18	116	125	46
H(1)	2	0·20	120	38	69
	3	0·13	41	79	51
	1	0·23	51	105	43
H(2)	2	0·25	128	67	47
	3	0·13	63	28	95
	1	0·20	17	90	107
H(3)	2	0·26	89	3	87
	3	0·14	73	93	17

Table 2. *Final fractional atomic coordinates together with the values of the thermal parameters, B_{ij} (Å^2) (Neutron refinement above, X-ray refinement below)*

Significant figures of estimated standard deviations are given in parentheses.

	$10^4x/a_0$	$10^4y/b_0$	$10^4z/c_0$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	6250 (9)	471 (3)	1829 (6)	0·49 (23)	1·51 (17)	1·44 (15)	0·01 (17)	0·05 (17)	0·00 (13)
	6263 (7)	476 (2)	1841 (6)	1·60 (16)	1·92 (15)	1·65 (16)	0·04 (17)	−0·20 (21)	0·39 (14)
As	1277 (7)	1090 (2)	590 (4)	B = 0·70					
	1283 (3)	1090 (1)	589 (3)	1·37 (9)	0·90 (6)	1·40 (8)	1·16 (8)	0·04 (11)	0·09 (8)
O(1)	2190 (8)	1996 (2)	1438 (6)	1·03 (21)	1·00 (13)	1·94 (15)	−0·16 (15)	−0·32 (18)	−0·14 (12)
	2249 (23)	2007 (8)	1428 (22)	3·56 (73)	1·15 (45)	1·96 (66)	0·78 (51)	−1·49 (69)	−0·32 (56)
O(2)	−372 (7)	736 (3)	1928 (5)	0·28 (20)	1·87 (15)	1·29 (13)	−0·15) (17)	0·14 (14)	0·18 (11)
	−413 (21)	744 (8)	1909 (21)	1·31 (57)	1·73 (53)	1·78 (60)	−0·48 (48)	0·25 (65)	−1·08 (54)
O(3)	483 (7)	1320 (2)	−1324 (5)	0·83 (21)	1·70 (15)	1·10 (12)	−0·04 (15)	−0·17 (14)	0·13 (10)
	547 (24)	1324 (9)	−1336 (20)	3·03 (69)	1·80 (54)	1·64 (57)	−0·33 (52)	1·31 (74)	0·04 (52)
O(4)	3029 (7)	359 (2)	594 (5)	0·32 (20)	1·24 (14)	1·73 (13)	0·20 (14)	−0·14 (14)	−0·20 (11)
	3005 (21)	365 (9)	549 (22)	2·04 (52)	1·66 (52)	2·37 (62)	1·29 (44)	−0·05 (67)	−0·36 (66)
W	6223 (8)	1595 (3)	−76 (6)	1·90 (26)	1·73 (19)	1·97 (18)	−0·34 (19)	−0·73 (19)	0·13 (14)
	6239 (23)	1603 (7)	−64 (19)	2·80 (53)	1·10 (48)	1·75 (53)	−0·85 (54)	−1·33 (64)	−0·28 (46)
H(1)	3121 (14)	1834 (5)	2342 (10)	1·94 (41)	2·82 (31)	2·14 (27)	−0·34 (33)	−0·73 (32)	−0·07 (23)
H(2)	6844 (16)	2113 (6)	111 (13)	3·84 (55)	2·14 (31)	4·44 (37)	−1·30 (38)	−0·26 (44)	0·46 (30)
H(3)	5806 (15)	1522 (7)	−1199 (11)	3·16 (51)	5·41 (46)	1·76 (30)	0·05 (40)	−0·47 (32)	0·20 (28)

values (except for As for which the isotropic B is given) in the expression

$$\exp\left\{-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_i \cdot h_j a^{*}_{i} \cdot a^{*}_{j}\right\}.$$

Parameters of the thermal ellipsoids for all atoms are given in Table 3.

