Short Communications

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The correlation between helical parameters and layer line distribution in the diffraction pattern of helical polymers.

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In the course of an X-ray investigation of poly-γ-benzylglutamate (Mitsui, Iitaka & Tsuboi, 1965), difficulty was experienced in indexing the layer lines without ambiguity because of their broadness. Besides, the determination of the identity period, c, is often disturbed by coexistence of another fibrous phase or by reflexions due to partial distortion of the helix. The value of c also changes largely and haphazardly with a slight twisting of the helix, namely by a slight change of P/p, where P denotes the pitch of the helix and p the axial climb per residue. In case of helical polymers, especially when the helix is non-integral, the parameter P/p or p/P seems to be more suitable than other parameters such as c/P or c/p for describing a helical structure. The parameters P/p and p/P represent the number of residues in one turn of the helix and the rotation angle per residue expressed as a fraction of 2π, respectively.

According to Cochran, Crick & Vand (1952), the value of ζ (the coordinate in reciprocal space) for a layer line relating to the nth order Bessel function is given by

$$\zeta(n, m) = n/P + m/p\,, \tag{1}$$

where m as well as n is an integer. We multiply P or p on both sides of (1) and define the following quantities,

$$\zeta_{\rm rel}(n, m) \equiv \zeta(n, m)P = n + m(P/p) \tag{2}$$

$$\zeta'_{\rm rel}(n, m) \equiv \zeta(n, m)p = n(p/P) + m\,. \tag{3}$$

Fig. 1 shows the relation between $\zeta_{\rm rel}(n, m)$ and P/p for the range $P/p = 2{\cdot}0 \sim 6{\cdot}0$, where each line is specified only by n

