TWO RIPPLED-SHEET CONFIGURATIONS OF POLYPEPTIDE CHAINS, AND A NOTE ABOUT THE PLEATED SHEETS

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About a year ago, in the course of the consideration of configurations of polypeptide chains with favored orientations around single bonds, we described two pleated-sheet structures.[1] These structures are suited to polypeptide chains constructed entirely of L amino-acid residues or of D amino-acid residues. In one pleated sheet alternate polypeptide chains are antiparallel, and in the other they are parallel. The amide groups have the trans configuration.

We have observed that closely related structures can be constructed in which polypeptide chains of D and L amino-acid residues alternate. The configuration of these layer structures is such as to make it appropriate to call them rippled sheets.

The Antiparallel-Chain Rippled Sheet.—The antiparallel-chain rippled sheet, represented in figure 1, is closely similar to the antiparallel-chain

TABLE 1

ATOMIC COORDINATES FOR THE ANTIPARALLEL-CHAIN RIPPLED SHEET

$a_0 = 9.44$ A, $b_0 = 7.00$ A, $c_0 = 1.00$ A (assumed). Four atoms in x, y, z; $1/2 - x, 1/2 + y, \bar{z}$; $\bar{x}, \bar{y}, \bar{z}$; $1/2 + x, 1/2 - y, z$

	x	y	z
C	0.287	0.040	0.64
C′	0.200	0.216	0.28
O	0.068	0.220	0.45
N	0.275	0.359	−0.22

pleated sheet, and the diagrammatic representation given in figure 4 of the earlier paper[1] applies to both structures. One structure is converted into the other by the reflection of alternate chains into their enantiomers, in the plane of the sheet. The unit of structure was determined by measurement of a model constructed of units precisely built on the scale 10 cm. = 1A. The value of the lateral translation was found to be 9.44 A, and that of the translation in the direction of the polypeptide chains 7.00 A. Atomic coordinates are given in table 1.

The Parallel-Chain Rippled Sheet.—The parallel-chain rippled sheet, shown in figure 2, is closely similar to the parallel-chain pleated sheet, and has the same diagrammatic representation, shown in figure 5 of the previous paper.[1] The unit of structure was found by measurement of a model to have lateral identity distance $a_0 = 9.60$ A, and identity distance along the fiber axis $b_0 = 6.50$ A. Atomic coordinates are given in table 2.

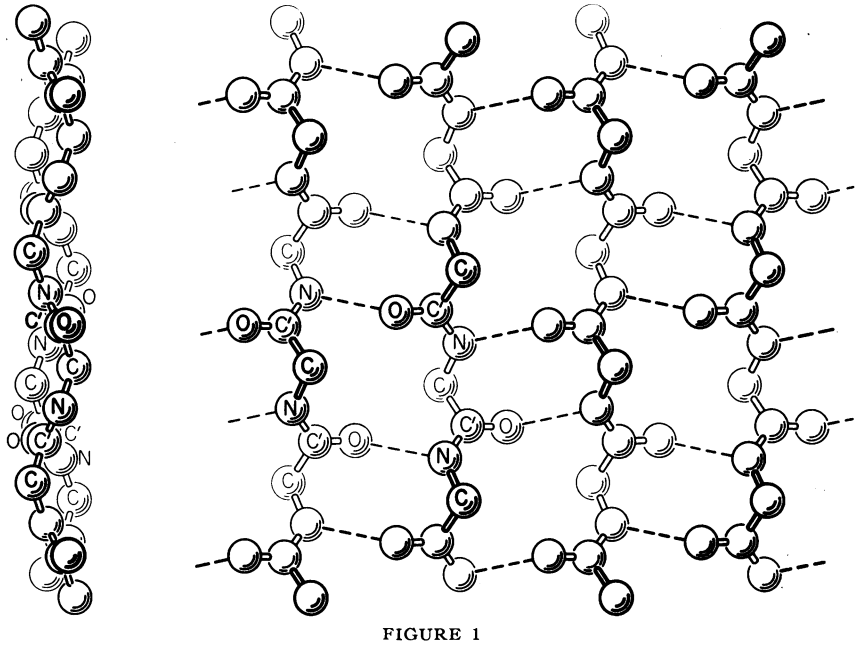

FIGURE 1

The antiparallel-chain rippled sheet of hydrogen-bonded polypeptide chains.

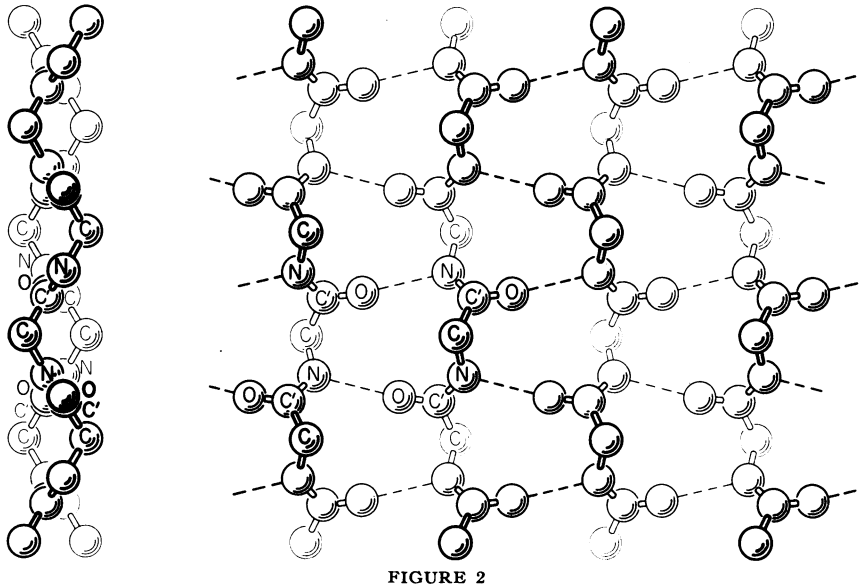

FIGURE 2

The parallel-chain rippled sheet of hydrogen-bonded polypeptide chains.

