This dislocation of the metal atoms, suddenly occurring after long periods, is evidently the cause of the peculiar X-ray pattern given by β tungsten oxide, and of the diffraction effects appearing in the electron-density function derived on the basis of the observed X-ray data.

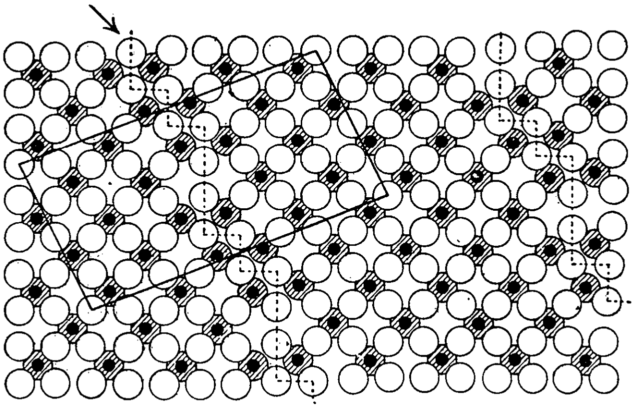

Fig. 6. The structure of β tungsten oxide. The tungsten atoms (black circles) are situated in planes normal to the *b* axis of the monoclinic unit cell. Oxygen atoms within these planes (open circles) and in interjacent planes (shaded circles) are octahedrally grouped around the metal atoms. The unit extension parallel to the *b* axis amounts to one octahedron. The WO_6 octahedra, joined by sharing corners, form blocks of almost regular $D0_9$ structure. The blocks, which are infinitely extended in two dimensions, are mutually connected by octahedra, sharing edges at folded 'planes of dislocation', the projections of which are indicated by broken lines. In the direction of the arrow the blocks show a characteristic extension of twenty octahedra.

The periodic dislocation of atoms found in structures of layer-lattice type shows certain similarities to the one described above. In single-crystal photographs of various modifications of silicon carbide obtained by Ramsdell (1947) and by Honjo, Miyake & Tomita (1950), a fine structure of the X-ray patterns analogous to that of β tungsten oxide is strikingly demonstrated. It is obvious that when carrying out Fourier calculations for such compounds due regard must be given to the influence of non-observed reflexions.

The author wishes to express his sincere gratitude to Prof. G. Hägg and Dr N. Norman for valuable discussions. The work has been carried out in connexion with investigations on certain oxide systems, financially supported by the Swedish Natural Science Research Council.

References

Bragg, W. L. & West, J. (1930). *Phil. Mag.* **10**, 823.

Honjo, G., Miyake, S. & Tomita, T. (1950). *Acta Cryst.* **3**, 396.

Magnéli, A. (1949). *Acta chem. scand.* **3**, 88.

Magnéli, A. (1950*a*). *Nature, Lond.*, **165**, 356.

Magnéli, A. (1950*b*). *Ark. Kemi*, **1**, 513.

Ramsdell, L. S. (1947). *Amer. Min.* **32**, 64.

Acta Cryst. (1951). **4**, 450

The Crystal Structure of Acetoxime

By T. K. Bierlein and E. C. Lingafelter

Department of Chemistry and Chemical Engineering, University of Washington, Seattle 5, Washington, U.S.A.

(*Received* 22 *September* 1950 *and in revised form* 10 *February* 1951)

The crystal structure of acetoxime has been determined by Fourier projections on (001). The structure consists of sheets of planar trimers having intermolecular OH...N hydrogen bonds.

Introduction

Since investigations of acetoxime in the melt and in solution (Caughlan, 1941) indicate association to a higher degree than dimers, the crystal structure has been investigated in order to determine the degree of association in the solid state as well as the configuration of the molecule.

Preliminary crystallographic data

Because of the appreciable vapor pressure of acetoxime at room temperature, suitable crystals were readily grown by sublimation. However, for the same reason, it was found necessary to enclose the crystals with a thin film of formvar (Roth & Harker, 1948).

X-ray diffraction data were obtained from oscillation and equi-inclination Weissenberg photographs taken about the *a* and *c* axes of the hexagonal lattice. The unit cell has dimensions

$$a_0 = 10{\cdot}61, \quad c_0 = 7{\cdot}02\ \text{A.}$$

and contains 6 molecules. (Calculated density, 1·057 g.cm.$^{-3}$; observed, 1·045 g.cm.$^{-3}$.) Copper radiation ($K\alpha = 1{\cdot}5418$ A.) was used and the camera diameter was calibrated with NaCl ($a_0 = 2{\cdot}8197$ A.).

