The synthetic polypeptide α-poly-L-alanine has been prepared as highly oriented and crystalline fibers by Bamford et al. (1954), and diffraction data obtained from these fibers are presented by Brown & Trotter (1956). Because the side chains of poly-L-alanine consist only of methyl groups whose positions are known, its diffraction pattern is particularly suitable for comparison with the calculated transforms of polypeptide models. Brown & Trotter have observed that the 1·5 Å reflection in α-poly-L-alanine can best be indexed as (0,0,0,47). This appears as a well resolved intense reflection, and is accompanied by the (1,0,$\bar{1}$,47) reflection, which is much weaker. The orientation of the fiber is such that this 1·5 Å reflection can only be meridional. In addition, consideration of the relative intensities of the equatorial reflections of α-poly-L-alanine clearly favor the α helix model. Thus, although there is a striking similarity between the transforms of the α and π helices, the differences are still sufficient so that a clear distinction can be made between them for comparison with well oriented diffraction data. It should be pointed out, however, that such a clear distinction cannot be made between an α and a π helix from an inspection of a poorly oriented fiber pattern.

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An Improved Method for Determining the Relative Positions of Molecules

By C. A. TAYLOR AND K. A. MORLEY

Physics Department, College of Science and Technology, Manchester 1, England

The molecular-location method described by Taylor (1954) has been found to fail under certain conditions. The method described in the present paper was designed to overcome these limitations and proves to be more satisfactory in other respects as well; it involves no approximations and the results are presented in the form of a contoured graph which is easier to assess than the pattern of bands produced in the earlier method.

Introduction

In using the Fourier or optical-transform approach to crystal-structure determination, the shape and orientation of a molecule or group of atoms is determined largely by considering the disposition of the stronger reflexions; consideration of the weaker and absent reflexions may then give information about the position of the molecule or group relative to others in the unit cell (Hanson, Lipson & Taylor, 1953).

A systematic method of solving the position problem was suggested by Taylor (1954) and has been successfully used on a number of structures. During its application to one particular structure, however, certain limitations were discovered (Crowder, Morley & Taylor, 1957). The essential requirement for success in the earlier method is that the reflexions to be used should be chosen to satisfy certain conditions which become more stringent as the symmetry of the cell increases.

In this structure, however, an accidental symmetry relationship in the molecule made it impossible to choose reflexions satisfying these conditions. The new method, briefly outlined at the Montreal Conference (Taylor, 1957) and now to be described in detail, was developed to overcome this difficulty. It has been found to have a number of additional advantages over the earlier method. In particular, the results are presented in a more elegant form. The final position

is found in the original method by studying the intersections of various lines and bands; this is fairly straightforward at the time of drawing the successive sets of bands but is rather confusing in subsequent study. The present method involves a final presentation in the form of a contoured map of which the lowest point indicates the molecular co-ordinates.

The new method has been tried successfully on a number of known and unknown structures and in this paper the structure which prompted the development of the method has been used to illustrate the procedure. Full details of this structure are given in the succeeding papers (Crowder, Morley & Taylor, 1959; Bartindale, Crowder & Morley, 1959).

Basic principles

The principle of the method is best illustrated by reference to the structure-factor graphs described by Bragg & Lipson (1936). These are contour maps representing the variation with position in the unit cell of the combined contribution to one particular reflexion by a single atom and its plane-group-related counterparts. If the projected shape of a molecule, or part of a molecule, is known, a similar structure-factor graph showing the variation with position in the unit cell of the combined contribution of the *molecule* and its plane-group-related counterparts, $G(h, k)$, to a particular reflexion could be prepared. If the reflexion chosen were observed zero, the zero contour of this graph would represent the locus of possible positions in the unit cell of the arbitrarily chosen origin of the molecule; if the reflexion were not zero, the zero contour of the graph of a quantity $||G(h, k)| - |F_o(h, k)||$ would give the locus of possible positions. If a number of such graphs were prepared, the point at which all were simultaneously zero could be found and would indicate the position of the molecule necessary to satisfy the observed intensities.

The present method involves the calculation of the sum of the functions $||G(h, k)| - |F_o(h, k)||$ for a few reflexions. The zero point of this combined graph will then indicate the molecular position. In practice, because of errors of various kinds, an actual zero value is not obtained, but there is usually a well-defined minimum. The computation is most easily performed with Beevers–Lipson strips.

