

One-Dimensional Disorder in Dodecahydrotriphenylene, $C_{18}H_{24}$

BY F. HALLA

Association pour les Études Texturales, 4 rue Montoyer, Brussels, Belgium

H. JAGODZINSKI

Max Planck-Institut für Silikatforschung, Würzburg, Germany

AND W. R. RUSTON

Association pour les Études Texturales, 4 rue Montoyer, Brussels, Belgium

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A modification of dodecahydrotriphenylene, $C_{18}H_{24}$, has been found, different from that investigated by Chorghade. Rotation diagrams about [0001] show diffuse row lines and those about [1000] show diffuse layer lines. The cell has the dimensions

$$a' = 10.45, c' = 15.50 \text{ \AA}; n = 4,$$

and may be reduced to a statistically occupied cell with the dimensions

$$a = 5.86, c = 7.75 \text{ \AA}; n = \frac{2}{3}.$$

The disorder phenomena are the same as occur in closest packings of spheres. The intensity distribution on the row lines can be interpreted quantitatively by Wilson's theory, as extended by Jagodzinski.

1. Introduction

The generally accepted structural formula of dodecahydrotriphenylene, $C_{18}H_{24}$, assumes a central benzene nucleus with three hydrogenated benzene rings symmetrically attached to it (Fig. 1). The hydro-

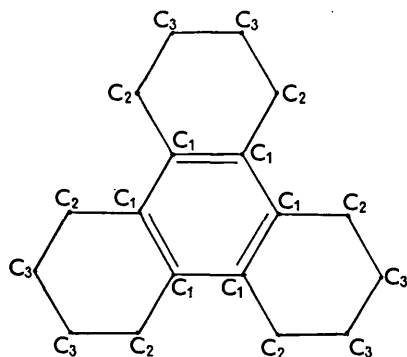


Fig. 1. $C_{18}H_{24}$, structural formula of dodecahydrotriphenylene.

aromatic bonds between the C_3 atoms could cause the occurrence of different geometrical isomers without trigonal symmetry, but the discussion of the space group will show that this symmetry is nevertheless preserved by the molecule.

The first sample was obtained from Dr E. Clar of Glasgow, and subsequent samples have later been synthesized from cyclohexanone by the method of Mannich (1907). According to the method of crystalli-

zation, different forms of crystals may be obtained (Fig. 2):

(a) Sublimation in a protective gas at atmospheric pressure and at a temperature just below its melting point, yields striped hexagonal needles, 2–3 cm. long and 0.3 mm. thick, built up by a rather regular succession of layers.

(b) Crystallization by the rapid cooling of a hot saturated solution in benzene yields the same form as (a).

(c) Crystallization by slow evaporation of a cold saturated solution in benzene yields hexagonal plates, hourglass-like striped double pyramids and clear prisms.

The density, averaged from literature data (Ziegler & Ditzl, 1929), and our own measurements, is $d_4^{20} = 1.145 \pm 0.003 \text{ g.cm.}^{-3}$. The molecular weight, M , is 240.

2. Unit cell and missing spectra

The dimensions of the unit cell were determined from rotation photographs about the hexagon edge a' and the needle axis c' . In the latter diagrams, taken from different crystals or of different parts of the same crystal, the row lines with $h-k \equiv 3n$ are sharp, the others diffuse (Figs. 3 and 4). If the diffuse reflexions are also taken into account, the diagrams give the following unit cell:

$$a' = 10.145 \pm 0.002, c' = 15.50 \pm 0.05 \text{ \AA}.$$



Fig. 2. $C_{18}H_{24}$, crystals of different habit.

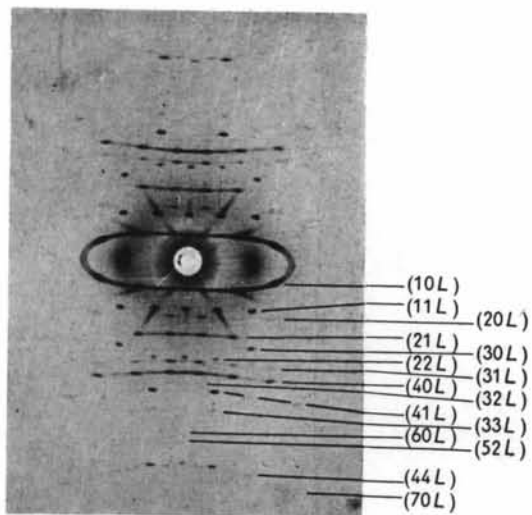


Fig. 3. $C_{18}H_{24}$, disordered crystal, 'hexagonal' variety, rotation diagram about [0001], showing diffuse row lines; $Cu K\alpha$ (Ni filter).

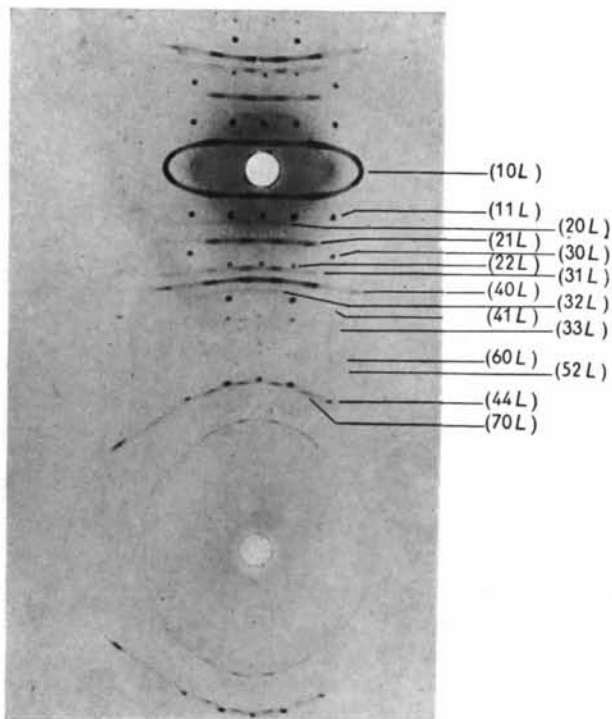


Fig. 4. $C_{18}H_{24}$, disordered crystal, 'cubic' (or rather rhombohedral) variety, rotation diagram about [0001], showing diffuse row lines; $Fe K\alpha_1$ (monochromatic).