The only extinction observed was $(00l)$ for l odd. This, combined with the Laue symmetry $C6/m$, indicated the space groups $C6_3$ or $C6_3/m$. The excellent cleavage parallel to (001), the exceptionally high intensity of the $(00l)$ diffractions, and the identity in the intensity distributions of the zero- and second- and of the first- and third-level equi-inclination Weissenberg photographs about the c axis indicate a layer structure, with all atoms having Z co-ordinates of $\frac{1}{4}$ or $\frac{3}{4}$. The space group was therefore assumed to be $C6_3/m$.

Intensities

The intensities of the reflections recorded on single and on multiple films were visually estimated by several observers and an average set, referred to a standard set of spots of proportionately increasing exposure times, was obtained. The observed intensities were corrected for the Lorentz and polarization effects according to Buerger & Klein (1945); absorption and extinction errors were considered to be negligible. Although a rather high anisotropic temperature factor is probably applicable, the ordinary isotropic factor was used, with a final value of $B=4\times10^{-16}$ cm.^{2}. The values used for the scattering factors of the atoms were obtained from the *Internationale Tabellen.* The positions of the hydrogen atoms were taken to be those of the bonding atoms.

Patterson section

After some preliminary trial-and-error calculations had been made, mainly using a Bragg–Lipson chart for $(h00)$, the Patterson section $P(x,y,0)$ was evaluated.

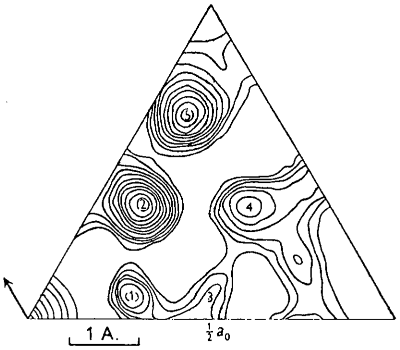

Fig. 1. Patterson section at $Z=0$. Contours are drawn at equal intervals on an arbitrary scale; all negative contours are omitted and the interval is increased by a factor of ten on the peak at the origin. Termination of vectors at peak 1 represent N–C_1, N–O, C_1–C_2, C_1–C_3 distances; at peak 2, O–C_1, C_2–C_3, N–C_2, N–C_3; at peak 3, O–C_2, OH...N; at peak 4, N–N, O–C_1; at peak 5, O–O, O–C_3. Notation refers to Fig. 3.

Because of the layer structure, only values of $|F(hk0)|^2$ (53 independent values) and $|F(hk1)|^2$ (33 independent values) were used. These were divided by the appropriate $(\bar{f}_r)^2$ as suggested by Patterson (1935), and Patterson–Tunell strips ($\frac{1}{60}$ths) were used for the calculation. This section (Fig. 1) could be interpreted in terms of the existence of trimers, held together by OH...N bonds. The threefold ambiguity arising from this section was resolved by comparison of calculated and observed values of $F(h00)$.

Fourier projection

Since the structure indicated by the Patterson section $P(x, y, 0)$ would give a well-resolved Fourier projection on (001), this projection was evaluated by means of the Patterson–Tunell strips. After three successive refinements, no further changes in signs were indicated by the projection illustrated in Fig. 2. The more accurate positions of the maxima were then calculated using the method of Donnay & Donnay (1949), and the final co-ordinates are listed in Table 1.

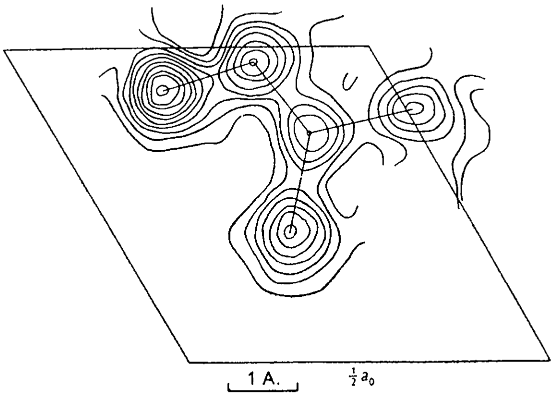

Fig. 2. Fourier projection on (001) containing one asymmetric unit. Contours are drawn at equal intervals on an arbitrary scale.

Table 1. *Atomic co-ordinates*

	x	y	z
O	0·432	0·245	$\frac{1}{4}$
N	0·474	0·143	$\frac{1}{4}$
C_1	0·362	0·013	$\frac{1}{4}$
C_2	0·203	0·963	$\frac{1}{4}$
C_3	0·403	0·892	$\frac{1}{4}$

The reliability index, $\Sigma||F_o|-|F_c||\div\Sigma|F_o|$, has a value 0·20 for the $(hk0)$ zone and 0·25 for the $(hk1)$ planes. If the calculated structure factors for the non-observable faint spots are omitted, the values become 0·18 and 0·14, respectively.

