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ATOMIC COORDINATES AND STRUCTURE FACTORS FOR TWO HELICAL CONFIGURATIONS OF POLYPEPTIDE CHAINS

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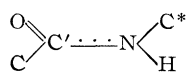
During recent years we have been gathering information about interatomic distances, bond angles, and other properties of simple substances related to proteins, and have been attempting to formulate configurations of the polypeptide chain that are compatible with this information and that might constitute a structural feature of proteins. We have reported the discovery of two helical configurations that satisfy these conditions.[1,2] In the following paragraphs we discuss the atomic positions for these configurations, and their form factors for diffraction of x-rays in the equatorial direction.

The γ Helix.—Let us first discuss the 5.1-residue helix. This configuration is obtained by coiling a polypeptide chain into a helical form, in such a way that the planar amide groups,



are in the trans configuration (the carbonyl group being almost directly opposed to the imino group), and each amide group forms hydrogen bonds with the fifth more distant group in each direction along the chain. The structure is represented diagrammatically in figure 1, and a drawing of it has been recently published.[2] We base our discussion on the values of interatomic distances and bond angles given in figure 4; these differ from those described earlier only in the change from 120° to 123° for the angle C′—N—C*.

The fifth amide group beyond a given group in the helix is nearly directly above it, and if the hydrogen bonds determine the orientation of the plane of the amide groups there seems to be no reason for this plane not to be parallel to the axis of the helix. The following calculations are made

with this assumption. It is found that the rise per residue—the magnitude of the translation associated with the rotatory translation that converts one residue into the adjacent one along the chain—is determined nearly exactly by the length of the hydrogen bond. For N—H···O distance 2.72 A the rise per residue is 0.97 A, for 2.78 A it is 0.98 A, and it continues to increase linearly by about 0.002 A for each 0.010 A increase in length of the hydrogen-bond distance. The number of residues per turn, on the other hand, is determined essentially by the N—C—C′ angle of the α carbon

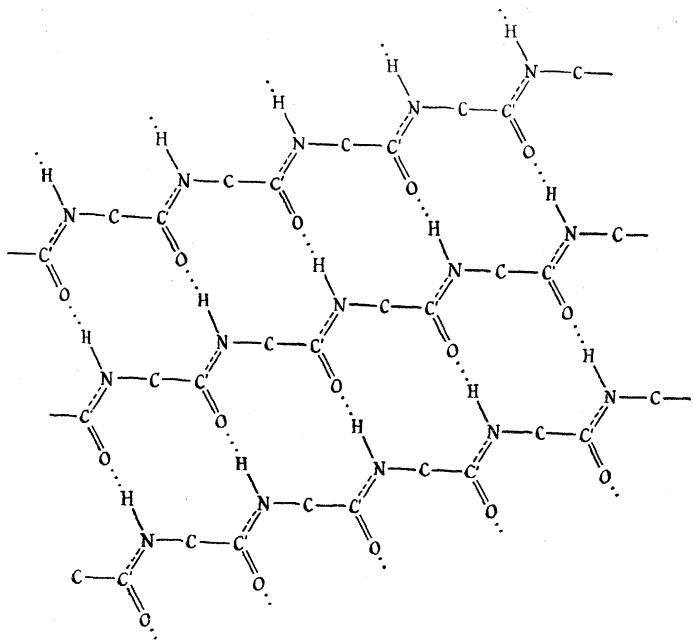


FIGURE 1

Diagrammatic representation of the 5.1-residue helical configuration of the polypeptide chain.

atom. For 21 residues in 4 turns (5.25 residues per turn) this angle has the value 111.2°, for 26 residues in 5 turns (5.20) its value is 110.6°, for 31 residues in 6 turns (5.17) 110.1°, and for 36 residues in 7 turns (5.14 residues per turn) 109.8°. These values are all within a reasonable range for this angle; the existing experimental evidence, for scores of molecules containing a tetrahedral carbon atom, suggests 110° as the best value for the angle, but a change by as much as 1° would introduce such a small amount of strain energy, in any case, that it should be allowed. There is, of course, no reason in an isolated molecule of a polypeptide or protein for the number of residues per turn to be rational. In a crystal, however, the

intermolecular forces might constrain the molecule to assume the symmetry of a position in the crystal. The most likely eventuality is that the cylindrical molecules would take up a hexagonal close-packed arrangement, and that the molecules would assume a sixfold screw axis. This is provided from among the foregoing possibilities only by the configuration with 36 residues in 7 turns, which has a 36-fold screw axis, with a sixfold screw axis contained within its symmetry group. We present in table 1 calculated atomic coordinates for this case, for which the angle of rotation of the fundamental rotatory-translational operation is exactly 70°. The coordinates have been calculated for a rise per residue 0.98 A, corresponding to the