Theory of the method

The theory will be developed for the plane group *pgg*, but the development for other plane groups follows the same general pattern, though becoming increasingly complex as the multiplicity of the general position of the group increases. Let x_n, y_n be the coordinates of the nth atom of a molecule with respect to an arbitrarily chosen origin and let X, Y be the co-ordinates of this origin with respect to the true

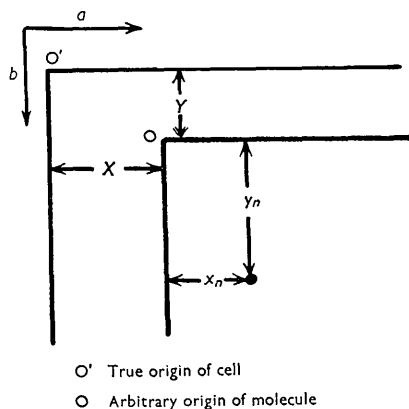O'   True origin of cell

O   Arbitrary origin of molecule

Fig. 1. The relationship between the co-ordinates of the nth atom of a molecule with respect to the arbitrary origin and with respect to the true origin of the unit cell.

origin of the unit cell (Fig. 1). The combined contribution of all the molecules to a reflexion h, k may then be written

$$G(h, k) = 2 \Sigma_n f_n \cos 2\pi \{h(X + x_n) + k(Y + y_n)\}$$
$$+ 2 \Sigma_n f_n \cos 2\pi \{h(X + x_n) - k(Y + y_n) + \tfrac{1}{2}(h + k)\} . \quad (1)$$

The first summation represents a contribution of the centrosymmetrically-related pair of molecules at the origin and the second that of the other pair centrosymmetrically-related about the point $\tfrac{1}{2}, \tfrac{1}{2}$ and related to the first pair, as far as orientation is concerned, by mirror planes. In the original method, reflexions were chosen such that the contribution of one of these pairs was large and the other very small; attention was then concentrated on the pair with the large contribution and the contribution of the second pair included as a possible error. In the determination of the structure of 5-methoxy-2-nitrosophenol, the benzene rings turn out to have planes of symmetry almost parallel with the sides of the cell and hence the strongest peaks from all four molecules occur in the same region. It therefore becomes impossible to fulfil the conditions of selection for the earlier method.

For the purpose of the present method equation (1) must be re-written as follows:

$$G(h, k)$$
$$= 4 \cos 2\pi k Y \{A(h, k) \cos 2\pi hX + B(h, k) \sin 2\pi hX\}$$
$$+ 4 \sin 2\pi k Y \{C(h, k) \sin 2\pi hX + D(h, k) \cos 2\pi hX\}$$
$$\text{if } (h + k) \text{ is even}$$

and

$$G(h, k)$$
$$= 4 \cos 2\pi k Y \{B(h, k) \cos 2\pi hX + D(h, k) \sin 2\pi hX\}$$
$$- 4 \sin 2\pi k Y \{A(h, k) \sin 2\pi hX + C(h, k) \cos 2\pi hX\}$$
$$\text{if } (h + k) \text{ is odd} , \quad (2)$$

where

$$A(h, k) = \Sigma_n f_n \cos 2\pi hx_n \cos 2\pi ky_n$$
$$B(h, k) = -\Sigma_n f_n \sin 2\pi hx_n \sin 2\pi ky_n$$

$$C(h, k) = \Sigma_n f_n \sin 2\pi h x_n \cos 2\pi k y_n$$
$$D(h, k) = -\Sigma_n f_n \cos 2\pi h x_n \sin 2\pi k y_n .$$