It is interesting to note that a Fourier projection evaluated using the signs calculated from one of the incorrect ambiguities from the Patterson section gave very satisfactory peaks in the positions corresponding to that structure, but the value of the reliability index remained at about 0·45.

Discussion of structure

The arrangement of the molecules in crystalline acetoxime is in quite satisfactory agreement with the properties of the substance. The existence of cyclic trimers, with only van der Waals forces between the trimers, accounts for the large vapor pressure. These trimers probably exist, in equilibrium with dimers and monomers, in the liquid state, giving rise to an association number approaching 3 in the more concentrated solutions. The parallel arrangement of these planar trimers explains the excellent (001) cleavage of the crystals. The O–H...N hydrogen bond distance, 2·78 A., indicates a fairly strong hydrogen bond.

The intramolecular distances and angles (Fig. 3), are not unreasonable. From a consideration of the variation of the reliability index with successive refinements, we estimate the distances to be accurate to ±0·03 A.

The average C–C bond distance, 1·52 A., compares favorably with the value 1·54 A., obtained from Pauling's (1944) covalent radii. It is probably unwarranted to attempt any discussion of the significance of the difference in the two C–C distances. The N–O bond distance, 1·36 A., is equal to the value obtained from Pauling's covalent radii, but the values of Schomaker & Stevenson (1941) yield a distance of 1·44 A., and the experimental results on hydrogen peroxide, hydrazine and the hydroxyl-ammonium ion (Jerslev, 1948; Giguère & Schomaker, 1943) indicate this higher value

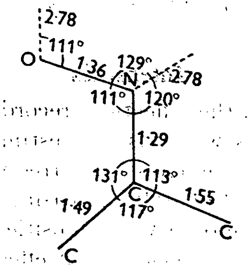

Fig. 3. Structure of the acetoxime molecule from co-ordinates in Table 1.

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c
100	16·0	−16·9
200	0	− 0·9
300	18·6	−18·2
400	8·3	8·7
500	16·4	12·3
600	7·8	5·0
700	5·2	− 5·1
800	5·0	4·3
900	3·1	3·5
110	22·9	27·7
120	17·3	18·1
130	13·2	8·8
140	24·5	24·4
150	16·8	−12·6
160	5·8	7·2
170	0	− 2·5
180	3·9	− 2·8
210	12·2	5·4
220	24·1	−23·9
230	6·7	0·9
240	0	1·1
250	12·2	7·7
260	2·6	− 3·1
270	6·4	7·7
280	4·4	6·4
310	11·8	− 7·0
320	14·1	−11·1
330	17·3	17·3
340	8·0	6·0
350	4·2	− 6·0
360	0	1·7
370	3·5	4·7
410	12·5	9·2
420	17·2	−17·6
430	9·5	11·4
440	13·1	10·9
450	7·0	10·5
510	5·6	3·8
520	8·6	− 8·2
530	14·8	15·7
540	0	5·5
550	4·5	1·5
610	14·2	13·2
620	17·2	16·9
630	6·7	8·6
710	7·7	8·2
720	10·0	− 9·3
730	0	− 0·9
740	3·0	3·4
810	3·9	3·8
820	0	− 1·6
830	2·9	2·8
10,2,0	2·6	3·8
101	20·3	−21·5
201	16·7	−17·8
301	47·4	52·9
401	12·6	− 9·9
501	14·7	13·4
601	0	4·0
701	0	0·6
801	0	− 0·2
901	0	− 3·2
111	49·0	−52·8
121	6·9	2·7
131	22·1	−23·3
141	20·3	−16·2
151	15·9	16·1
161	0	1·2
171	0	− 0·4
181	0	− 2·6
211	6·9	− 6·8
221	14·8	−15·6
231	12·0	11·9
241	5·9	− 6·8
251	0	− 4·2
261	0	4·9
271	6·2	5·6
281	0	0·6
311	4·6	− 4·6
321	18·9	19·8
331	15·1	16·1
341	5·4	− 3·6
351	11·8	12·8
361	0	3·2
371	0	1·9
411	0	1·2
421	4·9	−7·6
431	6·6	−0·5
441	4·1	1·9
451	0	1·4
511	13·3	10·9
521	6·7	11·0
531	4·1	3·0
541	0	2·5
551	0	3·5
611	6·9	7·6
621	4·2	6·3
631	4·4	− 5·1
711	15·0	−17·5
721	15·4	17·0
731	0	0·4
741	0	− 1·1
811	0	0·2
821	0	3·5
831	0	0·5
10,2,1	0	1·7

to be correct. Thus the N–O bond distance appears to be somewhat shorter than normal. The C–N distance, 1·29 A., is very slightly longer than the value of 1·27 A. given by Pauling's radii, which has been tentatively accepted by Cox & Jeffrey (1951). This shortening of the single bond and lengthening of the double bond may arise from resonance between $C{=}N{-}O$ and $C^{-}{-}N{=}O^{+}$. We hope soon to be able to make calculations of the bond orders to be expected in such a system.