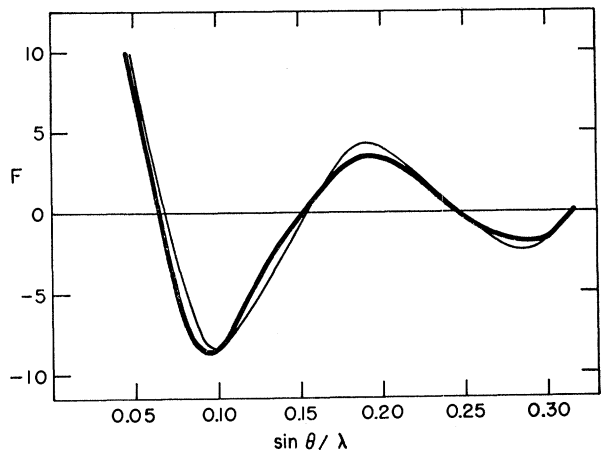


FIGURE 2

X-ray form factor for the 5.1-residue helix, calculated for equatorial reflections, and for cylindrical symmetry. The light line represents the scattering due to the four main-chain atoms of the amide group, and the heavy line includes the scattering of one β carbon atom per residue.

distance N—H···O equal to 2.78 A. The rise per turn is then 5.04 A, and the identity distance along the helical axis is 35.28 A.

The form factor for x-ray scattering for this molecule could, of course, be calculated from the coordinates of the atoms. A very good approximation for the equatorial reflections can be made by assuming cylindrical symmetry about the axis. The structure factor is then $F = \sum_i f_i J_0 (4\pi\rho_i \sin\theta/\lambda)$, in which J_0 is the Bessel function of order zero with the indicated argument, and ρ_i is the radius of the ith atom, in cylindrical coordinates, as given in table 1. (In this table there are given both cartesian coordinates, x, y, z, and cylindrical coordinates, ρ, ϕ, z, the latter being relative to the axis of the helix.) The form factor F as calculated by this method with use of the atomic form factors given in the International Tables for the

Determination of Crystal Structures is shown in figure 2, both for the residue alone, corresponding to polyglycine, and for a molecule with a β carbon atom in each residue. The two form factors do not differ very

TABLE 1

ATOMIC COORDINATES FOR THE 36-RESIDUE 7-TURN γ HELIX

x, y, z, ρ IN A

ATOM	x	y	z	ρ	ϕ
C	0.00	0.00	0.00	3.22	0.0°
C′	1.52	0.00	−0.15	2.66	27.8°
O	2.05	0.00	−1.26	2.65	39.3°
N	2.23	0.00	0.97	2.67	43.2°
C*	3.70	0.00	0.98	3.22	70.0°
βC	−0.50	−0.74	1.26	4.11	0.7°
or					
βC	−0.52	−0.72	−1.26	4.11	−0.7°
Axis	1.85	2.64	...	0.00	...

much. The square of F, which determines the intensity of reflection of x-rays, is shown in figure 3. It is seen that we predict that the equatorial

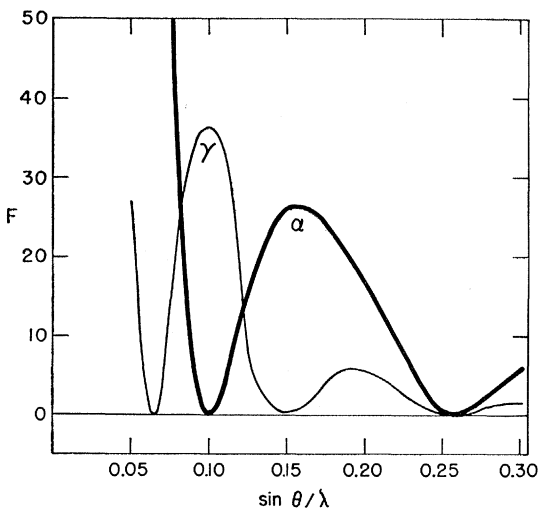


FIGURE 3

The square of the form factor for the 5.1-residue helix (γ) and the 3.7-residue helix (α), for equatorial reflections.

reflections from an array of molecules with this structure would be weak in the regions of interplanar distance 7.7 A, 3.3 A, and 2.0 A, and strong at

about 5.0 A and 2.4 A. A discussion of the question of possible existence of protein molecules with this structure will be given in a later paper.