Refinement with X-ray data

Since the bond lengths derived from the neutron refinement (Tables 4, 5 and 6) appeared to differ slightly from those derived from the CF X-ray refinement, a least-squares refinement of the X-ray data was undertaken with the hydrogen atoms included. With a local modification (for IBM 360/44, University of Turin) of the full matrix *ORFLS* program, parameters were refined anisotropically for all atoms except hydrogen. Nine scale factors were included and anomalous scattering by As and Ca w. s corrected for real and imaginary components. With $|F_o|$ values and weighting scheme as given by CF, R fell in two cycles from 0·085 to 0·073 over all reflexions with non-zero weight (or 0·118 to 0·107 for all reflexions listed by CF) to give parameters (e.s.d.'s in parentheses) shown in the lower rows of Table 2. The new apparent e.s.d.'s are about three times the apparent e.s.d.'s derived from the earlier CF block-diagonal least-squares program.

Table 4. *Interatomic distances and angles for arsenate ion, from neutron refinement*

Significant figures of estimated standard deviations are given in parentheses.

As–O(1)	1·729 (5) Å	O(3)–O(4)	2·796 (6) Å
As–O(2)	1·659 (6)	O(1)–H(1)	0·998 (10)
As–O(3)	1·657 (5)	O(1)–As–O(2)	107·1 (3)°
As–O(4)	1·691 (6)	O(1)–As–O(3)	106·7 (3)
O(1)–O(2)	2·725 (6)	O(1)–As–O(4)	109·3 (3)
O(1)–O(3)	2·718 (6)	O(2)–As–O(3)	115·9 (3)
O(1)–O(4)	2·790 (5)	O(2)–As–O(4)	104·4 (3)
O(2)–O(3)	2·811 (6)	O(3)–As–O(4)	113·3 (3)
O(2)–O(4)	2·647 (6)	As–O(1)–H(1)	107·3 (5)

Most of the changes involve the anionic oxygen atoms and the shifts tend to be towards the neutron coordinates. At first, it appeared that inclusion of the anionic hydrogen atom in the refinement significantly affects coordinates within the whole anion, whereas inclusion of hydrogen atom coordinates has little effect on the water-oxygen atom. However, a further series of full-matrix refinements of the X-ray data with the same weighting scheme showed that essentially the same parameters and final R value (0·074 for refined reflexions only, or 0·108 including those with zero weight) resulted, regardless of whether hydrogen atoms were included or whether anomalous scattering corrections were made for the real and imaginary parts of the As and Ca scattering f..ctors. Evidently, the type of matrix approximation adopted is much more important. In general, bond lengths and angles for the non-hydrogen atoms derived from this set of X-ray refinements do not differ significantly from those derived from the neutron analysis. Within the arsenate ion, the X-ray bond length with the largest discrepancy from the neutron analysis is As–O(1)=1·756 (14) Å* and the only discrepant intra-ionic oxygen separations are O(1)···O(2)=2·77 (2) Å and O(3)···O(4)= 2·74 (2) Å (*cf.* Table 4). Hydrogen-bond lengths for the water molecule derived from the X-ray refinement are W···O(1,3')=2·75 (2); W···O(2,5')=2·84 (2) Å (*cf.* Table 6). Some differences between coordinates derived from X-ray and neutron refinements would not be unexpected, as Coulson (1969) has pointed out; the centroid of the charge distribution in a bound atom need not coincide with the centre of gravity of the nucleus. Any comparisons between results from X-ray

* The labelling of the atoms is as follows: a single figure in parentheses (or no figure) denotes an atom of the asymmetric unit; a second figure ranging from 2 to 8, is included for atoms in the positions $\tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z; -x, \tfrac{1}{2}-y, z; \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z; \tfrac{1}{2}-x, y, \tfrac{1}{2}+z; x, \tfrac{1}{2}+y, -z; \tfrac{1}{2}+x, -y, \tfrac{1}{2}-z$; and $-x, -y, -z$, respectively. A prime denotes an atom shifted by lattice vectors.

Table 5. *Interatomic distances and angles in calcium coordination polyhedron, from neutron refinement*

Significant figures of estimated standard deviations are given in parentheses.

