

# One-Dimensional Disorder in the Structure of Sodium 2-Oxocaprylate\*

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Sodium 2-oxocaprylate gives a pattern of sharp and diffuse X-ray reflexions. The reflexions with  $h+k+l$  even are sharp and those with  $h+k+l$  odd are diffuse; further the diffusion of intensity takes place along the  $a^*$  reciprocal axis, thereby suggesting one-dimensional disorder. An expression for the diffracted intensities from the crystal as a function of the probability of occurrence of the fault has been derived on the postulate that the fault consists in the appearance of any layer of molecules as a twin on (001) with (100) as the composition plane, and assuming interaction among the neighbouring layers only.

## Introduction

The crystal structure of sodium 2-oxocaprylate is described in the preceding paper (Tavale, Pant & Biswas, 1964). The oscillation and Weissenberg photographs about the  $c$  axis show a pattern of sharp and diffuse spots as shown in Fig. 1 and Fig. 2 respectively. It is seen that the reflexions with  $h+k+l$  even are sharp, and those with  $h+k+l$  odd are diffuse. Further, the diffusion of intensity takes place along the  $a^*$  reciprocal axis, thereby suggesting it to be a case of one-dimensional disorder. Examples of such disorder are given by Dornberger-Schiff (1956) and Wooster (1962). This paper describes the type of disorder in the crystal of sodium 2-oxocaprylate and presents the results of a calculation of diffracted intensities, based on the postulated disorder and assuming interaction among the neighbouring layers only. The method of calculation is similar to that of Wilson (1942) and of Jagodzinski (1949).

## The disorder phenomenon

As shown in the preceding paper, this structure belongs to the space group  $Pbcn$ , which has the following eight equivalent positions:

$$\begin{array}{ll} (x, y, z); & (\frac{1}{2}-x, \frac{1}{2}+y, z); & (x, \bar{y}, \frac{1}{2}+z); \\ & (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z) & A_1 \\ -(x, y, z); & -(\frac{1}{2}-x, \frac{1}{2}+y, z); & -(x, \bar{y}, \frac{1}{2}+z); \\ & -(\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z) & B_1 \end{array}$$

Each equivalent position corresponds to one molecule, which is the asymmetric unit in this case. The four molecules marked  $A_1$  form the repeat unit of one layer of molecules, and the other four molecules marked  $B_1$  and related to  $A_1$  by a centre of inversion form the repeat unit of the neighbouring layer. Only van der Waals bonds operate between the layers and

there is a certain probability  $\alpha$  that during crystal growth a mistake occurs in the stacking of the layers. The calculation of diffracted intensities in the next section shows that the observed diffraction pattern can be explained if it is postulated that the mistake consists in the appearance of any layer as a twin on (001) with (100) as the composition plane. Let us call the layers which appear as the twins of  $A_1$  and  $B_1$ ,  $A_2$  and  $B_2$ , respectively. The four equivalent positions, corresponding to  $A_2$  and  $B_2$  would be as follows:

$$\begin{array}{ll} (x, y, \bar{z}); & (\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}); & (x, \bar{y}, -\frac{1}{2}-z); \\ & (\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{2}-z) & A_2 \\ -(x, y, \bar{z}); & -(\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}); & -(x, \bar{y}, -\frac{1}{2}-z); \\ & -(\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{2}-z) & B_2 \end{array}$$

In the disordered structure, there are thus four types of unit cell possible, namely  $A_1B_1$ ,  $A_2B_1$ ,  $A_1B_2$  and  $A_2B_2$ . Using the notation of Dornberger-Schiff (1956), the  $\sigma$  operation connecting the  $p$ th layer to the  $(p+1)$ th layer is either a centre of inversion ( $A_1$  to  $B_1$  and  $A_2$  to  $B_2$ ) or body-centring ( $A_1$  to  $B_2$  and  $A_2$  to  $B_1$ ), and the  $\sigma$  operation connecting the  $p$ th layer to the  $(p+2)$ th layer is either identity ( $A_1$  to  $A_1$  and  $B_1$  to  $B_1$ ) or reflexion on the (001) plane ( $A_1$  to  $A_2$  and  $B_1$  to  $B_2$ ).

