

φ_1 may be chosen to be a φ_{ugg} . Then the values of all phases φ_{ugg} and φ_{gug} , being linearly semi-dependent on φ_1 , are determined. Next, φ_2 may be chosen to be a φ_{uuu} . Then the values of all phases φ_{uuu} and φ_{ggg} , linearly semi-dependent on φ_2 , are determined. Finally the values of all phases φ_{ugu} and φ_{guu} , linearly semi-dependent on the pair φ_1, φ_2 , are determined.

6.2. Type $2P_1$

The first paragraph of 6.1 carries over verbatim for Type $2P_1$ with the single exception that the seminvariant phases are now of the form φ_{ggg} and φ_{uuu} .

As an illustration of the specification of origin, φ_1 may be chosen to be a φ_{uug} . The values of all phases φ_{uug} and φ_{ggg} , linearly semi-dependent on φ_1 , are determined. Next, φ_2 may be chosen to be a φ_{guu} . Then the values of all phases φ_{guu} and φ_{ugg} , linearly semi-dependent on φ_2 , are determined. Finally the values of all phases φ_{ugu} and φ_{gug} , linearly semi-dependent on the pair φ_1, φ_2 , are determined.

6.3. Type $3P_2$

The phases which are the structure seminvariants are of the form φ_{ggg} , φ_{uug} , φ_{ugu} and φ_{guu} . The value of any phase φ_1 , not of this form, may be specified arbitrarily. Once this is done, the values of all phases, of necessity linearly semi-dependent on φ_1 , are determined. For example, φ_1 may be chosen to be φ_{ggg} .

6.4. Type $3P_3$

The phases which are the structure seminvariants are of the form φ_{ggg} , φ_{ggg} , φ_{uug} , and φ_{uuu} . The value of any phase φ_1 , not of this form, may be specified arbitrarily. Once this is done, the values of all phases,

of necessity linearly semi-dependent on φ_1 , are determined. For example, φ_1 may be chosen to be φ_{ugu} .

6.5. Type $4P$

Every phase is a structure seminvariant and its value is determined by the observed intensities. The value of no phase may be specified arbitrarily. In this type, the choice of the functional form of the structure factor is equivalent to the unique selection of the origin.

7. Concluding remarks

Monograph I (1953) and this paper present a detailed procedure for specifying the origin in any centrosymmetric space group. This has been done by demonstrating the existence of relationships between the observed intensities and values of the phases via the structure seminvariants. With the specific statement of the nature of these relationships, it is possible to go directly from observed intensities to the values of phases. It will be the aim of future publications to employ the formulas of our two recent papers (1958) to obtain specific procedures for phase determination for all the space groups.

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Structure Factor Calculations for some Helical Polypeptide Models

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Structure factors have been calculated for some helical polypeptide models, assuming random angular orientations of the molecules about the helical axis. The computations were carried out on IBM punched-card machines and a brief description is given of the method of computation.

Introduction

The theory of X-ray diffraction by helical molecules has been developed by Cochran, Crick & Vand (1952), who applied it to verify the presence of the α -helix (Pauling, Corey & Branson, 1951) in the synthetic polypeptide, poly- γ -methyl-L-glutamate. Since then, helical structures have been proposed for a number of

molecules, e.g. desoxyribose nucleic acid (Watson & Crick, 1953); collagen (Rich & Crick, 1955). Although many helical structures have been proposed with no more than a qualitative prediction of the calculated intensities, it is important to point out that a structure with satisfactory screw dimensions will not necessarily result in a correct distribution of layer-line

intensities. A quick method of obtaining calculated helical intensities is therefore desirable so that trial structures obtained from model building may be checked by comparing the calculated with the observed intensities.

The calculated intensity of diffraction by a proposed fiber structure can be obtained either by computation, using the structure-factor expression of Cochran *et al.* (1952); or it can be obtained optically with the optical diffraction spectrometer (Hughes & Taylor, 1953). Stokes (1955) has discussed the theoretical background for the use of the optical diffraction spectrometer for producing the optical transform of a helical structure. This method provides only approximate structure factors for comparison with the observed X-ray diffraction photograph, because of the difficulty of dealing with overlapping atoms and with the differences in scattering factors. In addition, a number of projected views must be summed if one wishes to produce a transform in which there is random angular orientation of the molecules about the helical axis. The time spent in calculating and plotting these views can be considerable.

We have therefore prepared a punched-card method for calculating fiber diffraction patterns for helical structures with random angular orientation.