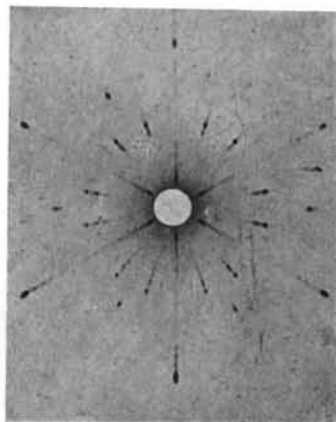


Fig. 5. $C_{18}H_{24}$, disordered crystal, 'hexagonal' variety, Laue diagram in direction [0001].

The volume of the unit cell, V , is 1394 \AA^3 and the number of molecules in the unit cell, n , is $4.01 = 4$.

Using Cu $K\alpha$ radiation, the quadratic form for this cell reads:

$$\sin^2 \theta \times 10^3 = 7.67(H^2 + HK + K^2) + 2.47L^2.$$

Zero-layer and equi-inclination Weissenberg photographs about c' , up to the fifth layer line, have the symmetry C_{6l} ; those about a' have the symmetry C_{2l} (classification after Buerger, 1942) which gives the Laue symmetry D_{6h} , in agreement with a Laue photograph (Fig. 5).

The asterisms in Fig. 5 (and still more the diffuse row lines in Figs. 3 and 4) make it apparent that a disorder of the lattice is involved, similar to that already described by Wilson (1942) and Jagodzinski (1949*a, b, c*), and that a statistically occupied superlattice must be present. The fact that diffuse and sharp lattice rods coexist, leads to the conclusion that we have to deal with simple statistics of position.

A more detailed inspection of the rotation photographs of crystals grown by different methods shows differences in the degree to which the two main types of closest packing, hexagonal or cubic*, are approached. In crystals grown by sublimation at 200° C. , a temperature just below the melting point, hexagonal packing (Fig. 3) predominates, while in crystals grown by rapid cooling of a hot concentrated solution cubic packing (Fig. 4) prevails. In the original diagram of Fig. 4 special conditions of the focused beam have produced a direct image of different parts of the crystal on the weaker lattice rods (HKL) = $(20L)$ and $(31L)$ in a direction perpendicular to the c axis. In these spots the maximum has different values, owing to variations of the degree of disorder within the same crystal. (This detail is not visible in the reproduction.)

The reflexions may be arranged in two groups:

- I. Sharp reflexions: where $h-k = 0 \pmod{3}$ and $l = \text{even}$.
- II. Reflexions on the diffuse row lines: where $h-k = 0 \pmod{3}$ and $l = \text{odd}$.

The subsidiary weak maxima which appear on certain diagrams—on Fig. 3 but not on Fig. 4—will not be considered for the moment.

A law which would satisfy I and II simultaneously does not exist in the *International Tables* among the criteria of missing spectra. Compatible with it, however, is the less specialized condition:

- III. $(h, h, 2h, l)$ present only if $l = \text{even}$.

The following additional law of missing spectra is strictly obeyed:

- IV. $(3h, 0, 3h, l)$ present only if $l = 0 \pmod{4}$.

* Or rather rhombohedral in this case.

All these facts* show that a discussion of the space group cannot lead to a result free from contradiction if the disorder phenomena are not taken into account.

3. The space group

The marked similarity between the rotation photographs of $\text{C}_{18}\text{H}_{24}$ (Fig. 3) and wurtzite (Jagodzinski, 1949*c*, p. 300, Fig. 1) suggested strongly the assumption that in both cases one-dimensional disorder phenomena are involved, with the sole difference that in $\text{C}_{18}\text{H}_{24}$ molecules take the place of the ions of wurtzite.

It appears that in the case of one-dimensional disorder the hk values of the sharp reflexions are such that the phases of the diffracted waves are independent of the statistical occupation of the lattice points. For $\text{C}_{18}\text{H}_{24}$ the reflexions with $h-k \equiv 0 \pmod{3}$ have this property.

In order to interpret the diffuse reflexions, let us make the assumption that it is possible to occupy simultaneously in each layer of a closest packing of spheres (Fig. 6*a*)) not only the positions A (and the translationally identical three positions) but also the positions $B(\frac{1}{3}, \frac{2}{3})$ and $C(\frac{2}{3}, \frac{1}{3})$. The content of the original cell would be tripled, but this filled-up cell could then be reduced to a simple cell with one-third of its volume, in the same manner as a hexagonal cell oriented as H -groups can be reduced to the simple cell oriented as C -groups (see *International Tables*, vol. 1, p. 7).

In $\text{C}_{18}\text{H}_{24}$ the original large cell G plays with respect to the reduced cell g the role of a superstructure or superlattice. The reflexions common to both cells are sharp, those of the superstructure alone appear diffuse.

The reduced cell g has the dimensions

$$a = a'/\sqrt{3} = 5.86, \quad c = c'/2 = 7.75 \text{ \AA}.$$

The quadratic form of the cell g for Cu $K\alpha$ radiation reads:

$$\sin^2 \theta \times 10^3 = 23.01(h^2 + hk + k^2) + 9.88l^2.$$

The halving of the c axis results from the limitation upon the sharp reflexions. The volume of the cell g is one-sixth of that of the cell G , the number of the molecules per cell is $\frac{1}{3}$ or $\frac{2}{3}$.

The transformation of the indices h, k, l of the cell g into the indices H, K, L of the cell G is:

$$h = \frac{1}{3}(-H - 2K), \quad k = \frac{1}{3}(2H + K), \quad l = \frac{1}{3}(-H + K), \\ l = \frac{1}{2}L.$$

We thus obtain the following corresponding index quadruples:

* The existence of these special laws of extinction strongly suggested an attempt at the calculation of the parameters by the method of Ott-Seyfarth (Ott, 1927; Seyfarth, 1928*a, b*). However, this led to the impossible result that all the 72 carbon atoms should be arranged, one above the other, along the axis $[00]$ and $[\frac{1}{3} \frac{2}{3}]$, respectively $[\frac{1}{3} 0]$ etc.