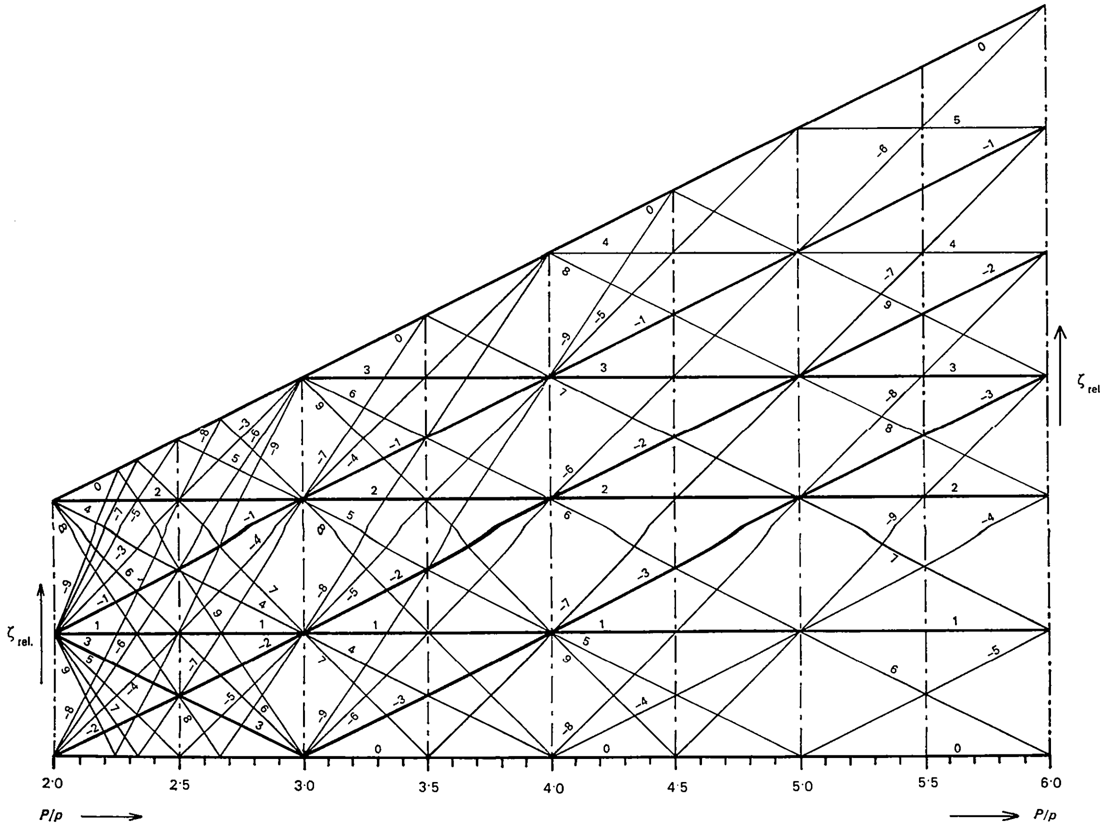

Fig. 1. The $\zeta(n) - P/p$ diagram. A graphical representation of equation (2). Numbers inscribed denote the value of n.

because m is not explicitly related to the diffraction intensity. We call this diagram the $\zeta(n)-P/p$ diagram. A similar one has been utilized by the author for discussing the helical structure of polypeptides (Mitsui, 1963). The $\zeta'(n)-p/P$ diagram corresponding to equation (3) is also shown in Fig. 2 for the range $p/P=0{\cdot}0\sim0{\cdot}4$. Extension of the diagram to higher layer lines may easily be made by taking account of the symmetry of the diagram. Dickerson (1964), in his review on fibrous proteins, gave a similar diagram to Fig. 2, but with P/p as abscissa in place of p/P.

From these diagrams, we can easily see how the relative ζ and the intensity distribution of the layer line vary with P/p or p/P. The relative positions of the layer lines corresponding to higher n are more sensitive to the change in P/p or p/P, and this fact may be utilized for an accurate determination of P/p, say, by the following procedures. (1) Plot the observed ζ's on a rubber tape and mark the relative intensities of the layer lines. (2) Set the tape parallel to the ordinate of the diagram and try to find out the best fit by expanding or shortening the tape and at the same time by sliding it along the P/p axis, until a satisfactory agreement between ζ_{obs} and ζ_{rel} and a reasonable correspondence of n to the relative intensities are obtained.

Once the (n, m) have been assigned to each layer, the layer line number, l, can be calculated by using the relation $l=tn+um$, where u is the number of residues in a period and is calculated as the smallest possible integral multiple of P/p. The parameter t denotes the number of turns of the helix in a period. The period c may then be calculated as the weighted average of l/ζ_{obs}'s.

The following are some examples of application of the $\zeta'(n)-p/P$ diagram to the helical synthetic α-polypeptides, for which the fitting procedure is greatly simplified because p can be accurately determined from the Perutz line (Fig. 3).

(1) Poly-γ-benzyl-L-glutamate (PBG), with ζ_{obs} values obtained by the present author. The best fit was obtained for $P/p=3{\cdot}600$.

(2) Poly-L-alanine (PAla), with ζ_{obs} values by Brown & Trotter (1956). Some discrepancies were found to occur for the proposed value $P/p=3{\cdot}615$, although no other better solution was found.

(3) Poly-γ-methyl-L-glutamate (PMG), with ζ_{obs} values by Bamford, Elliott & Hanby (1956). The Perutz line spacing is taken as 1·495 Å. They proposed various helices having $P/p\simeq3{\cdot}63$, *i.e.* the 29 residue/8 turn (3·625), 98/27 (3·630), 69/19 (3·631) and 91/25 (3·640) helices. However, it is apparent from Fig. 3 that the agreement is better with $P/p=3{\cdot}61$. From this value we obtain $c=97{\cdot}2_6$ Å by assuming a 65/18 (3·611) helix. The calculated ζ values are shown in Table 1 together with the ζ_{obs} and ζ_{cal} of Bamford *et al.* (1956).