The Fourier transforms  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  at the reciprocal point  $(h+\omega, k, l)$ , where  $h, k, l$  are integers and  $h+k+l$  is odd, of the unit cells  $A_1B_1$ ,  $A_2B_1$ ,  $A_1B_2$  and  $A_2B_2$  respectively are given by the following formulae:

$$F_1 = A \sin \frac{1}{2}\pi\omega + B \cos \frac{1}{2}\pi\omega, \quad (1)$$

$$F_4 = A \sin \frac{1}{2}\pi\omega - B \cos \frac{1}{2}\pi\omega, \quad (2)$$

$$F_2 = (A - iB) \sin \frac{1}{2}\pi\omega \quad (3)$$

$$F_3 = (A + iB) \sin \frac{1}{2}\pi\omega, \quad (4)$$

where

$$\begin{aligned} A = & -8 \sin 2\pi\{hx + \omega(x - \frac{1}{4})\} \cdot \cos 2\pi ky \cdot \cos 2\pi lz \\ & \text{for } l \text{ even, and} \\ & -8 \cos 2\pi\{hx + \omega(x - \frac{1}{4})\} \cdot \sin 2\pi ky \cdot \cos 2\pi lz \\ & \text{for } l \text{ odd; } \quad (5) \end{aligned}$$

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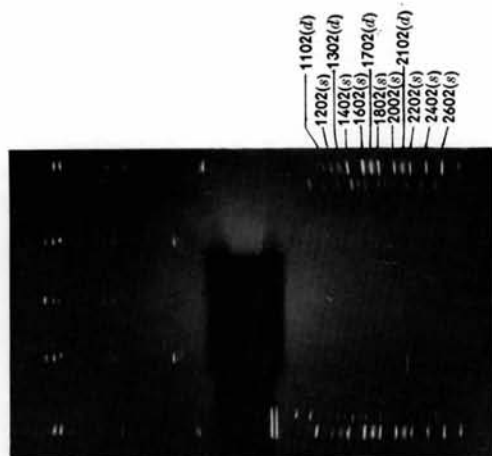


Fig. 1. 10° oscillation photograph; *c*: oscillation axis; Cu  $K\alpha$  radiation; 34 kV, 20 mA; exposure 9 hr.

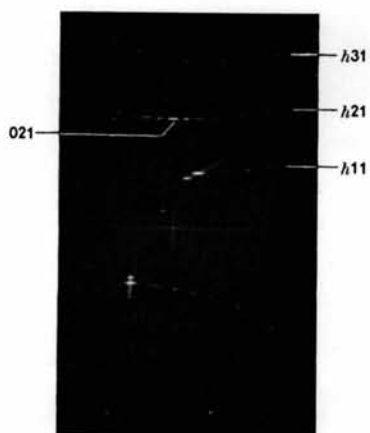


Fig. 2. First layer Weissenberg photograph; *c*: oscillation axis; Cu  $K\alpha$  radiation, 34 kV, 20 mA; exposure 9 hr.

$$B = -8 \sin 2\pi\{hx + \omega(x - \frac{1}{4})\} \cdot \cos 2\pi ky \cdot \sin 2\pi lz$$

for  $l$  even, and

$$-8 \cos 2\pi\{hx + \omega(x - \frac{1}{4})\} \cdot \sin 2\pi ky \cdot \sin 2\pi lz$$

for  $l$  odd. (6)

For  $\omega$  an odd integer, *i.e.* for  $(\omega + h) + k + l$  even,

$$|F_1|^2 = |F_4|^2 = A^2, \quad \text{and} \quad |F_2|^2 = |F_3|^2 = A^2 + B^2, \quad (7)$$

and for  $\omega$  an even integer, *i.e.* for  $(\omega + h) + k + l$  odd,

$$|F_1|^2 = |F_4|^2 = B^2, \quad \text{and} \quad |F_2|^2 = |F_3|^2 = 0. \quad (8)$$

### The intensity formula

It may be assumed that a structure starting  $A_1B_1A_1B_1\dots$  has a tendency to continue thus, but at each added layer there is a probability  $\alpha$  of a fault and the sequence continuing  $A_2B_2A_2B_2\dots$  till another mistake changes the sequence back to  $A_1B_1A_1B_1\dots$

Let the  $i$ th layer be of the  $A_1$  type. The probability of the  $(i+1)$ th layer being  $B_1$  is then  $(1-\alpha)$ , and of its being  $B_2$  is  $\alpha$ . Calling layers of the type  $A_1, B_1$  alike and  $A_2, B_2$  alike, but  $A_1, B_1$  unlike  $A_2, B_2$ , we find that the probability of the  $(i+m)$ th layer being like the  $(i+m-1)$ th layer is  $(1-\alpha)$ , and the probability of the  $(i+m)$ th layer being unlike the  $(i+m-1)$ th layer is  $\alpha$ .