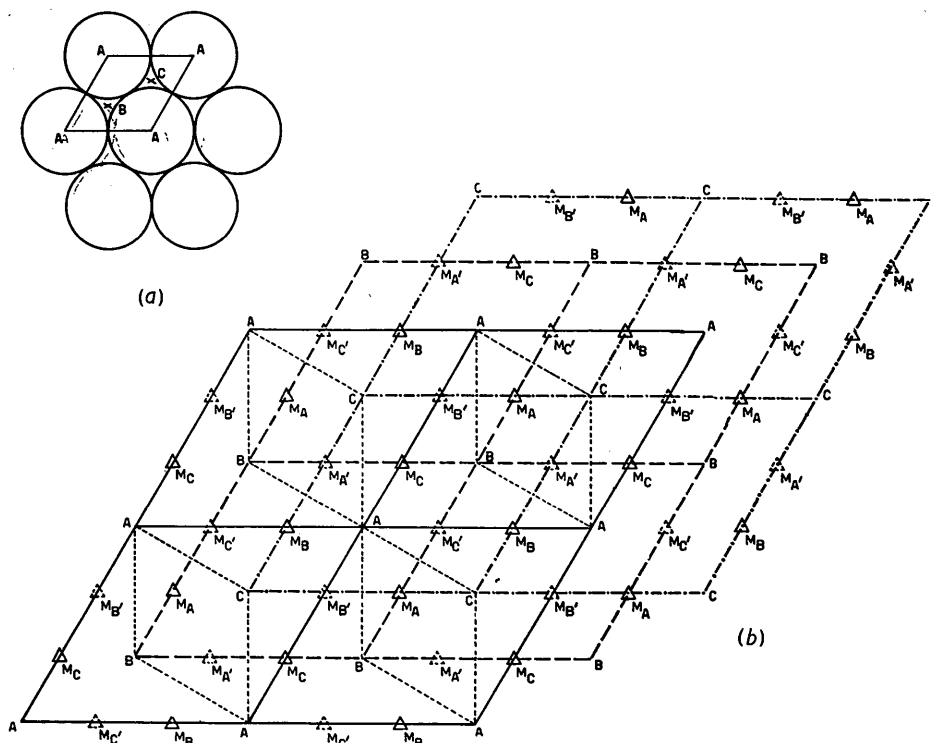


Fig. 6. (a) Single layer of a close-packed arrangement. $AAAA$: base of the hexagonal unit cell. B and C : possible positions for the origin in the neighbouring layer. (b) Relative positions of the molecules in two neighbouring layers, the origin occupying statistically the three possible positions A, B, C . The reduced cell g ($ABCA$) is marked in dotted lines.

$G(HKIL)$	$g(hkil)$	
$(H, H, 2H, L)$	$(H, 0, \bar{H}, \frac{1}{2}L)$	
$(3, 0, \bar{3}, 4n)$	$(1, 1, \bar{2}, 2n)$	
$(41\bar{5}L)$	$(2, 1, \bar{3}, \frac{1}{2}L)$	etc....

$\bar{3}m-D_{3d}$	would require (a) in $C6/mmc$,
$3m-C_{3v}$	would require (a) or (b) in $C6mc$,
$32-D_3$	would require (a) in $C\bar{6}2c$,
$\bar{6}-C_{3h}$	would require (b), (c) or (d) in $C\bar{6}2c$,
$\bar{6}m2-D_{3h}$	would require (b), (c) or (d) in $C6/mmc$.

By this transformation of indices, law IV of missing spectra is changed into

IV'. $(h, h, \bar{2}h, l)$ present only if $l = \text{even}$.

The fact that such a law is also valid for g shows that this cell must be doubly primitive. The content of the cell g has been found to be $\frac{2}{3}$, but the statistics triple the occupation and we thus obtain $3 \times \frac{2}{3} = 2$ molecules per cell, which is in agreement with the law of missing spectra.

Taking into account that $(h\bar{h}0l)$ is present in all orders, law IV' leads to the space groups $C\bar{6}2c$, $C6mc$, $C6/mmc$. The centres of the two molecules must be located at twofold sets of homologous points.

The same result is obtained by considering the molecular symmetry (Fig. 1) which must be at least C_3 and which requires that the centres of the molecules lie on an axis which is at least trigonal. The choice of the correct space group depends, therefore, on an exact knowledge of the molecular symmetry.

The cell g

In the reduced cell g a molecular symmetry

The molecule cannot be perfectly planar for the intensities on the sharp row lines (with $h-k=3n$) alternate slightly but perceptibly; this would not occur if $|F|$ were the same for all values of l apart from the regular atomic f -factor decline (see also p. 485). The inner ring (C_1 in Fig. 1) is most probably planar, owing to its benzene character, and the C_2 atoms may perhaps also lie in the same plane. The C_3 atoms, however, certainly lie above or below that plane.

The missing centre of symmetry in the structural formula excludes the symmetry $\bar{3}m$. There remain only the molecular symmetries $\bar{6}m2$, $\bar{6}$, 32 and $3m$ for discussion; $\bar{6}$ and $\bar{6}m2$ depend upon the presence of a horizontal mirror plane in the molecule and make the space groups $C6/mmc$ or $C\bar{6}2c$ more probable. However, if the molecule is supposed to be non planar but is nevertheless to contain a horizontal symmetry plane, the protruding atoms have to be distributed statistically above or below this plane. Such a 'molecule' has only a statistical significance. If the protruding atoms lie in all molecules on one side of the plane, the point symmetry $3m$ would automatically result, leading to the space group $C6mc$. The molecular symmetry 32

can occur only in the space group $C\bar{6}2c$ (position (a)) and symmetry $\bar{6}m2$ only in space group $C6/mmc$ in positions (b), (c), (d). The latter, however, can be realized only statistically.