The quantities $A(h, k)$, $B(h, k)$, $C(h, k)$ and $D(h, k)$ depend only on the molecular shape and orientation and are constant throughout the process of molecular location. They may be calculated for the chosen reflexions by any of the normal computational methods for structure factors. The required molecular structure-factor graph for a given reflexion is then obtained by computing the values of $G(h, k)$ given by equation (2) for all possible values of X and Y within the unit cell. So far we have not made any restrictions on the choice of reflexions; the method could thus be applied to 5-methoxy-2-nitrosophenol. In theory, the sum of the functions $||G(h, k)| - |F_o(h, k)||$ for all possible reflexions could be calculated and used to find the molecular position. Apart from the labour involved, there are other reasons which make this undesirable. First, the method is usually applied at a stage when the scale and temperature factors are not known accurately; errors from this source are minimized if attention is confined to reflexions for which $|F_o(h, k)|$ is as small as possible. Secondly, the projected shape of the molecule may not be known with great precision. Errors from this source can be minimized if reflexions are chosen which lie in the centre of strong peaks of the transform of one of the single molecules; such reflexions will be comparatively insensitive to small changes in the shape of the molecule.

It is usually necessary to use only 6 or 7 reflexions;

a small amount of experience in applying the method soon makes it fairly easy to select the most useful ones. It should be noted, however, that, whereas with the earlier method selection of reflexions to fulfil special conditions was essential, with the present method all the reflexions could be used if the shape and orientation were correct; selection is now necessary to improve the chance of success when the shape or orientation is uncertain.

Method of computation

The computation may conveniently be done with Beevers–Lipson strips, and it is then necessary to re-write the equations once more as follows:

$$G(h, k) = P(h, k) \cos 2\pi k Y + Q(h, k) \sin 2\pi k Y$$

where

$$P(h, k) = 4\{A(h, k) \cos 2\pi h X + B(h, k) \sin 2\pi h X\}$$

and

$$Q(h, k) = 4\{C(h, k) \sin 2\pi h X + D(h, k) \cos 2\pi h X\}$$
$$\text{if } (h+k) \text{ is even} \qquad (3)$$

or

$$P(h, k) = 4\{B(h, k) \cos 2\pi h X + D(h, k) \sin 2\pi h X\}$$
$$Q(h, k) = -4\{A(h, k) \sin 2\pi h X + C(h, k) \cos 2\pi h X\}$$
$$\text{if } (h+k) \text{ is odd.}$$

After computing the values of $A(h, k)$, $B(h, k)$, $C(h, k)$ and $D(h, k)$ for the reflexions to be considered, pre-

Index hkl	F_o	P or Q for X = 5/60ths		k	Z in 1/60ths																		For Z = 3/60ths
					0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
200	33	$\overline{45}$	C	0	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	$(\overline{720})$	$||\overline{45}+ 0|-33| = 12$
101	7	$\overline{77}$	C	1	77	77	75	73	70	67	62	57	52	45	38	31	24	16	8	0	$(\overline{772})$	$||\overline{73}+23|- 7| = 43$
		76	S	1	0	8	16	23	31	38	45	51	56	61	66	69	72	74	76	76	(762)	
902	—	34	C	2	34	33	31	28	23	17	11	4	$\overline{4}$	$\overline{11}$	$\overline{17}$	$\overline{23}$	$\overline{28}$	$\overline{31}$	$\overline{33}$	$\overline{34}$	(0)	$||28+\overline{16}|- 0| = 12$
		$\overline{28}$	S	2	0	$\overline{6}$	$\overline{11}$	$\overline{16}$	$\overline{21}$	$\overline{24}$	$\overline{27}$	$\overline{28}$	$\overline{28}$	$\overline{27}$	$\overline{24}$	$\overline{21}$	$\overline{16}$	$\overline{11}$	$\overline{6}$	0	$(\overline{266})$	
12,0,4	4	28	C	4	28	26	19	9	$\overline{3}$	$\overline{14}$	$\overline{23}$	$\overline{27}$	$\overline{27}$	$\overline{23}$	$\overline{14}$	$\overline{3}$	9	19	26	28	(30)	$|| 9+ 8|- 4| = 13$
		8	S	4	0	3	6	8	8	7	5	2	$\overline{2}$	$\overline{5}$	$\overline{7}$	$\overline{8}$	$\overline{8}$	$\overline{6}$	$\overline{3}$	0	(0)	
13,0,5	5	3	C	5	3	3	1	0	$\overline{1}$	$\overline{3}$	$\overline{3}$	$\overline{3}$	$\overline{1}$	0	1	3	3	3	1	0	(7)	$|| 0+56|- 5| = 51$
		56	S	5	0	28	48	56	48	28	0	$\overline{28}$	$\overline{48}$	$\overline{56}$	$\overline{48}$	$\overline{28}$	0	28	48	56	(132)	
0,0,10	5	64	C	10	64	32	$\overline{32}$	$\overline{64}$	$\overline{32}$	32	64	32	$\overline{32}$	$\overline{64}$	$\overline{32}$	32	64	32	$\overline{32}$	$\overline{64}$	(0)	$||\overline{64}+ 0|- 5| = 59$
		14	S	10	0	12	12	0	$\overline{12}$	$\overline{12}$	0	12	12	0	$\overline{12}$	$\overline{12}$	0	12	12	0	(24)	