Ca——O(2,1')	2·373 (8) Å	O(3,5)–O(4,7)	3·685 (6) Å
Ca——O(2,7)	2·456 (7)	O(3,5)–O(2,7)	3·358 (6)
Ca——O(3,5)	2·337 (6)	O(3,5)–O(4)	3·074 (6)
Ca——O(4)	2·437 (7)	W——Ca-O(2,1')	83·7 (2)°
Ca——O(4,7)	2·737 (6)	O(2,1')–Ca–O(4,7)	67·8 (2)
Ca——O(4,8')	2·396 (6)	O(4,7)–Ca–O(2,7)	61·0 (2)
Ca——W	2·363 (7)	O(2,7)–Ca–O(4)	71·7 (2)
O(2,1')–W	3·160 (7)	O(4)——Ca-W	78·0 (2)
W——O(4)	3·023 (7)	O(4,8')–Ca–O(2,1')	85·6 (2)
O(4)——O(2,7)	2·867 (6)	O(4,8')–Ca–O(4,7)	103·4 (2)
O(2,7)–O(4,7)	2·647 (6)	O(4,8)–Ca–O(2,7)	88·4 (2)
O(4,7)–O(2,1')	2·867 (6)	O(4,8')–Ca–O(4)	79·9 (2)
O(4,8')–O(2,1')	3·240 (6)	O(4,8)–Ca–W	85·4 (2)
O(4,8')–W	3·226 (6)	O(3,5)–Ca–O(2,1')	112·1 (3)
O(4,8')–O(4)	3·105 (6)	O(3,5)–Ca–O(4,7)	92·8 (2)
O(4,8')–O(4,7)	4·034 (5)	O(3,5)–Ca–O(2,7)	88·9 (2)
O(4,8')–O(2,7)	3·383 (6)	O(3,5)–Ca–O(4)	80·2 (2)
O(3,5)–W	3·232 (6)	O(3,5)–Ca–W	86·9 (2)
O(3,5)–O(2,1')	3·907 (7)		

and neutron data collected by the commonly used procedures should be undertaken with care (Cooper, 1969).

Discussion

Bond lengths and angles derived from the neutron refinement are given in Tables 4, 5 and 6. Since most features of the structure, including the overall hydrogen-bonding system (Figs. 1 and 2), do not differ materially from the description of CF, discussion here is concerned largely with the configuration of the water molecule and with details of the hydrogen bonds.

The H–O–H angle of 113° in the water molecule of haidingerite is one of the largest reported; 115° was found in $CuF_2.2H_2O$ (Abrahams & Prince, 1962). The water molecule in haidingerite can be described approximately in terms of type D of the classification by Chidambaram, Sequeira & Sikka (1964). However, since the Ca atom is considerably (0·41 Å) out of the water-molecule plane (equation $6·091X - 6·633Y - 1·831Z = 2·746$) and makes an angle of about 10° with the bisector of the lone-pair of the water oxygen atom, a better description of the water molecule in haidingerite would be a hybrid between types D and J. Much the same situation holds for the $W(2)$ water molecule in pharmacolite (Ferraris, Jones & Yerkess, 1971a), where the Ca atom is 0·19 Å out of the plane and the Ca$\cdots W \cdots$lone-pair-bisector angle is 4·5°.

For sodium arsenate heptahydrate, $Na_2HAsO_4.7H_2O$ (Ferraris, Jones & Yerkess, 1971b), in particular, but also for pharmacolite, we have emphasized the planarity of the group comprised of the water molecule and the acceptor oxygen atoms. As for one of the water molecules [$W(2)$] in pharmacolite, the group consisting of the water molecule and the two oxygen acceptor atoms of the hydrogen bonds in haidingerite does not form a true plane; the five atoms $W(2)$, H(2), H(3), O(2,5) and O(1,3) are distant 0·05, 0·05, −0·19, 0·08 and 0·01 Å, respectively, from their best least-squares plane (equation $6·107X - 7·510Y + 0328Z = 2·549$) The pharmacolite and haidingerite results would appear to suggest that, when the water molecule is of type D, or at least of a pseudo-type D, the planarity requirement is less strict than in other cases; in particular, both pharmacolite and haidingerite have one hydrogen atom significantly out of the plane.