Therefore, if  $P_m$  is the probability of the  $(i+m)$ th layer and the  $i$ th layer being alike, we get

$$P_m = (1-\alpha)P_{m-1} + \alpha(1-P_{m-1}).$$

Solving this difference equation, we get

$$P_m = \frac{1}{2} + \frac{1}{2}(1-2\alpha)^m.$$

If the  $i$ th layer is  $A_1$ , the  $(i+2m)$ th layer will be either  $A_1$  or  $A_2$  while the  $(i+2m+1)$ th layer will be either  $B_1$  or  $B_2$ ; and the probability of the  $(i+2m)$ th layer being  $A_1$  is  $\frac{1}{2} + \frac{1}{2}(1-2\alpha)^{2m}$ , and of its being  $A_2$  is  $\frac{1}{2} - \frac{1}{2}(1-2\alpha)^{2m}$ . Similarly, the probability of the  $(i+2m+1)$ th layer being  $B_1$  is  $\frac{1}{2} + \frac{1}{2}(1-2\alpha)^{2m+1}$ , and of its being  $B_2$  is  $\frac{1}{2} - \frac{1}{2}(1-2\alpha)^{2m+1}$ . The probability of the  $(i+1)$ th layer being  $B_1$  is  $(1-\alpha)$  and of its being  $B_2$  is  $\alpha$ .

Let us call the unit cell, consisting of the repeat units of  $i$ th and  $(i+1)$ th layers, the  $j$ th unit cell. In general, the  $(j+m)$ th unit cell will consist of the repeat units of  $(i+2m)$ th and  $(i+2m+1)$ th layers. The probability of the  $j$ th unit cell being  $A_1B_1$  is  $(1-\alpha)$ , and of its being  $A_1B_2$  is  $\alpha$ . Further,

the probability of the  $(j+m)$ th unit cell being  $A_1B_1$   
 $= \{\frac{1}{2} + \frac{1}{2}(1-2\alpha)^{2m}\} \{\frac{1}{2} + \frac{1}{2}(1-2\alpha)^{2m+1}\} = \alpha_1$  (say),  
the probability of the  $(j+m)$ th unit cell being  $A_2B_1$   
 $= \{\frac{1}{2} - \frac{1}{2}(1-2\alpha)^{2m}\} \{\frac{1}{2} + \frac{1}{2}(1-2\alpha)^{2m+1}\} = \alpha_2$ ,  
the probability of the  $(j+m)$ th unit cell being  $A_1B_2$   
 $= \{\frac{1}{2} + \frac{1}{2}(1-2\alpha)^{2m}\} \{\frac{1}{2} - \frac{1}{2}(1-2\alpha)^{2m+1}\} = \alpha_3$ ,  
and the probability of the  $(j+m)$ th unit cell being  $A_2B_2$   
 $= \{\frac{1}{2} - \frac{1}{2}(1-2\alpha)^{2m}\} \{\frac{1}{2} - \frac{1}{2}(1-2\alpha)^{2m+1}\} = \alpha_4$ .

It can similarly be shown that if the  $i$ th layer is  $A_2$ , the probabilities of the  $(j+m)$ th unit cell being  $A_1B_1, A_2B_1, A_1B_2$  and  $A_2B_2$  would be  $\alpha_4, \alpha_3, \alpha_2$  and  $\alpha_1$  respectively, and those of the  $j$ th unit cell being  $A_2B_2$  and  $A_2B_1$  would be  $(1-\alpha)$  and  $\alpha$  respectively. Hence  $J_m$ , the mean value of  $F_j F_{j+m}^*$ , as defined by Wilson (1942) is given by

$$J_m = \frac{1}{2} \{ (1-\alpha)F_1 + \alpha F_3 \} \{ F_1^* \alpha_1 + F_2^* \alpha_2 + F_3^* \alpha_3 + F_4^* \alpha_4 \} \\ + \frac{1}{2} \{ (1-\alpha)F_4 + \alpha F_2 \} \{ F_1^* \alpha_4 + F_2^* \alpha_3 + F_3^* \alpha_2 + F_4^* \alpha_1 \}, \quad (9)$$