The antiparallel-chain rippled sheet and the parallel-chain rippled sheet are satisfactory structures, in that they involve linear hydrogen bonds, the interatomic distances and bond angles have the accepted values, and the amide groups are planar. The orientations of the bonds around the α carbon atoms are such that there is room for a side chain, projecting out nearly perpendicularly to the sheet, if alternate chains are constructed of D amino-acid residues and L amino-acid residues. These structures are accordingly satisfactory ones for equimolal mixtures of D polypeptides and L polypeptides.

Moreover, mixtures of D polypeptides and L polypeptides in which the enantiomeric polypeptide chains are present in unequal numbers can assume sheet structures which represent a mixture of a pleated-sheet configuration and a rippled-sheet configuration. Irregular sequences of polypeptide chains with positive and negative orientations can also lead to reasonably satisfactory hydrogen-bonded layer structures. The value of the identity distance in the fiber-axis direction would be intermediate between the value

TABLE 2

ATOMIC COORDINATES FOR THE PARALLEL-CHAIN RIPPLED SHEET

$a_0 = 9.60$ A, $b_0 = 6.50$ A, $c_0 = 1.00$ A (assumed). Four atoms in x, y, z; $\bar{x}$, $1/2 + y$, $\bar{z}$; $1/2 + x, y, \bar{z}$; $1/2 - x, 1/2 + y, z$

	x	y	z
C	−0.006	0.000	0.98
C′	0.059	0.185	0.28
O	0.188	0.205	0.25
N	−0.027	0.314	−0.26

7.00 A corresponding to linear hydrogen bonds for the antiparallel-chain sheets and the value 6.50 A corresponding to linear hydrogen bonds for the parallel-chain sheets. An intermediate value of this identity distance would require that all hydrogen bonds be somewhat bent, and presumably also somewhat strained.

A Note on the Pleated Sheets.—In the earlier discussion of the pleated-sheet configurations of the polypeptide chains[1] the assumption was made that certain orientations around the bonds between the α carbon atom and adjacent atoms in the amide group are favored over other orientations. The assumed favored orientations around these single bonds led to the predicted value 6.68 A for the identity distance in the fiber-axis direction (the direction of the polypeptide chains). Although the existence of a potential function causing certain orientations around these bonds to be favored is likely from *a priori* considerations, the magnitude of the effect is uncertain, and it may well be that very little strain (less than 0.1 kcal. mole^{-1} per residue) is involved in rotating the chain from favored to less favored configurations.

We have now found through the construction of large-scale models that other values of the identity distance in the direction of the polypeptide chains are indicated for the two pleated sheets, corresponding to slightly different orientations about the single bonds to the α carbon atom. The new configurations, described by the coordinates in tables 3 and 4, involve linear hydrogen bonds—that is, the angle N—H $\cdots$ O is equal to 180°. The fiber-axis identity distance for the antiparallel-chain pleated sheet is 7.00 A, and that for the parallel-chain pleated sheet is 6.50 A; these values are the same as for the corresponding rippled sheets.

The two pleated sheets provide satisfactory structures for proteins and for polypeptides composed exclusively of L amino-acid residues (or D amino-acid residues). We think that it is likely that silk fibroin, for which the

TABLE 3

ATOMIC COORDINATES FOR THE ANTIPARALLEL-CHAIN PLEATED SHEET

$a_0 = 9.50$ A, $b_0 = 7.00$ A, $c_0 = 1.00$ A (assumed). Four atoms in x, y, z; $\bar{x}, 1/2 + y, \bar{z}$; $1/2 - x, \bar{y}, z$; $1/2 + x, 1/2 - y, \bar{z}$

	x	y	z
C	0.034	−0.005	−0.70
N	−0.030	0.173	−0.20
C′	0.051	0.320	0.21
O	0.180	0.326	0.22
βC	0.024	−0.005	−2.24

TABLE 4

ATOMIC COORDINATES FOR THE PARALLEL-CHAIN PLEATED SHEET

$a_0 = 4.85$ A, $b_0 = 6.50$ A, $c_0 = 1.00$ A (assumed). Two atoms in x, y, z; $\bar{x}, 1/2 + y, \bar{z}$

	x	y	z
C	0.012	0.000	−0.98
N	−0.066	0.186	−0.26
C′	0.118	0.315	0.28
O	0.371	0.295	0.25
βC	−0.093	0.014	−2.45

observed fiber-axis identity distance is 7.0 A, has the antiparallel-chain pleated-sheet structure, and that the β-keratin proteins, for which the observed fiber-axis identity distance is about 6.6 A, have the parallel-chain pleated-sheet structure, or a structure in which a considerable number of adjacent polypeptide chains have parallel orientations.

The atomic coordinates given in tables 3 and 4 differ only slightly from those previously reported.[1]

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[1] Pauling, L., and Corey, R. B., these PROCEEDINGS, **37**, 729 (1951).