All the above-mentioned possible homologous points for the center of the 'molecule' have in common that to each 'molecule' there belongs always another 'molecule' translated by $\frac{1}{2}c \pm \frac{1}{3}(a_2 - a_1)$ and turned by 180° . (In $C6/mc$ (a) only the vertical shift occurs. However, this latter position may be excluded for statistical reasons.)

If we consider the equivalent homologous points (c) and (d) in $C6/mmc$, we immediately see (Fig. 1) that C_1 would occupy the homologous points 12(j), C_2 a similar position but with other parameters x', y' , while C_3 would occupy the homologous points 24(l): (x, y, z) ; however, this occupation can occur only statistically with weight $\frac{1}{2}$ if the horizontal symmetry required by the space group is to be achieved; the number of atoms per double 'molecule' is then 12 for each kind of C atom, C_1 , C_2 and C_3 .

The analogous case of the homologous points (b) in the space group $C6/mc$ (inherent symmetry $3m$) requires that each of the three kinds of carbon occupies twelvefold homologous points (d).

For statistical reasons (see p. 485) we can exclude the homologous points (a) and (b) in the space group $C6/mmc$ and $C\bar{6}2c$, as well as the homologous points (a) in $C6/mc$. This, too, is in agreement with the accepted molecular structure.

The space group $C\bar{6}2c$ seems improbable for another reason. Locating the molecular centers in (a) or (b), we had to accommodate the 12 C_1 atoms and the 12 C_2 atoms in the two different sixfold equivalent positions 6(g) or 6(h), twelvefold points not being available in this space group. This would be contradictory to the very probable equivalence of all C_1 or C_2 atoms. In this space group, too, all atoms being outside the horizontal mirror plane have to be doubled by the statistics. One degree of freedom of rotation about the trigonal axis still exists.

The final conclusion favours (c) or (d) in $C6/mmc$ with $\bar{6}m2$ as point-group symmetry. It has therefore been used as a basis for all the subsequent work.

4. The disorder phenomena

For a statistical discussion we may start from a horizontal sheet of (fourfold) primitive unit cells G . By horizontal planes it can be subdivided into four single layers of molecules. Because of the mutual coupling of two molecules (say A and A' , B and B' etc.) in consecutive layers, as already mentioned on p. 481, the whole crystal splits into two interpenetrating systems of alternating layers, an 'unprimed' one containing all odd layers, and a 'primed' one containing all even layers. The three possible positions A, B, C (or A', B', C') occur in each system (see

p. 479 and Fig. 6(a)). Each system contains only half the total number of layers, $\nu = \frac{1}{2}N$.

We will call m the order number of subsequent layers in the crystal and μ that within each of the two partial systems.

In order to obtain the statistical cell g we may put the origin A of a 'generating' or 'carrier' cell $AAAA$ (Fig. 6(b)) in the three possible positions A, B, C (see Fig. 6(a)). The height of this 'generating' cell is only $\frac{1}{2}c' = c$. In this cell the two molecules M_A and $M_{A'}$ must be located on the two trigonal axes \triangle and \triangle' . In $C\bar{6}m2$ they would lie in z and $\frac{1}{2}+z$, in $C6/mmc$ in $\frac{1}{4}$ and $\frac{3}{4}$; they always differ in level by $\frac{1}{2}c$. Fig. 7

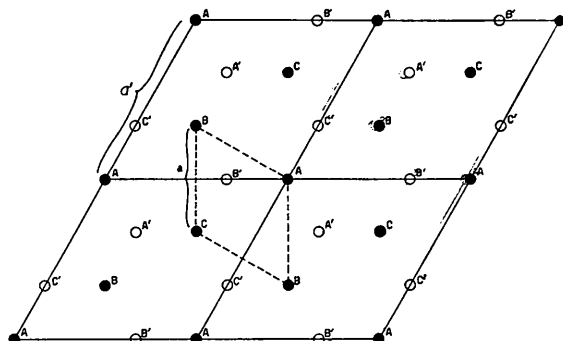


Fig. 7. Relative positions of molecules in two consecutive layers (representation equivalent to Fig. 6(b)) ●: molecules in level z . ○: molecules in level $z + \frac{1}{2}$.

differs from Fig. 6(b) in that the origin of the generating cell is moved into the positions M_A and $M_{A'}$. Fig. 7 shows immediately that the positions A', B', C' are perfectly equivalent relative to any one of the positions A, B, C and vice versa. (In reality they cannot be occupied simultaneously.)

If we begin to build up the crystal layer by layer, and if we put the origin of the first layer in any of the positions A, B, C , the origin of the next layer may be put with uniform probability $\frac{1}{3}$ in one of the positions A', B', C' . Correspondingly, if the interactions between the layers reach only as far as one layer, the origin of the third layer may be put in one of the positions A, B, C with the same probability $\frac{1}{3}$. In this case the statistics are independent of the arrangement of preceding layers. Conditions change, however, if the direct interaction reaches from the first to the third layer. Here a discrimination between the possible positions becomes necessary. For, if we had given the $(m-2)$ th layer a position A , the probability, $P(A)$, of finding the m th layer also in position A would no longer match $P(B)$ and $P(C)$, which, however, remain equal.

The insertion of layers with a definite probability between the consecutive layers of one system brings about a statistical independence of the possible positions in the two systems, and that without regard to the range of interaction. The insertion also allows us to make the μ th and the $(\mu \pm 1)$ th layer identical within a single system without violating the principle of

closest packing of spheres for the crystal as a whole. This is allowed for by introducing a partial probability γ .

We see from the foregoing how mutual coupling of positions A, A' , etc. causes the difference between our problem and that of simple closest packing, e.g. cobalt (Edwards & Lipson, 1942). The statistical treatment may, therefore, be reduced to that of two identical partial systems.

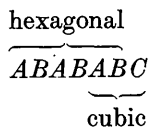
5. The partial probabilities

According to the range of interaction on which we base the mathematical analysis, we have to choose different partial probabilities. For the case $\sigma = 3$, i.e. interactions over three layers (Jagodzinski, 1949*b*), they are given in Table 1.