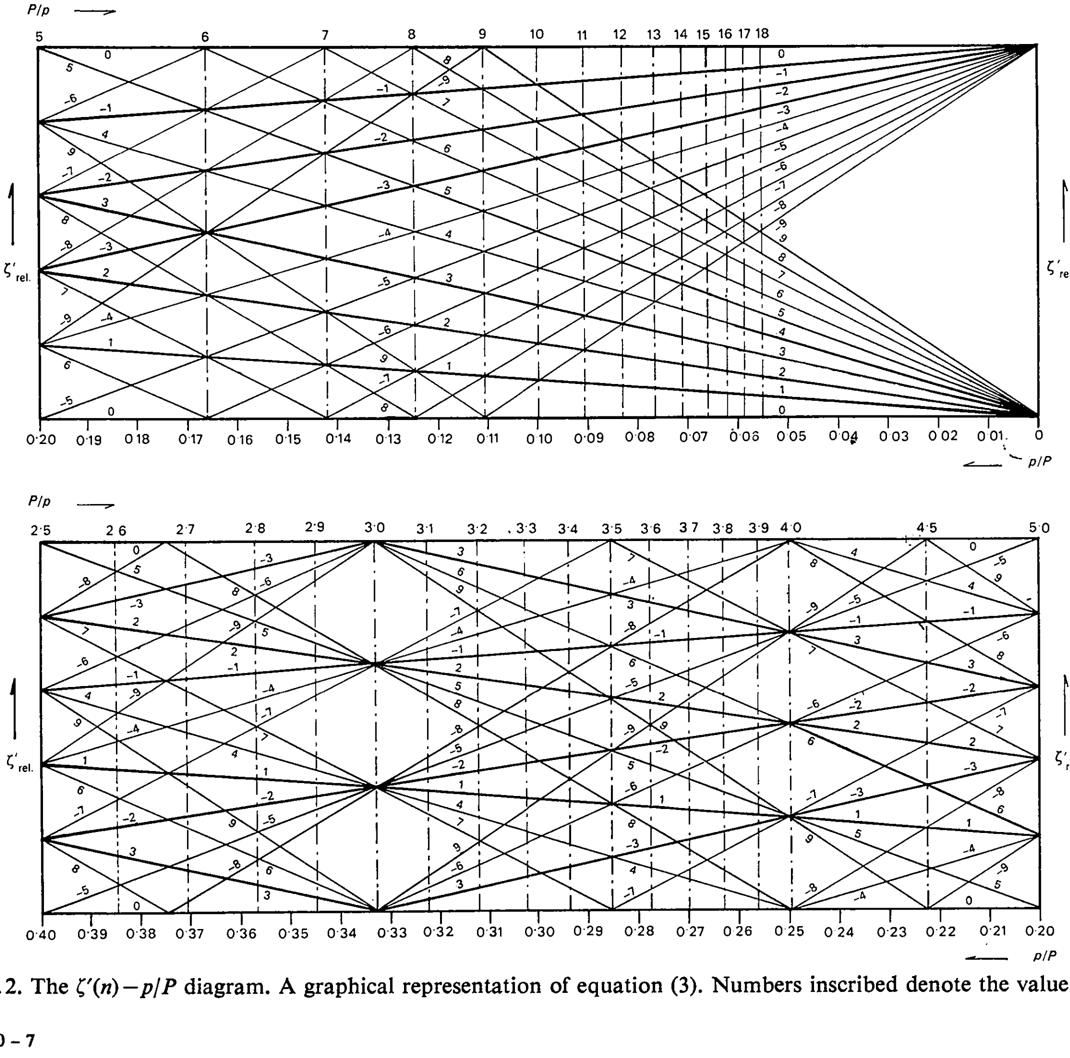

Fig. 2. The $\zeta'(n)-p/P$ diagram. A graphical representation of equation (3). Numbers inscribed denote the value of n.