The abnormally large H–O–H angle may result from two cooperating effects: first, angle O$\cdots W \cdots$O [147·7 (2)°] is large; and second, the Ca atom position would tend to decrease the angle of the lone pair. The second effect requires an increase of the H–O–H angle (see, e.g. Coulson, 1970, and Coppens, 1970). With regard to the first effect, we have found (Ferraris, Jones & Yerkess, 1971a, b) that lack of correspondence between O$\cdots W \cdots$O and H–W–H angles chiefly affects the linearity of the hydrogen bond; however, one may also note that in $Na_2HAsO_4.7H_2O$ (Ferraris, Jones & Yerkess, 1971b) the larger H–O–H angles (about 110°) are associated with the larger O$\cdots W \cdots$O angles. In haidingerite, not only is the O$\cdots W \cdots$O angle unusually large, but also the two W–H$\cdots$O hydrogen bonds [2·798 (6) and 2·815 (6) Å] are fairly strong for a water molecule; an unusual distorting effect of the O$\cdots W \cdots$O angle on the H–W–H angle is to be expected. Both hydrogen bonds from the water molecule are markedly non-linear [155 (1)° and 147 (1)°].

Corrections for thermal motion (Busing & Levy, 1964) have been made to the three O–H bonds. Table 7 gives the lower (A) and upper (B) limits, together with the length (C) on the assumption of the O–H 'riding' model.

Table 7. O–H *bond lengths corrected for thermal motion*: *lower* (A) *and upper* (B) *limits and 'riding' model* (C)

	A	B	C
O1–H(1)	0·999 Å	1·085 Å	1·008 Å
W–H(2)	0·958	1·118	0·983
W–H(3)	0·950	1·107	0·975

The anionic hydrogen, H(1), is attached to O(1), the oxygen atom with the longest As–O bond [1·729 (5) Å, compared with 1·669 (4) Å for the mean of the other three]. As in pharmacolite (Ferraris, Jones & Yerkess, 1971a), the (uncorrected) O(1)–H(1) distance of 1·00 (1) Å is slightly longer than the water-molecule O–H distances. H(1) forms a hydrogen bond to O(3,5) of comparable strength [2·632 (6) Å] and non-linearity [O(1)–H(1)$\cdots$O(3,5) is 164·6 (8)°] with those in other acidic arsenates we have studied (Ferraris, Jones & Yerkess, 1971a, b). For the three structures haidin-

Table 6. *Interatomic distances and angles for atoms engaged in hydrogen bonds, from neutron refinement*

Significant figures of estimated standard deviations are given in parentheses.

W———H(2)	0·952 (11) Å	H(2)———W———H(3)	113 (1)°
W———H(3)	0·944 (10)	O(1)———H(1)———O(3,5)	164·6 (8)
O(1)——H(1)	0·998 (10)	As———O(1)———H(1)	107·3 (5)
H(2)…H(3)	1·584 (14)	W———H(2)…O(1,3′)	155·3 (10)
W……O(1,3′)	2·798 (6)	W———H(3)…O(2,5′)	146·7 (10)
W……O(2,5′)	2·815 (6)	O(1,3′)…W……O(2,5′)	147·7 (2)
O(1) .. O(3,5)	2·632 (6)	Ca ……W———H(2)	125·0 (7)
H(1)…O(3,5)	1·657 (10)	Ca ……W———H(3)	120·7 (8)
H(2)…O(1,3′)	1·904 (11)	Ca ……W……O(1,3′)	110·4 (2)
H(3)…O(2,5′)	1·978 (11)	Ca ……W……O(2,5′)	99·4 (2)

gerite, pharmacolite, and $Na_2HAsO_4.7H_2O$, the dimensions associated with the hydrogen bond of the anionic hydrogen are remarkably similar; the average values for As–O–H, O–H (uncorrected), O$\cdots$O, and O–H$\cdots$O are, respectively, 110°, 1·01 Å, 2·67 Å and 164°.

The authors thank Mr D. H. C. Harris and members of the University Support Group, and Mr K. D. Rouse, A.E.R.E., for advice. We are grateful to the S.R.C. for making available neutron-beam and computational facilities, the Italian C.N.R. for the award of a N.A.T.O. Fellowship to GF, and Bradford University for the award of a scholarship to JY.