Table 1. *Partial probabilities for the case $\sigma = 3$*

Initial state hexagonal		Partial probability
Three layers in hexagonal order are followed by a fourth layer in hexagonal order	$ABA B$	$1 - \alpha$
Three layers in hexagonal order are followed by a fourth layer in cubic order (probability of a mistake in a hexagonal sequence)	$ABA C$	α
Initial state cubic		Partial probability
Three layers in cubic order are followed by a fourth layer in hexagonal order (probability of a mistake in a cubic sequence)	$ABC B$	$1 - \beta$
Three layers in cubic order are followed by a fourth layer in cubic order	$ABC A$	β

For sake of simplicity we will restrict ourselves to the case $\sigma = 2$ in which the hexagonal arrangement is considered the normal state of order and each deviation from it is regarded as a mistake (e.g. C in the following scheme):



For the sequence $A-B-X$ the partial probabilities are:

γ for finding $X \equiv B$ ('first' layer interaction, $\sigma = 1$),

$1 - \alpha$ for finding $X \equiv A$ ('second' layer interaction, $\sigma = 2$);

and consequently

$\alpha - \gamma$ for finding $X \equiv C$.

This new scheme may be compared with that for

the earlier problem in which closest packing was adhered to strictly so that $\gamma = 0$. Then $\alpha = 0.5$ and $\gamma = 0$ implies a continuation of a given (hexagonal) arrangement with equal probability in either the hexagonal or the cubic sense, while for $\alpha > 0.5$ the hexagonal arrangement tends to turn into the cubic.

6. The intensity formulae

The intensity of the sharp and the diffuse reflections are determined by the formula of Wilson in its extended form (Jagodzinski, 1949*a*). In this, the mean values $\overline{S_j S_{j+m}^*}$ enter and for their formation every layer of both systems has to be taken in turn as the zero layer.

In order to interpret the intensity behaviour in the sharp and diffuse lattice rods, we shall calculate explicitly the mean value $\overline{S_j S_{j+m}^*}$ separately for m odd and m even.

For the first case we introduce the hitherto unknown probability P_m for the occurrence of the same position after m steps, its calculation being shown later.

1. m odd

$$\begin{aligned} \overline{S_j S_{j+m}^*} &= \frac{1}{2} \left(\frac{1}{3} [F_A + F_B + F_C] \frac{1}{3} [F_{A'}^* + F_{B'}^* + F_{C'}^*] \right. \\ &\quad \left. + \frac{1}{3} [F_{A'} + F_{B'} + F_{C'}] \frac{1}{3} [F_A^* + F_B^* + F_C^*] \right) \\ &= \frac{1}{18} (F_A K F_A^* K^* + F_{A'} K F_{A'}^* K^*) . \end{aligned}$$

F_A is the amplitude of the molecule, $F_{A'}$ the structure amplitude of the same molecule but translated as in Fig. 6(b) and also turned by 180°, and

$$K \equiv 1 + \exp [2\pi i(h-k)/3] + \exp [-2\pi i(h-k)/3] = K^* .$$

K becomes 0 for $h-k \equiv 0 \pmod{3}$ and hence also $\overline{S_j S_{j+m}^*} = 0$.

For $h-k \equiv 0 \pmod{3}$ we obtain, however, $\overline{S_j S_{j+m}^*} = \frac{1}{2} (F_A F_A^* + F_{A'} F_{A'}^*)$.

2. m even

$$\begin{aligned} \overline{S_j S_{j+m}^*} &= \frac{1}{2} \left(\frac{1}{3} F_A [P_m F_A^* + (1 - P_m)(F_B^* + F_C^*)/2] \right. \\ &\quad \left. + \frac{1}{3} F_B [P_m F_B^* + (1 - P_m)(F_C^* + F_A^*)/2] + \frac{1}{3} F_C [P_m F_C^* \right. \\ &\quad \left. + (1 - P_m)(F_A^* + F_B^*)/2] + \text{analogous terms with} \right. \\ &\quad \left. A', B', C' \text{ instead of } A, B, C \right) . \quad (1) \end{aligned}$$

For $h-k \equiv 0 \pmod{3}$, and because then

$$F_A = F_B = F_C ,$$

we obtain $\overline{S_j S_{j+m}^*} = |F_A|^2$.

From these results we see immediately that the calculation of the intensities splits into two distinctly different cases:

(a) $h-k \equiv 0 \pmod{3}$ and

(b) $h-k \not\equiv 0 \pmod{3}$.

One equally recognizes the result, already known, that in the first case the mean value becomes statisti-

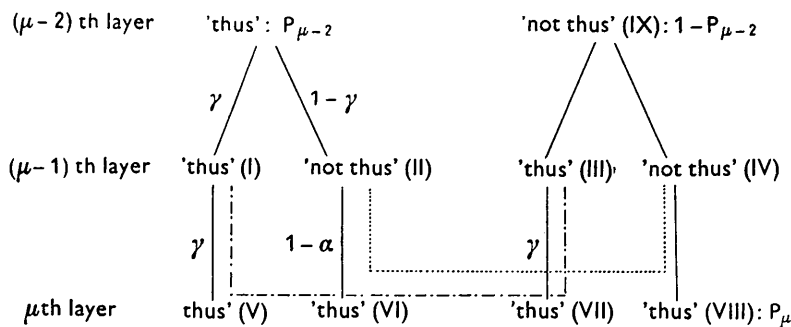


Fig. 8. Scheme for the probabilities of transitions from a given position 'thus' to the same or other positions ('thus' or 'not thus') in neighbouring layers. Roman numerals in parentheses designate partial probabilities.