There have been several helical configurations proposed for polypeptide chains, including the α and γ helices (Pauling *et al.*, 1951), the π -helix (Low & Baybutt, 1952) and several others. With the exception of the α helix, Fourier transforms have not been calculated for these models. In order to show the differences in diffraction patterns to be expected from them, we have computed the helical transforms for several such helices.

The averaged intensity expression

The Fourier transform of a helical molecule with periodicity c along its axis may be expressed as the sum of a series of Bessel function J_n for each layer line l (Cochran *et al.*, 1952). Thus, at a point in reciprocal space with cylindrical coordinates $(R, \psi, l/c)$, the Fourier transform is

$$F(R, \psi, l/c) = \sum_n \sum_j f_j J_n(2\pi r_j R) \times \exp \left[i \left\{ n(\psi - \varphi_j + \frac{1}{2}\pi) + \frac{2\pi l z_j}{c} \right\} \right], \quad (1)$$

where r_j, φ_j, z_j are the cylindrical coordinates of the j th atom of the asymmetric unit which has atomic scattering factor f_j , and the summation over n is for all the allowed values of n on the layer line of index l .

This expression can be written

$$F(R, \psi, l/c) = \sum_n (A_n + iB_n) \exp in\psi, \quad (2)$$

where

$$A_n = \sum_j f_j J_n(2\pi r_j R) \cos \left\{ n \left(\frac{1}{2}\pi - \varphi_j \right) + \frac{2\pi l z_j}{c} \right\},$$

$$B_n = \sum_j f_j J_n(2\pi r_j R) \sin \left\{ n \left(\frac{1}{2}\pi - \varphi_j \right) + \frac{2\pi l z_j}{c} \right\}. \quad (3)$$

The intensity is then

$$FF^* = \sum_n \sum_m \{ (A_n A_m + B_n B_m) + i(A_m B_n - A_n B_m) \} \exp i(n-m)\psi. \quad (4)$$

This expression, being a function of ψ , is not cylindrically symmetrical. In a fiber diagram, where the molecules are parallel, but oriented at random about the fiber axis, the relevant intensity is cylindrically averaged; that is, averaged over all values of ψ . Equation (4), when averaged, is zero unless $n = m$, when

$$F_{\bar{\psi}}^2(R, l/c) = \sum_n (A_n^2 + B_n^2). \quad (5)$$

An equivalent expression has been derived by Franklin & Klug (1955), but the form of (5) is more suitable for machine computation.

The orders n , of the Bessel functions on each layer line are defined by the equation

$$l/c = n/P + m/p, \quad (6)$$

where P is the pitch of the helix, p is the axial translation per asymmetric unit, and m is an integer. For molecules where there are k residues per repeat unit along the fiber axis, successive orders of Bessel functions on a given layer line will differ in order by k . In general, except for helices with small integral screws, k is large enough so that the major contribution to the intensity on a given layer line is due to the lowest-order Bessel function which satisfies equation (6). Under these circumstances, it is not necessary to calculate more than the contribution of the lowest-order Bessel function on each layer line. However,

Table 1

Structure	(1) γ helix	(2) 3.0 residue helix	(3) π helix	(4) α helix	(5) Modified π helix
Residues per turn	36 residues in 7 turns	3 residues per turn	22 residues in 5 turns	18 residues in 5 turns	23 residues in 5 turns
c -axis (Å)	35.28	6.00	25.3	26.64	26.64
Interval k between successive Bessel orders on each layer line	36	3	22	18	23
Number of Bessel functions per layer line used in calculation	1	4	1	1	1