References

ABRAHAMS, S. C. & PRINCE, E. (1962). *J. Chem. Phys.* **36**, 50.
BACON, G. E. (1969). *Acta Cryst.* A**25**, 391.
BINAS, H. (1966). *Z. anorg. allg. Chem.* **347**, 133.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
CALLERI, M. & FERRARIS, G. (1967). *Per. Mineral,* **36**, 1.
CASSIEN, M., HERPIN, P. & PERMINGEAT, F. (1966). *Bull. Soc. franç. Minér. Crist.* **89**, 18.
CHIDAMBARAM, P., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616.
COOPER, M. J. (1969). *Acta Cryst.* A**25**, 488.
COPPENS, P. (1970). Chap. 6 in *Thermal Neutron Diffraction.* Edited by B. T. M. WILLIS. Oxford Univ. Press.
COULSON, C. A. (1970). Chap. 5 in *Thermal Neutron Diffraction.* Edited by B. T. M. WILLIS. Oxford Univ. Press.
CURRY, N. A., DENNE, W. A. & JONES, D. W. (1968). *Bull. Soc. Chim. France,* p. 1748.
DENNE, W. A. & JONES, D. W. (1969). *Acta Cryst.* A**25**, S125.
FERRARIS, G., JONES, D. W. & YERKESS, J. (1971*a*). *Acta Cryst.* B**27**, 349.
FERRARIS, G., JONES, D. W. & YERKESS, J. (1971*b*). *Acta Cryst.* B**27**, 354.
FISCHER, E. (1960). *Chem. der Erde,* **20**, 162.
GUÉRIN, H. (1941). *Ann. Chim.* **16**, 101.
MARTIN, C., DURIF, A. & AVERBUCH-POUCHOT, M.-T. (1970). *Bull. Soc. franç. Minér. Crist.* **93**, 397.

The Crystal Structure of All-*trans* Retinal₁

BY T. HAMANAKA* AND T. MITSUI*

Department of Physics, Faculty of Science, Hokkaido University, Sapporo, Japan

AND T. ASHIDA AND M. KAKUDO

Institute for Protein Research, Osaka University, Kita-ku, Osaka, Japan

The crystal structure of all-*trans* retinal₁ has been determined by the symbolic addition method and refined by block-diagonal least-squares calculations with three-dimensional data collected using diffractometers. The crystal is monoclinic, space group $P2_1/n$, with $a = 15\cdot270$, $b = 8\cdot264$, $c = 14\cdot942$ Å, $\beta = 104\cdot73°$, and 4 molecules in the unit cell. The introduction of some disorder in the cyclohexene ring gave the final discrepancy index R of 8·8%. With the exception of the nearly s-*cis* orientation about the single bond from the chain to the cyclohexene ring, the chain is in the all-*trans* configuration. The dihedral angle between the planes of the ring and the chain is 62°. The average values of single and double bonds of this conjugated linear chain are 1·460 and 1·336 Å respectively. The chain is markedly curved in its plane and slightly bent normal to its plane.

Introduction

Retinal (vitamin-A aldehyde) is the chromophore of the visual pigments. It is well known that the only action of light in vision is to isomerize the retinal molecule from 11-*cis* to the all-*trans* configuration (Hubbard & Kropf, 1958; Wald, 1968). To understand the initial process of visual excitation, it is necessary to disclose the mechanism of *cis-trans* isomerization of retinal combined with opsin.

The present study is the first part of a project which has been undertaken in order to explain the photoreceptor process on the basis of the molecular structure of stereoisomers of retinal and retinal-related compounds. The numbering of the atoms is shown in Fig. 1.

Experimental

Crystals of all-*trans* retinal₁ were obtained as pale yellow parallelepipeds from light petroleum below 0°C.

Two sets of three-dimensional intensity data were used in this work. The first set of data was recorded by the Rigaku Denki AFC-I, an automatic four-circle diffractometer operated in a open-loop manner by a

* Present address: Department of Biophysical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.