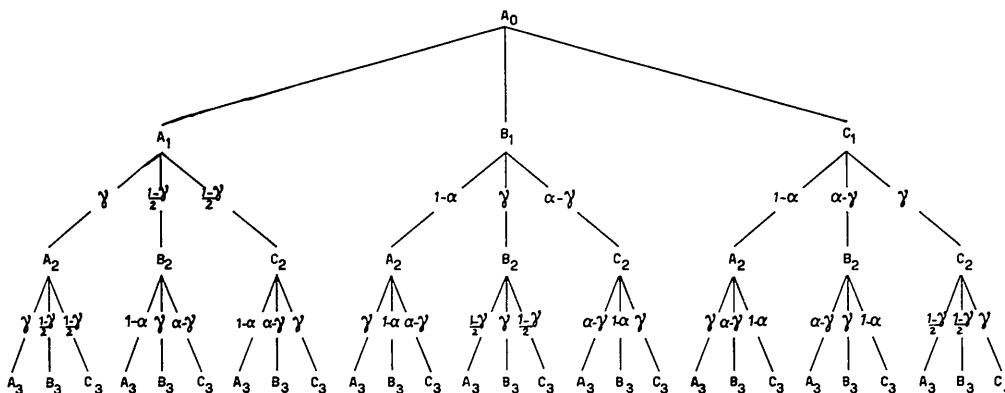


Fig. 9. Scheme of probabilities for the coincidences of molecular positions in succeeding layers.

cally independent, giving sharp reflexions, while in the second case the reflexions become more or less diffuse owing to the dependence upon $\cos \pi L$ (see formula (8)).

We now examine the two cases separately:

(a) $h-k \equiv 0 \pmod{3}$

It appears from the foregoing results that the intensities of these reflexions can be calculated as though one had to deal with the reduced cell g in an orderly lattice.

It is therefore possible for the calculation of these reflexions to use the conventional methods of structure analysis; in order to obtain absolute intensities it is necessary to multiply the structure amplitudes of the molecule by $\frac{1}{3}$ because of the statistical occupation.

(b) $h-k \not\equiv 0 \pmod{3}$

Because of the disappearance of $\overline{S_j S_{j+m}^*}$ for m odd it seems useful to return to the conception of the two systems and to use μ as summation index.

Wilson's formula now contains two equal terms, each having the form

$$I = R \sum_{\mu=-\frac{1}{2}N-1}^{\frac{1}{2}N-1} (\frac{1}{2}N - |\mu|) \overline{S_j S_{j+\mu}^*} \exp [2\pi i \mu A_3], \quad (2)$$

where

$$A_3 \equiv (\beta - \beta_0)c/\lambda = \frac{1}{2}L = l;$$

$|c| = c$ corresponds here to the cell g and not to the single interlayer distance.

In order to use equation (2) we need a recurrence formula for the probability P_μ , i.e. the probability of finding in the layer μ the same position as in the zero layer.

Fig. 8 shows the scheme for the interactions in this case. A notation independent of the special positions A or B or C is obtained when we denote always the position of the layer of reference by t ('thus') and the remaining two indiscriminately by nt ('not thus'). If far-reaching interactions are to be considered, however, e.g. in a sequence $nt-nt-t$, we must discriminate between the possibilities $nt' = nt''$ and $nt' \neq nt''$, and so on. Fig. 8 also differs from Jagodzinski's (1949*b*, p. 209) Table 1, in that sequences $t-t$ are not excluded.

The probabilities for the coincidences of the molecular positions in succeeding layers are shown in Fig. 9.

According to Fig. 8 we have

$$(I) \equiv \gamma \cdot P_{\mu-2}, \quad (II) \equiv (1-\gamma) \cdot P_{\mu-2},$$

and by definition

$$(I) + (III) = P_{\mu-1},$$

so that

$$(III) = P_{\mu-1} - \gamma \cdot P_{\mu-2}.$$

Similarly

$$(II) + (IV) = 1 - P_{\mu-1},$$

and hence

$$(IV) = 1 - P_{\mu-1} - (1 - \gamma)P_{\mu-2}.$$

The following relations are also evident from Fig. 8:

$$(V) = \gamma \cdot (I) = \gamma^2 \cdot P_{\mu-2},$$

$$(VI) = (1 - \alpha) \cdot (II) = (1 - \alpha)(1 - \gamma)P_{\mu-2},$$

$$(VII) = \gamma \cdot (III) = \gamma \cdot P_{\mu-1} - \gamma^2 \cdot P_{\mu-2}.$$

In order to obtain (VIII) from (IV), two transition probabilities still have to be defined. Corresponding to the two possibilities $nt' = nt''$ and $nt' \neq nt''$, there are two ways leading from (IX) via (IV) to (VIII); (IV) may be expressed as the sum of two partial probabilities:

$$(IV) = 1 - P_{\mu-1} - (1 - \gamma)P_{\mu-2} = (IV)_1 + (IV)_2.$$

For the first possibility we have between (IX) and (IV) the transition probability γ and hence

$$(IV)_1 = (1 - P_{\mu-2})\gamma,$$

so that

$$(IV)_2 = 1 - P_{\mu-1} - (1 - \gamma)P_{\mu-2} - (1 - P_{\mu-2})\gamma.$$

Reference to Fig. 9 shows that the last step towards VIII ($B_1 \rightarrow B_2 \rightarrow C_3$) occurs in case (IV)₁ with the partial probability $\frac{1}{2}(1 - \gamma)$ and in case (IV)₂ ($B_1 \rightarrow C_2 \rightarrow A_3, C_1 \rightarrow B_2 \rightarrow A_3$) with $\alpha - \gamma$. We therefore have

$$(VIII) = (IV)_1 \cdot \frac{1}{2}(1 - \gamma) + (IV)_2(\alpha - \gamma).$$

Finally we obtain

$$P_\mu = (V) + (VI) + (VII) + (VIII)$$

and, by introducing the expressions deduced for the individual summands, we obtain the recurrence formula

$$P_\mu - P_{\mu-1}(2\gamma - \alpha) - P_{\mu-2}[1 - 2\alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{1}{2}) - (1 - \gamma)(\alpha - \frac{1}{2}\gamma)] = 0.$$

By substitution of $\mu - 1$ for μ and by subtraction of the resulting expression from the former, one obtains the homogeneous equation

$$P_\mu - P_{\mu-1}(1 + 2\gamma - \alpha) - P_{\mu-2}[1 - \alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{5}{2}) + P_{\mu-3}[1 - 2\alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{1}{2})]] = 0.$$