where  $F_1, F_2, F_3$  and  $F_4$  are defined in the previous section. It can easily be shown after substituting the values of  $\alpha_s$  and  $F_s$  in the above expression that the same result will be obtained if the  $i$ th layer is assumed to be of the  $B$  type ( $B_1$  and  $B_2$ ) instead of the  $A$  type. In the case of one-dimensional disorder along the  $a$  direction, the scattered intensity falls off to zero, as in the case of ordered crystal when  $k$  or  $l$  (or both) depart from integral values by  $1/n_2$  and  $1/n_3$  respectively, where  $n_1, n_2$  and  $n_3$  are the numbers of unit cells along the  $a, b$  and  $c$  axes respectively (Wilson, 1942). We are therefore interested in the values of  $J_m$  only at points on the reciprocal lattice rods with  $k$  and  $l$  integral. Substituting the values of  $\alpha_s$  and  $F_s$  in the above, we obtain the following expression for  $J_m$  at the reciprocal point  $(h+\omega, k, l)$  where  $h, k, l$  are integers and  $h+k+l$  is odd:

$$J_m = A^2 \sin^2 \frac{1}{2}\pi\omega + B^2 \{ (1-\alpha)^2 \cos^2 \frac{1}{2}\pi\omega \\ + \alpha^2 \sin^2 \frac{1}{2}\pi\omega \} (1-2\alpha)^{|2m|}. \quad (10)$$

The above relation is derived for positive  $m$ , but it can be shown that it holds for negative values of  $m$  as well. The expression for the scattered intensity will then be (Wilson, 1942)

$$\mathcal{I}(h+\omega, k, l) = n_2^2 n_3^2 \left[ A^2 \sin^2 \frac{1}{2}\pi\omega \cdot \frac{\sin^2 \pi(h+\omega)n_1}{\sin^2 \pi(h+\omega)} \right. \\ \left. + B^2 \{ (1-\alpha)^2 \cos^2 \frac{1}{2}\pi\omega + \alpha^2 \sin^2 \frac{1}{2}\pi\omega \} \right. \\ \left. \times \Sigma (n_1 - |m|) (1-2\alpha)^{|2m|} \exp [2\pi i m a \cdot s / \lambda] \right]. \quad (11)$$

### Discussion

The term  $\Sigma (n_1 - |m|) (1-2\alpha)^{|2m|} \exp [2\pi i m a \cdot s / \lambda]$  in equation (11) reduces to

$$\frac{\sin^2 [\pi(h+\omega)n_1]}{\sin^2 [\pi(h+\omega)]}$$

for  $\alpha=0$  and unity, and becomes zero for  $\alpha=0.5$ . Therefore, the intensity expressions for these three special cases would be as follows:

For  $\alpha=0$ ,

$$\mathcal{I}(h+\omega, k, l) = n_2^2 n_3^2 \frac{\sin^2 \pi(h+\omega)n_1}{\sin^2 \pi(h+\omega)} \\ \times \{ A^2 \sin^2 \frac{1}{2}\pi\omega + B^2 \cos^2 \frac{1}{2}\pi\omega \}.$$

As expected, this reduces to  $n_1^2 n_2^2 n_3^2 |F_1|^2 (= n_1^2 n_2^2 n_3^2 |F_4|^2)$

at the reciprocal lattice points (*i.e.*  $\omega$  integral) and zero elsewhere (equations 7 & 8). This situation corresponds to the ordered structure  $A_1B_1A_1B_1\dots$  (or  $A_2B_2A_2B_2\dots$ ) of space group  $Pbcn$ .

For  $\alpha=1$ ,

$$\mathcal{I}(h+\omega, k, l) = n_2^2 n_3^2 \frac{\sin^2 \pi(h+\omega)n_1}{\sin^2 \pi(h+\omega)} (A^2 + B^2) \sin^2 \frac{1}{2} \pi \omega.$$

This reduces to  $n_1^2 n_2^2 n_3^2 \cdot |F_2|^2$  ( $=n_1^2 n_2^2 n_3^2 \cdot |F_3|^2$ ) at the reciprocal lattice points with the sum of indices, even (*i.e.*  $\omega$  odd) and zero elsewhere (equations 7). This situation corresponds to the ordered structure  $A_1B_2A_1B_2\dots$  (or  $A_2B_1A_2B_1\dots$ ) of space group  $Iba2$ .

For  $\alpha=0.5$ ,

$$\mathcal{I}(h+\omega, k, l) = n_2^2 n_3^2 \frac{\sin^2 \pi(h+\omega)n_1}{\sin^2 \pi(h+\omega)} \cdot A^2 \sin^2 \frac{1}{2} \pi \omega.$$

This reduces to  $n_1^2 n_2^2 n_3^2 \cdot |F_1|^2$  ( $=n_1^2 n_2^2 n_3^2 \cdot |F_4|^2$ ) at the reciprocal lattice points with the sum of indices even (*i.e.*  $\omega$  an odd integer) and zero elsewhere (equations 7). This situation corresponds to the statistically ordered structure  $(\frac{1}{2}A_1\frac{1}{2}A_2)(\frac{1}{2}B_1\frac{1}{2}B_2)\dots$  of space group  $Ibam$ .

