

(0.02 Å) is greater than the standard deviations. There are significant changes in the atomic co-ordinates, due to the cooling; these are recorded in Table 1. Despite these changes, however, the molecular dimensions show no significant differences from those of the molecule at room temperature. The hydrogen-bonding distance of the dimers is also unaffected.

Table 1. *Differences in atomic coordinates (Å)*

The authors' values are subtracted from those of Nardelli *et al.* The final column contains the estimated standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	
S	0.028	-0.007	-0.036	0.002
O ₁	0.048	-0.012	-0.037	0.006
O ₂	0.046	0.008	0.011	0.006
C ₁	0.044	-0.009	-0.028	0.008
C ₂	0.025	-0.021	-0.022	0.007
C ₃	0.045	-0.045	-0.008	0.008
C ₄	0.038	-0.101	-0.019	0.007
C ₅	0.036	-0.026	-0.008	0.007

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The structure of poly-L-proline II. By R. E. BURGE, P. M. HARRISON* and S. MCGAVIN,† *Wheatstone Physics Laboratory, University of London King's College, Strand, W. C. 2, England*

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Poly-L-proline has been shown (for references see Downie & Randall, 1959; Steinberg, Harrington, Berger, Sela & Katchalski, 1960) to exist in solution in two configurations characterized respectively by a small positive (I) or a large negative (II) optical rotation. It was shown (Cowan & McGavin, 1955) by X-ray diffraction methods that poly-L-proline II in the solid state consists of three-fold left-handed spirals, the peptide groups having the *trans* configuration.

A three-fold (or nearly three-fold) spiral structure for poly-L-proline I has also been proposed (Cowan & Burge, 1957) but the screw sense is right-handed and the imide groups have the *cis* configuration.

Cowan & McGavin (1955) found a trigonal unit cell for poly-L-proline II, space group $P3_2$, with $a=6.62$, $c=9.36$ Å. A similar structure has been published by Sasisekharan (1959) with some modification of co-ordinates and unit-cell dimensions ($a=6.68$, $c=9.36$ Å). Sasisekharan found, from stereochemical considerations and by a comparison of optical diffraction patterns and the X-ray powder pattern, the range of the possible orientations of the chain axis of the polymer in the *c* plane.

It is proposed here to present the results of a comparison between calculated intensities and measured X-ray intensities giving more specifically the orientation of the poly-L-proline II helix.

The polar co-ordinates for the poly-L-proline II chain used in these calculations are the previously published values (Cowan & McGavin, 1955). The atoms in the imide group and proline ring are planar except for the β -carbon atom which is 0.4 Å out of the plane. Bond lengths and angles are respectively within ± 0.02 Å and $\pm 3^\circ$ of the values for the amide groups published by

A three dimensional difference map computed with our data enabled three of the hydrogen atoms to be satisfactorily identified, but the carboxyl group hydrogen could not be adequately sited. Our work confirms the displacement of the sulphur atom from the plane of the ring, by 0.02 Å at the low temperature.

We should like to record our thanks to Dr E. G. Cox for his initiation of the problem and to Prof. Challenger for his interest and instructive discussions, and also to the Department of Scientific and Industrial Research for a maintenance grant to one of us (P. H.).

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Corey & Pauling (1953) and of those found for hydroxy-L-proline by Donohue & Trueblood (1952). The configuration of the prolyl residue is also close to that occurring in L-leucyl-L-prolyl-glycine subsequently published by Leung & Marsh (1958).