By introduction of

$$P_\mu = x^\mu$$

there results

$$x^{\mu-3}\{x^3 - x^2(1 + 2\gamma - \alpha) - x[1 - \alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{5}{2}) + 1 - 2\alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{1}{2})]\} = 0.$$

One trivial root of the equation is

$$x_1 = 1.$$

Division by $x - 1$ then gives the quadratic equation

$$x^2 - (2\gamma - \alpha)x - [1 - 2\alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{1}{2})] = 0 \quad (3)$$

with the roots

$$x_2, x_3 = v \pm w,$$

where

$$w = \frac{1}{2}\{(\alpha - 2\gamma)^2 + [1 - 2\alpha + \gamma(3\alpha - \frac{3}{2}\gamma - \frac{1}{2})]\}^{\frac{1}{2}} \quad (4)$$

and

$$v = \frac{1}{2}(2\gamma - \alpha). \quad (5)$$

By putting in general

$$P_\mu = \Gamma + \Delta x_2^\mu + E x_3^\mu \quad (6)$$

and by specializing for $\mu = 0$, and considering that

$$\Gamma = \frac{1}{3},$$

we obtain

$$1 = \frac{1}{3} + \Delta + E. \quad (7)$$

Further, for $\mu = 1$ we obtain

$$\frac{1}{3} + \Delta x_2 + (\frac{2}{3} - \Delta)x_3 = \gamma$$

and thence for the coefficients

$$E, \Delta = \frac{1}{3} \left(1 \pm \frac{1 - \alpha - \gamma}{2w} \right). \quad (7a)$$

Thereby we have obtained P_μ and are able to evaluate Wilson's equation.

For the diffuse lattice rods ($h - k \equiv 0 \pmod{3}$) we obtain

$$\overline{S_j S_{j+\mu}^*} = \frac{1}{2} |F|^2 [3P_\mu - 1] = \frac{3}{2} |F|^2 (\Delta x_2^\mu + E x_3^\mu),$$

and the combination of the two terms like equation (2) gives

$$I = 3 |F|^2 R \sum_{\mu = -(\frac{1}{2}N-1)}^{\frac{1}{2}N-1} (\frac{1}{2}N - |\mu|) (\Delta x_2^\mu + E x_3^\mu) \exp [2\pi i \mu \frac{1}{2}L] \\ \cong 3RN |F|^2 \left\{ \Delta \frac{1 - x_2^2}{1 - 2x_2 \cos \pi L + x_2^2} + E \frac{1 - x_3^2}{1 - 2x_3 \cos \pi L + x_3^2} \right\} \dots \quad (8)$$

This expression has been obtained by neglecting two terms which become infinitely small for large values of N_3 . They correspond to the 3rd and 5th terms in Wilson's (1942) equation (14).

Equation (8) differs from that, valid for the normal closest packing of spheres, only by the term $+\gamma$ in v (see equation (5)) and by the additional term multiplied by γ under the root of equation (4). The effect of the latter is relatively unimportant, but the influence of γ in v is much more marked.

The quantity in brackets $Q \equiv I/3RN|F|^2$ has, from its dependence on L , extreme values if L is an integer. It may be supposed that

$$0 \leq \gamma \leq \frac{1}{3} \quad \text{and} \quad 0 \leq \alpha \leq \frac{1}{2} \quad (\text{see p. 482}).$$

Within these two ranges the absolute term of equation (3) remains negative. The two roots x_2 and x_3 must therefore have opposite signs.

So long as $2\gamma < \alpha$, i.e. the structure approaches a closest packing of spheres ($\gamma = 0$), v is negative from (5) and thus

$$|x_3| > |x_2|.$$

In any case E is $> \Delta$ because w in (7a) is always positive and $\alpha + \gamma < 1$.

Because x_2 is positive, the first term in (8) gives maxima at points where L is even, and because x_3 is negative the second term gives maxima where L is odd. It is easily seen that the maxima of the second term are much more pronounced since $E > \Delta$ and $|x_3| > |x_2|$.

We have

$$\text{for } L \text{ odd } Q_{\text{odd}} = \Delta \frac{1-x_2}{1+x_2} + E \frac{1-x_3}{1+x_3},$$

$$\text{for } L \text{ even } Q_{\text{even}} = \Delta \frac{1+x_2}{1-x_2} + E \frac{1+x_3}{1-x_3}.$$

The first formula shows that, for the appearance of the maxima for L odd on the diffuse lattice rods, the strict prohibition of an immediate sequence of identical positions ($\gamma = 0$), which is true of a closest packing of spheres, is not required.

However, the maxima become more and more diffuse as the value of γ increases. Equation (8) shows the influence which the value of γ exerts on the intensity distribution. So long as $2\gamma < \alpha$, $|x_3| > |x_2|$, i.e. the maxima for L odd are sharper. The reverse is also true but has never been observed on the photographs.

7. Discussion

From equation (8) it follows that the intensities on the diffuse row lines are determined by the structure factor of the single molecule and not by that of the unit cell. This is in accordance with the facts: for low values of L , the intensities on all diffuse row lines behave approximately identically, but for $L = 5$ and more, discrepancies become evident; e.g. the rod ($20L$) is considerably weaker than ($21L$) at the point $L = 0$; but for $L = 5$ the intensities are comparable. This is evidence for the non-planarity of the molecule (cf. p. 480).

This result also justifies the exclusion of the homologous points (a) in the space group $C6mc$ and (a), (b) in the space groups $C6/mmc$ and $\bar{C}62c$, because there the molecules would lie directly one above the other and the positions $A'B'C'$ and ABC would be equivalent and hence not statistically independent of one another. But just this independence explains the striking property that the intensity on the diffuse lattice rods alternates with a double period.

The behaviour of the sharp reflexions, too, can easily be understood qualitatively. Here we have to deal with a doubly primitive cell, g , and because of the translation of the molecular centers by $\frac{1}{2}c$ we have to expect intensities totally different from those obtained by using the simple structure factors of the molecule (see the lattice rod ($41L$) in Fig. 3).