When  $\alpha$  differs from zero, 0.5 and unity by an amount  $\geq 1/n_1$ , the intensity expression becomes

$$\begin{aligned} \mathcal{I}(h+\omega, k, l) = n_2^2 n_3^2 A^2 \sin^2 \frac{1}{2} \pi \omega \cdot \frac{\sin^2 \pi(h+\omega)n_1}{\sin^2 \pi(h+\omega)} \\ + n_1 n_2^2 n_3^2 B^2 \frac{\{(1-2\alpha) \cos^2 \frac{1}{2} \pi \omega + \alpha^2\} \{1 - (1-2\alpha)^4\}}{1 - 2(1-2\alpha)^2 \cos 2\pi \omega + (1-2\alpha)^4}. \end{aligned} \quad (12)$$

In the above expression, one term whose value is inappreciable for large values of  $n_1$  has been left out. The first term in the above corresponds to the sharp reflexions in the X-ray photographs. These reflexions do not appear when the sum of the indices is odd (*i.e.*  $\omega$  even) because of the factor  $\sin^2 \frac{1}{2} \pi \omega$ . When the sum of indices is even (*i.e.*  $\omega$  odd),  $A^2 = |F_1|^2$  (equations 7), so that these reflexions appear with the same intensity and sharpness as from an ordered crystal.

The second term in equation (12) corresponds to the diffuse reflexions in the X-ray photographs. The diffuse term is proportional to  $n_1$  while the sharp term is proportional to  $n_1^2$ . The diffuse reflexions, though weaker are not as faint as one would expect from the above expression. For a comparison between the intensities of the sharp and the diffuse spots, the problem should, as mentioned by Jagodzinski (1949) be treated on the basis of the dynamical theory, unless the sharp reflexions are themselves broadened owing to smallness of  $n_1$ .

The diffuse term can be written

$$I_d = n_1 n_2^2 n_3^2 B^2 Q,$$

where

$$Q = \frac{\{(1-2\alpha) \cos^2 \frac{1}{2} \pi \omega + \alpha^2\} \{1 - (1-2\alpha)^4\}}{1 - 2(1-2\alpha)^2 \cos 2\pi \omega + (1-2\alpha)^4}.$$

The plots of  $Q$  against  $\omega$  are shown in Fig. 3 for  $\alpha=0.1, 0.3, 0.7$  and  $0.9$ , respectively. The curves are

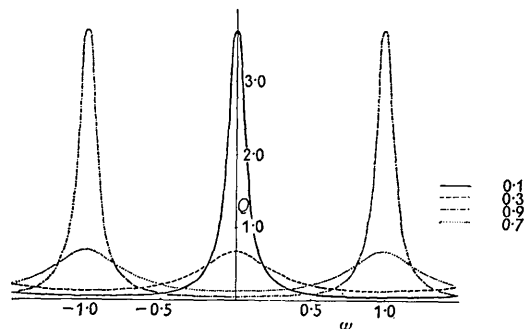


Fig. 3.  $Q$  versus  $\omega$  curves for  $\alpha=0.1, 0.3, 0.7$ , and  $0.9$ .

symmetrical about  $\omega=0$ , and they have maxima at  $\omega=0$  for  $\alpha < 0.5$  and at  $\omega=1$  for  $\alpha > 0.5$ ; in other words, for  $\alpha < 0.5$  the curves have maxima at the reciprocal lattice points with the sum of indices odd, while for  $\alpha > 0.5$ , the maxima appear at the reciprocal lattice points with the sum of indices even. The curves go on becoming broader and lower as  $\alpha$  approaches 0.5, whereas they show pronounced maxima as  $\alpha$  approaches zero or unity. Since the diffuse spots in the X-ray photographs show maxima near reciprocal lattice points with the sum of indices odd, it is clear that  $\alpha$  is close to zero (0.1 or so); this implies that the structure is closer to the ordered structure of space group  $Pbcn$  than to the ordered structure of space group  $Iba2$  ( $\alpha=1.0$ ) or to the statistically ordered structure of space group  $Ibam$  ( $\alpha=0.5$ ).