The orientation of the polymer chain was fixed with

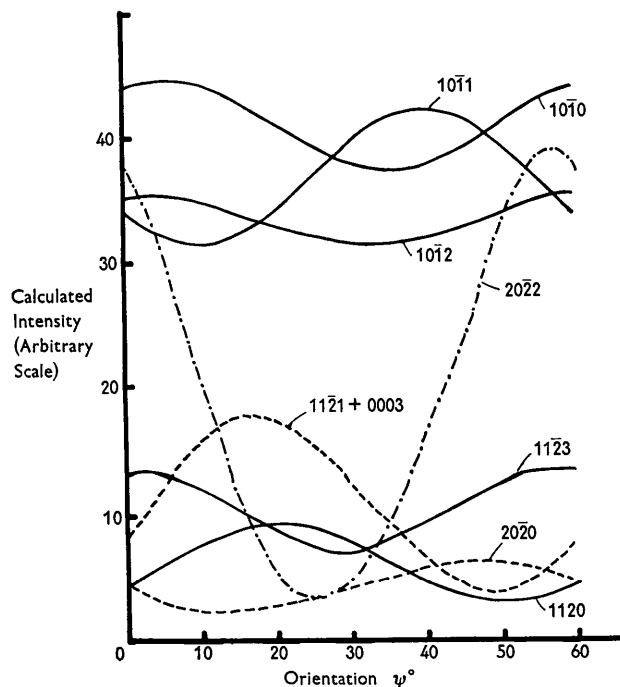


Fig. 1. The calculated variation, with orientation ψ of the poly-L-proline II helix in the unit cell, of the intensities of reflections corresponding to those observed in the X-ray powder diagram. A graph corresponding to $I_{hkl} + I_{\bar{h}\bar{k}\bar{l}}$ is marked with the hkl indices. Ordinate: Calculated intensity (arbitrary scale). Abscissa: Orientation ψ° .

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respect to the a axis of the unit cell by the angle ψ between this axis and the perpendicular to the chain axis passing through the α -carbon atom; full details of this procedure are given by Sasisekharan (1959). For each ψ the intensities of the hkl and $hk\bar{l}$ reflections were calculated for all reflections with spacings greater than 2.2 Å. Calculations were made at 5° intervals between $\psi = 0$ and $\psi = 60^\circ$; this range includes all possible orientations of the chain.

The average degree of polymerization of the material in the specimens was 20. The measured intensities were obtained from several X-ray powder photographs using a densitometer; the intensities were corrected for Lorentz and polarization factors and for an assumed isotropic temperature factor with $B = 4 \text{ \AA}^2$.

The variations of the calculated intensities for the $10\bar{1}0$, $11\bar{2}0$, $20\bar{2}0$, $10\bar{1}1 + 10\bar{1}\bar{1}$, $10\bar{1}2 + 10\bar{1}\bar{2}$, $20\bar{2}2 + 20\bar{2}\bar{2}$, $11\bar{2}1 + 11\bar{2}\bar{1} + 0003 + 000\bar{3}$, $11\bar{2}3 + 11\bar{2}\bar{3}$, powder pattern rings, allowing for multiplicities, are plotted against ψ in Fig. 1.

The only other measurable reflection at about 2.73 Å involves the overlapping $20\bar{2}1$, $20\bar{2}\bar{1}$, $11\bar{2}2$, $11\bar{2}\bar{2}$, $10\bar{1}3$, $10\bar{1}\bar{3}$, reflections which according to the calculated results varied little with ψ and has been omitted from the analysis of the orientation.

It is clear that most of the reflections shown in Fig. 1 vary significantly in intensity according to the helix orientation.

The calculated and observed intensities were correlated

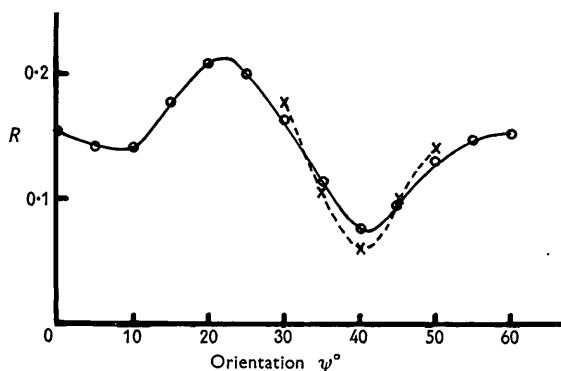


Fig. 2. The variation of the residual R according to the orientation of the helix in the unit cell. Full line—Cowan & McGavin's co-ordinates; dotted line—Sasisekharan's co-ordinates. Ordinate: R . Abscissa: Orientation ψ° .