Fig. 2. The arrangement of strips in the final summation for $X = 5/60$. The column on the right illustrates the method of summation for the column $Z = 3/60$.

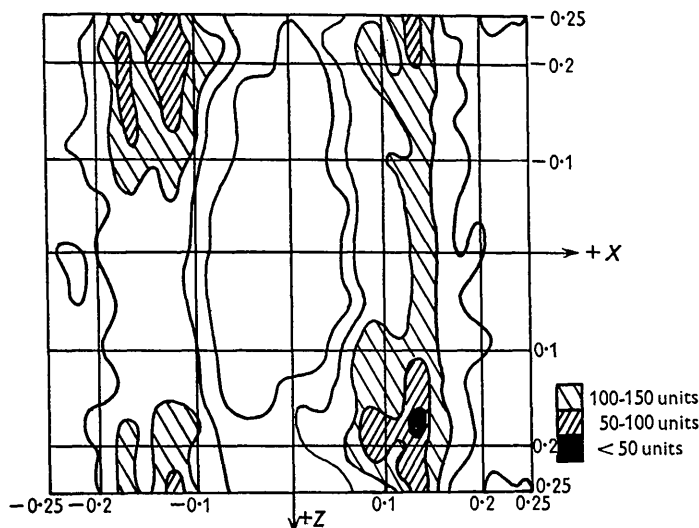Value of function at $X = 5/60$ths, 190 $Z = 3/60$ths

Fig. 3. The final function for the red form of 5-methoxy-2-nitrosophenol.
Contours are drawn at intervals of 50 units.

liminary tables are prepared giving values of $P(h, k)$ and $Q(h, k)$ for different values of X. This may conveniently be done by using sine and cosine strips together; for example, to calculate $P(h, k)$ when $(h+k)$ is even a cosine strip of amplitude $A(h, k)$ and index h, and a sine strip of amplitude $B(h, k)$ and index h are selected and added to give the values of $P(h, k)$ at intervals of $1/60$ (or $1/120$ if the unit cell is very large) in X.

Final tables giving the variations of the function with both X and Y are then prepared by selecting a cosine strip of amplitude $P(h, k)$ and a sine strip of amplitude $Q(h, k)$, both of index k, for each reflexion used. The final quantity to be summed is $||G(h, k)| - |F_o(h, k)||$; the modulus summation is used because minima due to fortuitous equality between positive and negative values are of no interest. The strips are therefore placed in pairs—that is, the sine and cosine strips for the same reflexion are kept together—and a note of $|F_o(h, k)|$ made by the side of each pair. The modulus of the difference between $|F_o(h, k)|$ and the modulus of the algebraic sum of the digits on the sine and cosine pair is then used in the summation. The layout for this stage of the computation described in the next paragraph is shown in Fig. 2. For the vertical column $Z = 3/60$ the actual quantities added would be those given at the right of the figure.

In practice it is not necessary to perform the summation over the whole of the unit cell, particularly if one or two low-order reflexions have been used; with a little experience the portions of the cell for which low values of the summation are possible may be recognized, and the summation is necessary only in the vicinity of these portions. Fig. 3 shows the resulting summation for six reflexions as used in the structure determination described in the succeeding

papers; the complete map for one quarter of the unit cell is shown (symmetry considerations make this sufficient) and it can be seen that there is only one small region where the value of the function is less than 50 units. In practice the summation need have been performed only in the region of the shaded portions; the function for the 200 reflexion alone indicates that the position sought can lie only in these regions.