A careful look at the photographs shows that the diffuse spots have peaks which are often shifted slightly from the reciprocal lattice points. Thus, in Fig. 1, the diffuse reflexion (17, 0, 2) is closer to (18, 0, 2) than to (16, 0, 2) and the diffuse reflexion (21, 0, 2) is closer to (22, 0, 2) than to (20, 0, 2). This is obviously because the values of  $B^2$  (equation 6) are not symmetrical about  $\omega=0$  except for reflexions of the type  $0kl$ . For such reflexions, the diffuse spots are expected to show two peaks symmetrically on either side of the reciprocal lattice points; however, being too close, these peaks would merge into a broad maxima, symmetrical about the reciprocal lattice point. As expected, the strong diffuse spot (021) in Fig. 2 shows a broad maximum, symmetrical about the reciprocal lattice point.

It is thus clear that the postulated disorder explains the observed pattern of sharp and diffuse reflexions qualitatively. This sort of disorder appears reasonable from geometrical considerations as well, because the van der Waals contacts linking the methyl groups of the neighbouring layers of type  $A_1$  and  $B_2$

respectively are normal. These contacts are as follows:

$C(x, y, z) - C(\bar{x}, \bar{y}, z)$	4.02 Å
$C(x, y, z) - C(\bar{x}, 1 - y, z)$	4.29
$C(x, y, z) - C(\bar{x}, y, z - \frac{1}{2})$	4.12
$C(x, y, z) - C(\bar{x}, y, z + \frac{1}{2})$	4.12

The structure analysis has been only recently completed, and it has therefore not yet been possible to compare quantitatively the observed and calculated intensities along the reciprocal lattice rods ( $h + \omega, k, l$ ).

Such a comparison and a proper estimate of  $\alpha$  will be published later.

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## X-ray Diffraction Analysis of *o*-Nitrobenzaldehyde and Some Substituted *o*-Nitrobenzaldehydes

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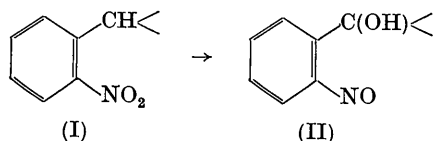
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The structures of three halogen-derivatives of *o*-nitrobenzaldehyde have been partially determined in their short-axis projections while the structure of *o*-nitrobenzaldehyde itself has been analysed from partial three-dimensional data. Molecular distortions due to the proximity of the bulky *ortho* substituents are discussed and compared with the corresponding effects in *o*-chloro- and *o*-bromobenzoic acid.

The X-ray determination is to be supplemented by a neutron-diffraction analysis.

### Introduction

The structure analyses of *o*-nitrobenzaldehydes reported in this paper form part of a research program on the chemistry of the solid state. One of us has pointed out elsewhere (Schmidt, 1957) that the aim of our combined X-ray and physico-chemical studies is the analysis of reaction mechanisms in terms of topochemical factors controlling solid-state reactions. The reaction type analysed here is the photochemical reaction of the system I  $\rightarrow$  II such as *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid (Ciamician & Silber, 1901; Leighton & Lucy, 1934).



To this end partial crystal-structure analyses of substituted *o*-nitrobenzaldehydes were undertaken in parallel with kinetic work (Cohen & Schmidt, unpublished). When this system was first being studied in 1951 we attempted to correlate reaction rates in the solid state with the distances between the reacting centres (CH and NO) in *o*-nitrobenzaldehyde, and its

4-iodo-, 5-bromo-, and 6-chloro derivatives. However, this approach had to be abandoned mainly because of the difficulty of establishing reproducible rates in the solid-state reaction. Parallel work on both the light-sensitive and the light-stable modifications of *p*-nitrophenol (Coppens & Schmidt, to be published) indicated that the geometry of the reacting centres rather than their distances was the controlling factor in the oxygen transfer reaction. Accordingly it became of interest to investigate the detailed structure of *o*-nitrobenzaldehydes; for the obvious reason the unsubstituted derivative was chosen for a three-dimensional X-ray analysis. One of us has followed up this work with a two-dimensional neutron-diffraction analysis (Coppens, 1964). No further X-ray work is contemplated on the three halogen derivatives.

### Halogen derivatives

*5-Bromo-2-nitrobenzaldehyde* was prepared according to Einhorn & Gernsheim (1895). It crystallizes from aqueous ethanol in long colourless needles elongated along [010]. The crystallographic constants are listed in Table I. The  $h0l$  intensities were estimated visually from Weissenberg photographs by means of the multiple-film technique. The Patterson projection