It has already been mentioned (p. 479) that different degrees of approximation to both types of packing (hexagonal and cubic) exist. They differ by the intensity distribution on the diffuse row lines. The diffuse lattice rods (row lines) of the 'hexagonal' variety show principal maxima at L odd and between them secondary maxima at L even. Fig. 10 shows the

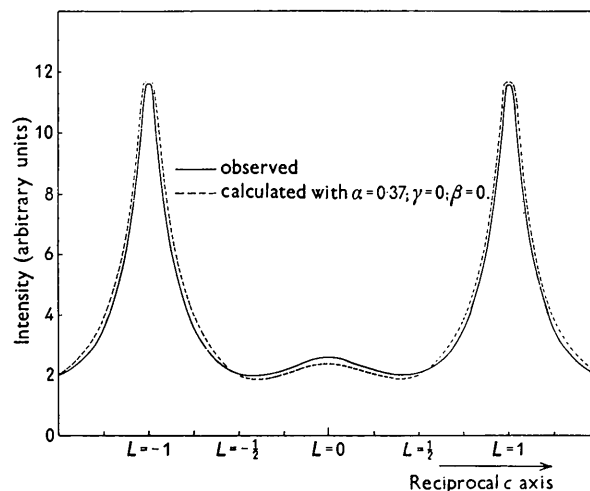


Fig. 10. Rectified photometric curve of the diffuse lattice rod ($40L$), 'hexagonal' variety, showing a secondary maximum at $L = 0$. Broken curve calculated with $\alpha = 0.37$, $\gamma = 0$ ($\beta = 0$).

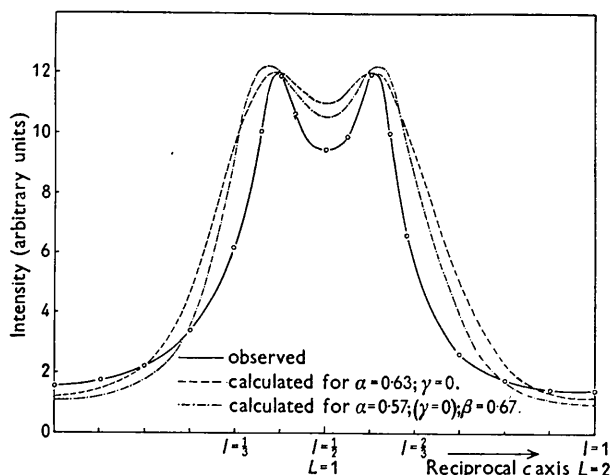


Fig. 11. Rectified photometric curve of the diffuse lattice rod ($40L$), 'cubic' variety, showing split maximum at $L = 1$; the dot-dash curve is calculated with $\alpha = 0.57$, ($\gamma = 0$), $\beta = 0.67$.

photometer curve* of the diffuse lattice rod (40L) of the 'hexagonal' variety, with the weaker maximum at $L = 0$.

The curve, calculated with $\alpha = 0.37$, $\gamma = 0$ ($\beta = 0$) is in best agreement with the observed values.

In the photometer curve (Fig. 11) of the 'cubic' variety (Fig. 4) the maximum at $L = 0$ is missing and the maximum at $L = 1$ is split. According to the conception hitherto employed of a stack of three double layers, the intensity distribution may be satisfied by the partial probabilities $\alpha = 0.63$; $\gamma = 0$. From (3) it follows that x_2, x_3 are complex for $\alpha = 0.63$, and this results in the split maximum (see Wilson, 1942, p. 281). A still better agreement is achieved if a stack of four double layers is considered. The respective formulae have already been developed in an earlier paper (Jagodzinski, 1949b). In Fig. 11 the dot-dash curve has been calculated using the parameters $\alpha = 0.57$; $\beta = 0.67$ (with the auxiliary condition of $\gamma = 0$). In the 'cubic' variety α as well as β must be greater than 0.5. The condition

$$\alpha = 1 - \alpha = \beta = 1 - \beta = 0.5$$

would mean the purely statistical arrangement of the layers, i.e. the absence of any influence of the order already achieved, upon the arrangement of the remaining layers.

The mean value between $\alpha = 0.57$ and $\beta = 0.67$ is 0.62, which represents the mean partial probability for the cubic continuation of either a hexagonal or a cubic arrangement.

This value is practically identical with that obtained by the previous method of calculation. The absolute value of the difference, $\frac{1}{2}(\alpha + \beta) - 0.5 = 0.62 - 0.5 = 0.12$, is practically identical with the corresponding

* The photometer curves along a row line were rectified by plotting them on a linear scale after subtraction of the background fogging in the immediate neighbourhood of the measured points. The asymmetry due to the atomic scattering factor and the structure amplitude were equalized in such a way that the shape of the curve in the middle and the end became nearly symmetrical. The broadening effect due to the finite size of the crystal was also taken into account.

difference $\alpha - 0.5 = 0.37 - 0.5 = -0.13$ of the 'hexagonal' variety (Fig. 10), i.e. the pure probability of the occurrence of a mistake with respect to either a hexagonal or a cubic arrangement is the same. The deviations have hence the same values, but opposite signs. This is in accordance with experience obtained with SiC and ZnS (Jagodzinski, 1949d) and it means that the continuance of growth is not specific with respect to the degree of order already achieved. There is, however, no indication that this can be explained by the entropy of vibration of the lattice as has been suggested by one of us (Jagodzinski, 1949d).

The principle of closest packing $\gamma = 0$ together with Wilson's results suffice to represent both kinds of curves. There is therefore no need to consider the more complicated case of $\gamma \neq 0$. The reason why the condition of closest packing is so closely obeyed for both 'varieties' is not obvious. Because of the insertion of the second layer system there is no apparent necessity for this.

The complete structure analysis could not be included in this paper, because the ordered crystals have been obtained only after the completion of the present work. The relations which exist between Chorghade's form (1944) and this modification will be discussed in a later paper.

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