The α Helix.—The α helix is a configuration of the polypeptide chain in which each amide group forms hydrogen bonds with the amide groups removed by three from it in either direction along the chain. The α helix and the γ helix are the only helical configurations in which the residues are all equivalent and in which the stereochemical requirements, including formation of intramolecular hydrogen bonds, are satisfied. The structure is represented diagrammatically in figure 4. With the structural parameters described above, we find that a translation per residue of 1.47 A corresponds to a hydrogen-bond distance 2.75 A, and that the translation increases by 0.01 A for every 0.03 A increase in the hydrogen-bond distance. The number of residues per turn is fixed primarily by the bond angle at the α carbon atom; it varies from 3.60 for bond angle 108.9° to 3.67 for bond angle 110.8°. α-Helixes with these numbers of residues per turn have been found (see the following paper[3]) to explain the x-ray reflections[4] from highly oriented fibers of poly-γ-methyl-L-glutamate and poly-γ-benzyl-L-glutamate, respectively. The first ratio corresponds to 18 residues in 5 turns and the second to 11 residues in 3 turns.

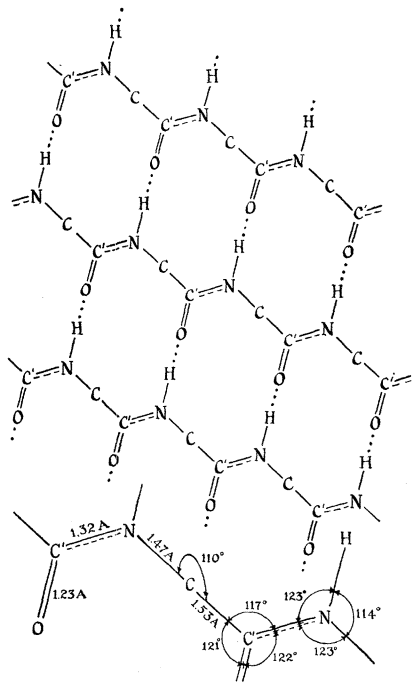


FIGURE 4

Diagrammatic representation of the 3.7-residue helical configuration of the polypeptide chain.

We have chosen to present parameters for the 18-residue 5-turn helix, which has a sixfold screw axis that would be stabilized in hexagonal packing. The parameters given in table 2 correspond to this helix, with a translation of 1.50 A per residue (5.40 A per turn, 27.0 A identity distance along the axis), these being the dimensions found for the polymethylglutamate. The corresponding hydrogen-bond distance is 2.86 A.

The structure factor for equatorial reflections calculated for cylindrical symmetry is shown in figure 5, and the corresponding intensity curve in figure 3. It is seen that the equatorial reflections should be very weak at about 5.0 A and 2.0 A, and strong at about 3.4 A. The correlation be-

tween theory and experiment for synthetic polypeptides and for proteins with the α-keratin structure is discussed in following papers of this series.

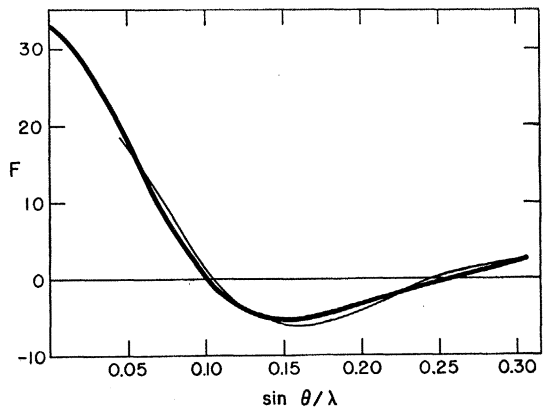


FIGURE 5

X-ray form factor for the 3.7-residue helix, calculated for equatorial reflections, and for cylindrical symmetry. The light line represents the scattering due to the main-chain atoms only, and the heavy line includes also the scattering of one β carbon per residue.

TABLE 2

ATOMIC COORDINATES FOR THE 18-RESIDUE 5-TURN α HELIX

x, y, z, ρ IN A

ATOM	x	y	z	ρ	ϕ
C	0.00	0.00	0.00	2.29	0.0°
N	1.16	0.00	0.89	1.59	27.8°
C′	2.42	0.00	0.44	1.61	73.8°
O	2.69	0.00	−0.76	1.74	82.0°
C*	3.52	0.00	1.50	2.29	100.0°
βC	−1.33	0.20	0.76	3.34	−17.6°
or					
βC	−0.03	−1.34	−0.76	3.34	17.6°
Axis	1.76	1.47	...	0.00	...

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* Contribution No. 1550.

[1] Pauling, L., and Corey, R. B., *J. Am. Chem. Soc.*, **72**, 5349 (1950).

[2] Pauling, L., Corey, R. B., and Branson, H. R., these PROCEEDINGS, **37**, 205 (1951).

[3] Pauling, L., and Corey, R. B., *Ibid.*, **37**, 241 (1951).

[4] Bamford, C. H., Hanby, W. E., and Happey, F., *Proc. Roy. Soc.*, **A205**, 30 (1951).