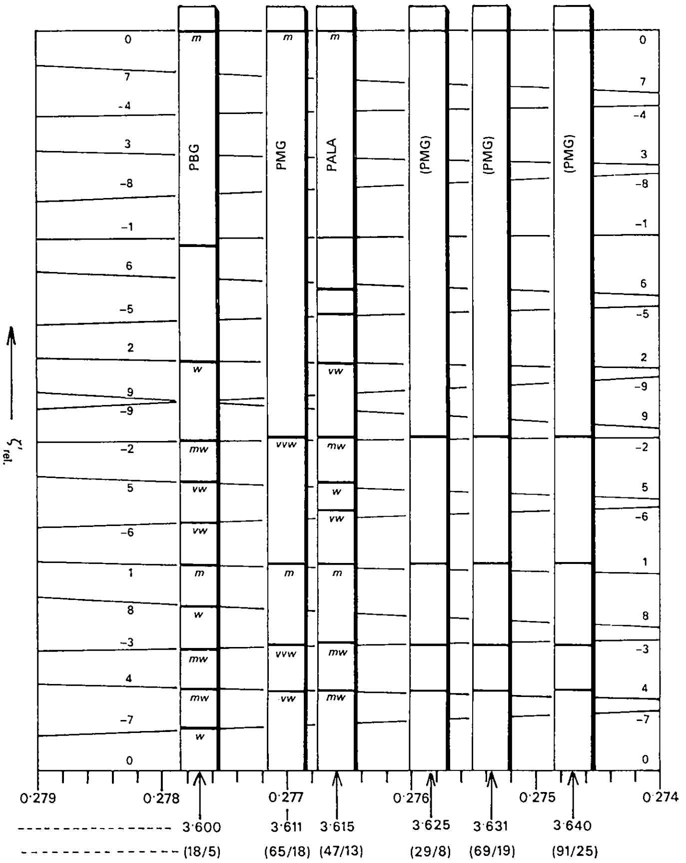

Fig. 3. The $\zeta'(n)-p/P$ diagram applied to the α-form of some synthetic polypeptides. Observed ζ and the relative intensities are marked in the strips.

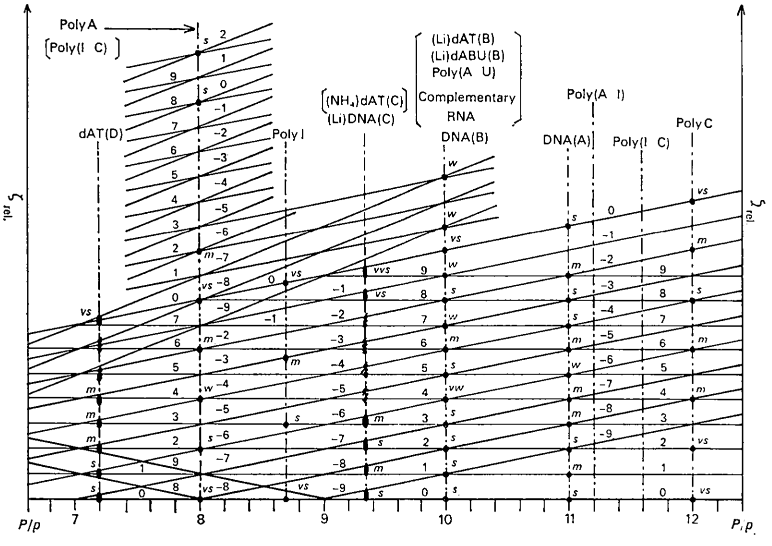

Fig. 4. The $\zeta(n)-P/p$ diagram applied to helical polynucleotides. Unless otherwise specified the polymers are in sodium salts. The observed layer lines are marked by black circles. The intensities are qualitatively indicated. Intensities marked at $P/p=10$, $P/p=8$, $P/p=9{\cdot}3$ are those for DNA(B), Poly A and (Li)DNA(C), respectively.

Abbreviations and references:

Poly C, Polyribocytidylic acid (protonated) (Langridge & Rich, 1963).
Poly I, Polyriboinosinic acid (three stranded) (Rich, 1958*a*).
Poly A, Polyriboadenylic acid (protonated) (Rich, Davies, Crick & Watson, 1961).
Poly (I+C), 1:1 mixture of Poly C and Poly I (Rich, 1958*b*).
Poly (A+U), 1:1 mixture of Poly A and Poly U (Rich & Davies, 1956; Rich, 1957).
Poly (I+C)$^+$, Protonated Poly (I+C) (Tomita & Rich, 1965).
dAT, Deoxyadenylic-thymidylic acid (Davies & Baldwin, 1963).
dABU, Deoxyadenylic-bromouridylic acid (Davies & Baldwin, 1963).
DNA(A), DNA(B), DNA in A form and in B form (Langridge, Wilson, Hooper, Wilkins & Hamilton, 1960).
(Li)DNA(C), Li salt of DNA in C form (Marvin, Spencer, Wilkins & Hamilton, 1961).
Complementary RNA: These include the following three examples.
(1) Wound tumor virus RNA (Tomita & Rich, 1964).
(2) Reovirus RNA (Langridge & Gomatos, 1963).
(3) Rice dwarf virus RNA (Sato, Kyogoku, Higuchi, Mitsui, Iitaka, Tsuboi, & Miura, 1965).