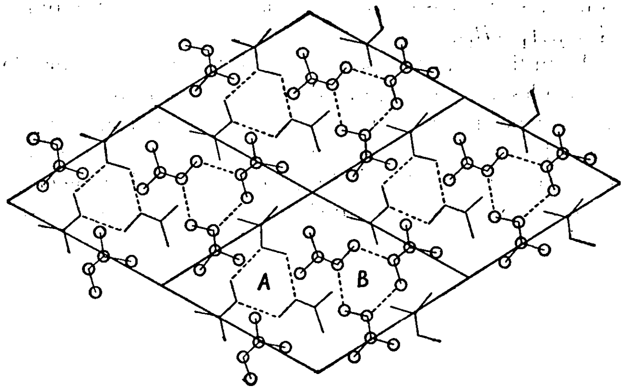

Fig. 4. Schematic projection of the crystal structure on (001). The symbols *A* and *B* represent trimers in the two layers separated by 3·51 A.

The difference between the two N–C–C bond angles may be due to a repulsion between the oxygen atom and the *cis*-methyl group.

The van der Waals contact distance between methyl groups in the same plane shows two quite different values. In the grouping about the 6_3 axis the distance is 4·09 A., in good agreement with the customary value of 2·0 A. for the van der Waals radius of the methyl group. On the other hand, the grouping about the threefold axis, which has the hydrogen-bonded rings above and below, shows a distance of only 3·67 A. (cf. Levy & Corey, 1941).

References

Buerger, M. J. & Klein, G. E. (1945). *J. Appl. Phys.* **16**, 408.

Caughlan, C. N. (1941). Thesis, University of Washington.

Cox, E. G. & Jeffrey, G. A. (1951). *Proc. Roy. Soc.* A, **207**, 110.

Donnay, J. D. H. & Donnay, G. H. (1949). *Acta Cryst.* **2**, 366.

Giguère, P. A. & Schomaker, V. (1943). *J. Amer. Chem. Soc.* **65**, 2025.

Jerslev, B. (1948). *Acta Cryst.* **1**, 21.

Levy, H. A. & Corey, R. B. (1941). *J. Amer. Chem. Soc.* **63**, 2095.

Patterson, A. L. (1935). *Z. Krystallogr.* **90**, 517.

Pauling, L. (1944). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Roth, W. L. & Harker, D. (1948). *Acta Cryst.* **1**, 34.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Acta Cryst. (1951). **4**, 453

Étude Théorique de la Diffusion de la Lumière par un Fluide présentant un seul Axe d'Isotropie: Application aux Cristaux Liquides du Type Nématique

Par Pierre Chatelain

Laboratoire de Minéralogie, Faculté des Sciences de Montpellier, Hérault, France

(*Reçu le 15 décembre 1950*)

A theoretical study is made of the diffusion of light by a liquid composed of anisotropic particles, which show fluctuations in orientation and are so distributed that the medium possesses a unique isotropic axis. Two cases are considered: (1) discrete anisotropic molecules; (2) large groups of parallel anisotropic molecules dispersed among isolated molecules. In the two cases the theory leads to depolarization factors greatly in excess of unity. Spherical groups, of radius 0·1 μ, containing 10^6 mclecules of azoxyanisole arranged parallel and inclined at an angle $\theta < 36°$ to the isotropic axis and single molecules inclined at an angle $\theta > 36°$ are discussed in detail, and the results obtained agree in order of magnitude with experiment. It can, therefore, be concluded that in nematic liquid crystals diffusion is due to fluctuations in the orientation of the molecules round the isotropic axis and that the fluctuations in two molecules can be treated as independent only if their separation exceeds 0·1 μ.

Introduction

Les résultats relatifs à la diffusion de la lumière polarisée par une lame orientée de para-azoxyanisol, dans sa phase nématique, ont été donnés, dans quatre cas principaux, accompagnés d'une ébauche d'interprétation théorique (Chatelain, 1948). Si l'hypothèse du