Discussion

The new method could be used in a completely objective way on structures for which the shape and orientation of the molecules is exactly known. It seems likely, however, that it may be more useful at an earlier stage in a structure determination when there is still considerable doubt about the precise shape or orientation of the molecule. It is then necessary to select reflexions lying on high peaks of the transform of the portion of the molecule which is best known. This selection requires a little experience, but increases the power of the method considerably.

An interesting feature is that in the final map there are often several minima, though one of them is usually lower than the rest. The remainder represent positions of the molecule which would give some measure of agreement between observed and calculated structure factors; they have been called 'pseudo-homometric' structures. If some doubt remains as to which is the correct minimum, an additional summation—in the manner of a 'correction synthesis' in normal Fourier work—using a further one or two reflexions will usually resolve the problem.

We wish to record our gratitude to Prof. H. Lipson for helpful discussions and advice.

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X-ray Diffraction by Assemblages of Line Scatterers with Application to Linear Polymers*

BY LEROY E. ALEXANDER AND E. R. MICHALIK†

Mellon Institute, Pittsburgh, Pennsylvania, U.S.A.

The principal halo in the X-ray scattering pattern of a densely packed amorphous linear polymer arises mainly from interferences between adjacent molecular chains. Therefore the relationship between the intensity distribution in the halo and the orientation of the molecules may be analyzed in terms of bundles of parallel line scatterers. This approach takes no account of diffraction effects arising from the structural features of an individual molecular chain.

An expression is derived giving the idealized intermolecular interference pattern as a function of the degree of preferred orientation assumed by the line scatterers. It is shown that the azimuthal intensity distributions predicted by the theory for the limiting cases of (1) randomly and (2) highly oriented molecular bundles are confirmed by experiment.

The theory of X-ray diffraction by assemblages of line scattering elements is of direct interest in connection with the phenomenon of preferred orientation of linear polymer molecules. It is now recognized that in some linear polymers various degrees of preferred orientation can be induced without the occurrence of crystallization (Hill, 1953; Alexander, Ohlberg & Taylor, 1955; Goldstein & Davies, 1955; Ohlberg, Alexander & Warrick, 1958). Thus, in certain elastomers a considerable amount of such 'amorphous' orientation occurs upon elongation of the specimens at temperatures above their melting points. Upon subsequent cooling, the rate of conversion of such oriented regions to the crystalline state is likely to differ from that in the sample as a whole.

Because of the intimate connection that necessarily exists between molecular orientation and actual crystallization, it was deemed worth while to investigate the nature of the X-ray scattering that might be expected from uncrystallized linear polymers. It was recognized that any success which might be achieved in this effort would provide some basis for the experimental evaluation of preferred molecular orientation from the distribution of intensity in the X-ray diffraction pattern.

The form of the X-ray scattering by well-oriented crystalline fibers has been investigated theoretically by a number of investigators (MacGillavry & Bruins, 1948; Vineyard, 1951; James, 1954, pp. 571–89; Norman, 1954). Oster & Riley (1952) have computed the scattering functions for assemblages of parallel solid cylinders and other cylindrically symmetric elements, with emphasis on aggregations of cylindrical particles oriented normally to the X-ray beam and arranged with various degrees of two-dimensional order. For complex aggregations of parallel cylinders displaying random orientations they demonstrated qualitatively that the X-ray interference function must be conically symmetrical about the direct X-ray beam vector, leading to circularly symmetric diffraction patterns when recorded on a flat film.

By analogy to the demonstrable relationship between the azimuthal intensity distribution, $I(\beta)$, in paratropic diffraction arcs and the distribution of orientations, $dN(\varphi)$, in a partially oriented crystalline fiber (Hermans, 1946), it has been proposed in a prior paper (Ohlberg, Alexander & Warrick, 1958) that $I(\beta)$ in the principal amorphous halo and $dN(\varphi)$ for a noncrystalline linear polymer should be related as follows:

$$dN(\varphi) = k \sin \beta I(\beta) d\beta . \tag{1}$$

In this expression $dN(\varphi)$ is the number of molecules

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* Contribution of the Department of Chemical Physics and the former Department of Applied Mathematics. Presented at the Fifteenth Annual Pittsburgh Diffraction Conference, Nov. 6, 1957.

† Present address: Glass Research Center, Pittsburgh Plate Glass Company, Pittsburgh, Pa.