Table 1. *Comparison of the two possible indexings of layer lines for poly-γ-methyl-*L*-glutamate*

	29 residue/8 turn Bamford *et al.* (1956) $c=43{\cdot}2$ Å, $P/p=3{\cdot}625$		65 residue/18 turn Present study $c=97{\cdot}2_6$ Å, $P/p=3{\cdot}611$	
ζ obs (Å^{-1})*	l	ζ cal	l	ζ cal
$0{\cdot}070_7$	3	$0{\cdot}069_4$	7	$0{\cdot}072_0$
$0{\cdot}112_2$	5	$0{\cdot}115_7$	11	$0{\cdot}113_1$
$0{\cdot}185_8$	8	$0{\cdot}185_1$	18	$0{\cdot}185_1$
$0{\cdot}299_0$	13	$0{\cdot}300_8$	29	$0{\cdot}298_1$
$0{\cdot}668_9$	29	$0{\cdot}671_1$	65	$0{\cdot}668_3$

* Bamford *et al.* (1956).

The $\zeta(n)-P/p$ diagram may be used in the study of helical polynucleotides as shown by Tsuboi (1964). In this case, the relation between the intensity and n is not always simple, especially for the multistranded helix owing to the exact or approximate extinction rules with respect to n. This fact, however, gives us a clue to infer the strandedness of the helix. Some of the results are shown in Fig. 4.

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Topotactic transition in C_4AlB_{24}.

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During the past 25 years considerable work has been carried out on determining the stoichiometry and structure of complex borides while properties and reactions of these materials have received little attention. Recently, a high temperature reversible disproportionation was reported for $C_2Al_3B_{48}$ (Matkovich, Economy & Giese, 1964). It was shown that $C_2Al_3B_{48}$ existed as a single phase only at elevated temperatures and that on cooling it disproportionated reversibly into two phases. The outer form of the high temperature crystal was retained, resulting in an intergrowth of the two low temperature phases. In the present work, an irreversible high temperature transformation of C_4AlB_{24} to a boron carbide type structure is described. In this case the morphology of the original single crystal is retained, yielding a single crystal of the new phase, even though significant changes occur in both the packing of the B_{12} icosahedra and placement of interstitial atoms. Several examples of similar rearrangements have recently been reported in the literature and are described as topotactic reactions (Lotgering, 1959; Shannon & Rossi, 1964).

Single crystals of C_4AlB_{24} prepared by a method reported earlier (Matkovich, Economy & Giese, 1964) were placed in a boron nitride crucible and fired in an argon atmosphere at temperatures ranging from 1700°C to 2000°C. At temperatures exceeding 2000°C recrystallization takes place and crystals assume the form of slightly distorted octahedra. This paper is concerned only with samples obtained below recrystallization temperatures.

Under the microscope it appeared that the outer form of the crystals changed very little, although the faces lost some of their luster in reflected light. X-ray examination of the product revealed that each specimen was still a single crystal; however, the orthorhombic unit cell of C_4AlB_{24} ($a=8{\cdot}88$ Å, $b=9{\cdot}10$ Å, $c=5{\cdot}69$ Å; space group *Bbmm*) could no longer be observed. Since the crystal retained its original outer form, the axis directions could be traced. It was found that there was no longer a crystallographic axis in the direction of the orthorhombic a and b axes. In the direction of the c axis, however, a period of about 5·63 Å was observed. By use of Weissenberg X-ray photographs the unit cell was found to be rhombohedral ($a=5{\cdot}23$ Å; $\alpha=65°10'$), B_4C type, with hexagonal dimensions of $a=5{\cdot}63$, $c=12{\cdot}29$ Å. It was established that one of the rhombohedral axes coincides with the [101] direction of the orthorhombic precursor crystal. (The transition of axes is illustrated in Fig. 1.) The density of crystals was