at each ψ by calculating the residual

$$[R = \Sigma |F|_o - |F|_c / \Sigma |F|_o]$$

after setting $\Sigma |F|_o^2 = \Sigma |F|_c^2$ for the 15 reflections concerned. The variation of R with ψ between 0° and 60° is shown in Fig. 2 for the helix with the Cowan-McGavin co-ordinates and values for R calculated from Sasisekharan's co-ordinates are also given for values of ψ near the minimum value of R .

The minimum value of R corresponds to an orientation of the poly-L-proline II helix relative to the a axis of the hexagonal cell such that (taking errors in the observed intensities into account) $\psi = 40 \pm 2^\circ$. This is true for both sets of co-ordinates, although the actual values of R do depend to some extent on the small configurational differences involved. The 'best value' of ψ obtained by calculation differs somewhat from the value $30\text{--}35^\circ$

Table 1. Comparison of observed and calculated structure factors for $\psi = 40^\circ$

Reflection	$ F _o$	$ F _c$
$10\bar{1}0$	12.9	13.8
$10\bar{1}1 + 10\bar{1}\bar{1}$	14.3	14.5
$10\bar{1}2 + 10\bar{1}\bar{2}$	12.7	12.6
$11\bar{2}0$	3.7	4.9
$11\bar{2}1 + 11\bar{2}\bar{1} + 1/6(0003) + 1/6(000\bar{3})$	7.2	5.2
$20\bar{2}0$	6.2	5.7
$20\bar{2}2 + 20\bar{2}\bar{2}$	9.5	9.1
$11\bar{2}3 + 11\bar{2}\bar{3}$	7.1	6.9
$20\bar{2}1 + 20\bar{2}\bar{1} + 11\bar{2}2 + 11\bar{2}\bar{2} + 10\bar{1}3 + 10\bar{1}\bar{3}$	12.9	18.0

estimated by Sasisekharan from qualitative observations of intensities in optical transforms. The observed and calculated structure factors normalized as already discussed for $\psi = 40^\circ$ are given in Table 1 and the co-ordinates for this position of the atoms in a single asymmetric unit along the poly-L-proline II chain are shown in Table 2.

Table 2. Co-ordinates of atoms in a single repeating unit

Atom	x	y	z
C_1	0.026	0.055	0.122
O_1	-0.186	-0.033	0.137
N_1	0.157	0.012	0.208
αC_1	0.077	-0.147	0.333
βC_1	0.278	-0.188	0.368
γC_1	0.492	0.028	0.306
δC_1	0.415	0.091	0.187

The calculation of intermolecular van der Waals contacts shows that all helix orientations other than those in the neighbourhood of $\psi = 35^\circ\text{--}40^\circ$ can be ruled out. For $\psi = 35^\circ$ there are contacts $\gamma C_1\text{--}O_1 = 2.92 \text{ \AA}$ and $\delta C_1\text{--}\gamma C_1 = 3.53 \text{ \AA}$. For $\psi = 40^\circ$, $\gamma C_1\text{--}O_1 = 2.80 \text{ \AA}$ and $\delta C_1\text{--}\gamma C_1 = 3.80 \text{ \AA}$. The short contact $\gamma C_1\text{--}O_1$ might be explained, as suggested by Sasisekharan, as a CH-O hydrogen bond. The distance is however rather short and the angles $\beta C_1\text{--}\gamma C_1\text{--}O_1$ and $\delta C_1\text{--}\gamma C_1\text{--}O_1$ are respectively 122° and 95° for $\psi = 40^\circ$. A diagram of the unit-cell arrangement with $\psi = 30^\circ$ has been given by Sasisekharan (1959).

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