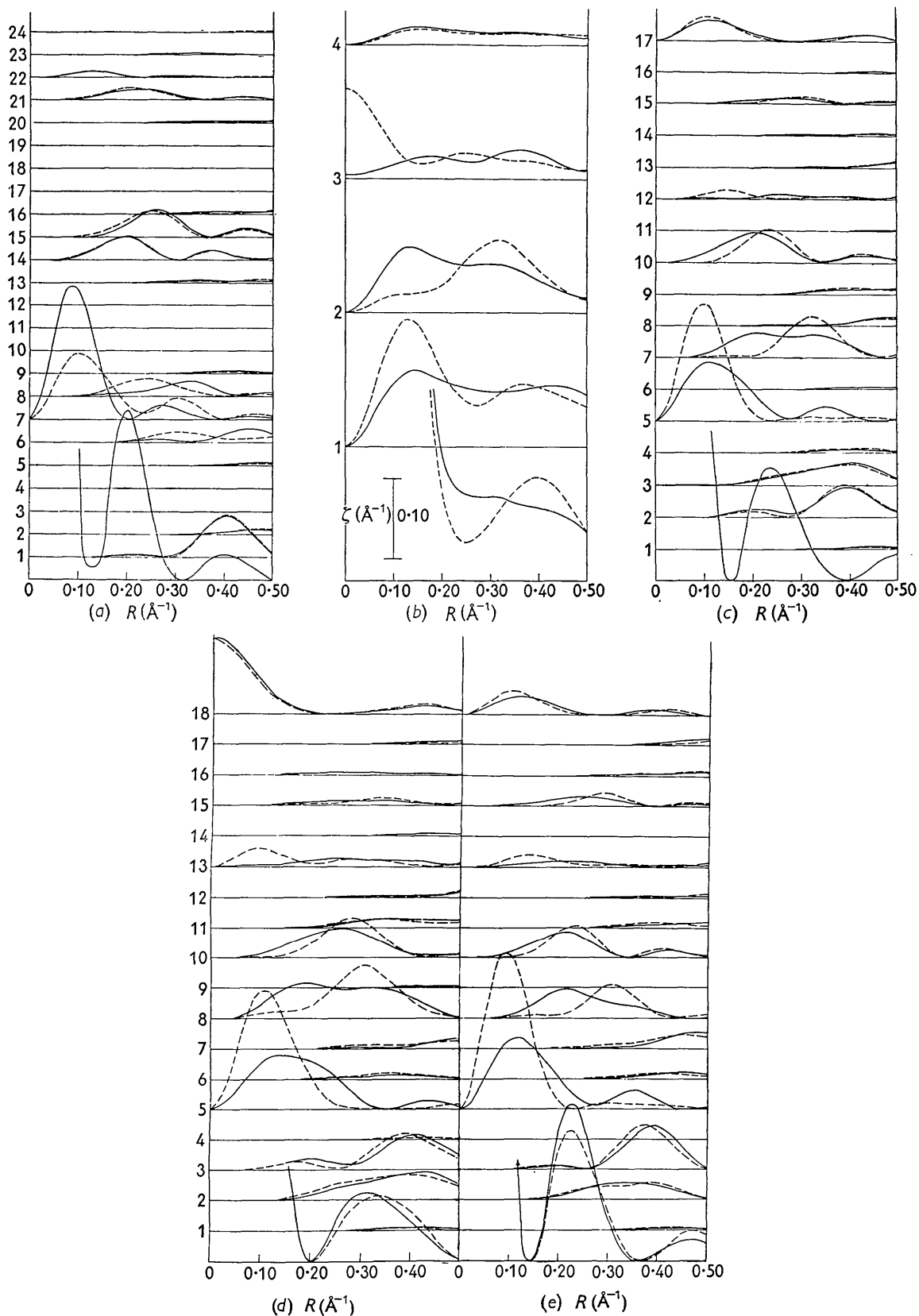


Fig. 1. The calculated averaged intensities for polypeptide models: (a) γ helix, (b) 3.0 residue helix, (c) π helix, (d) α helix, (e) modified π helix. The reciprocal lattice scale is the same for all five graphs. The ζ scale is shown in (b). The solid line represents the averaged intensity of a right-handed helix of L-amino acids (or a left-handed helix of D-amino acids). The dashed line represents a left-handed helix of L-amino acids.

if k is small, as in the 3.0 residue helix (see Table 1, p. 98), then more than one Bessel function makes a substantial contribution to a given layer line. These are simply added, as shown in equation (5).

Method of computation

A punched-card method has been prepared which uses the IBM 604 computer. In this procedure a detail card is prepared for each point in reciprocal space for each atom of the asymmetric unit of the helix. Each detail card contains the atomic coordinates, r_j , φ_j , z_j , a punch to distinguish the various atomic species, the reciprocal-space coordinates l and R , and the appropriate value of n for each l .

Values of $\sin \theta$, $2\pi r_j R$, $\cos \{n(\frac{1}{2}\pi - \varphi_j) + 2\pi l z_j / c\}$ and $\sin \{n(\frac{1}{2}\pi - \varphi_j) + 2\pi l z_j / c\}$ are then computed with the use of a simple power series and are punched on to the detail cards. Appropriate values of f_j ($\sin \theta$) and $J_n(2\pi r_j R)$, taken from master decks, are also punched on to the detail cards. Finally, the quantities A_n , B_n , and $A_n^2 + B_n^2$ of equation (5) are calculated and punched on to a deck of summary cards which are then listed and plotted in the form shown in Fig. 1.

The transforms were evaluated at intervals of 0.02 \AA^{-1} along R on all layer lines. The Bessel-function master deck contains $J_n(2\pi r_j R)$ to the nearest 0.001 over the range $0.00 \leq 2\pi r_j R \leq 25.00$ at intervals of 0.05. These were originally obtained from the *Tables of the Bessel Functions* (1947).

For these calculations, the asymmetric unit consists of five atoms, N, C α , C β , and carboxyl C and O. The atomic scattering factors were those obtained by graphical interpolation from the tables of McWeeny (1951) and contain no correction for thermal vibration. Values of f ($\sin \theta$) were chosen to the nearest 0.01, using intervals of $\sin \theta$ equal to 0.005 in the range $0.00 \leq \sin \theta \leq 0.600$ and 0.01 in the range $0.600 \leq \sin \theta \leq 1.000$.

For helical molecules which crystallize with one helix in the unit cell, the appropriate intensity expression becomes

$$FF^*(R, \psi, l/c) = \sum_n (A_n^2 + B_n^2) + 2 \sum_n^{\substack{n> \\ n}} \sum_m^{\substack{m \\ m}} \{ (A_n A_m + B_n B_m) \cos (n-m)\psi - (A_n B_m - A_m B_n) \sin (n-m)\psi \}. \quad (7)$$

This expression is a function of ψ and it is therefore incorrect to use the cylindrically averaged intensity expression for crystalline material. For helices like the α and π helix, however, where $(n-m)$ is 18 and 22 respectively, the ψ -dependent part of (7) will be small for the intense layer lines, and the cylindrically averaged expression (5) will provide a suitably accurate intensity pattern. However, computation of the trans-

form for a crystalline 3.0 residue helix would require the use of the expression (7).

Results

Fig. 1(a-d) shows the averaged intensities for right and left-handed helices of L-amino acids in the (a) γ helix, (b) 3.0 residue helix (Donohue, 1953), (c) π helix and (d) α helix. These are all calculated with the β -carbon atom present, hence they all represent possible models for poly-L-alanine. Various characteristics of these helices are listed in Table 1. The results for the α helix agree well with those of Pauling, Corey, Yakel & Marsh (1955), when allowance is made for the fact that Pauling *et al.* appear to have included a temperature factor in their calculation.

It is interesting to note that all of these transforms have an intense layer line near $\zeta = 0.2 \text{ \AA}^{-1}$. Furthermore, this layer line is a sensitive index of the handedness of the helix, since there are marked differences between right- and left-handed members of the same series.

Comparison of the transforms for the α and π helices shows that they have a remarkably similar general intensity distribution. This similarity can be greatly increased by adjusting the π helix to give 23 residues in 5 turns with $c = 26.64 \text{ \AA}$, as shown in Fig. 1(e). Examination of such a structure by the method of Low & Grenville-Wells (1953) shows a C-C α -N angle of $117\frac{1}{2}^\circ$ with a hydrogen-bond length of 2.86 \AA and with the hydrogen atoms displaced 5° from the N-O line. However, this method for constructing a polypeptide helix throws all the distortion into the α -carbon angle. By introducing small distortions in the rest of the molecule, e.g. removing the strict planarity of the peptide group, it is possible to effect a considerable reduction in the α -carbon angle distortion. For example, a 5° deviation from the planarity of the peptide group would reduce the α -carbon angle to $113\frac{1}{2}^\circ$. Donohue (1953) points out that there might exist certain conditions under which the π helix would be favored, although it is at first sight less stable than the α helix. We have, therefore, re-examined the data on synthetic polypeptides bearing in mind the striking similarity between the transforms of the α and π helices.

The main differences between the calculated diffraction patterns of the α and π helices occur on the equator and on the 18th layer line. The 18th layer line of the π helix is described by a first-order Bessel function and is therefore non-meridional in character, in contrast to the zero-order Bessel function of the α -helix, which is meridional. In addition, the peak intensity of the 18th layer line of the π helix is between one-quarter and one-third that of the α -helix. The equatorial patterns, however, differ greatly; in particular, the α -helix transform has its first minimum at $R = 0.16 \text{ \AA}^{-1}$.

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 (1,0,1,47) 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

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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