ELASTIC MODULI OF HELICAL POLYPEPTIDE CHAIN STRUCTURES

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ABSTRACT The elastic moduli of the α-helix, polyglycine II, and the parallel-chain and antiparallel-chain pleated sheet structures have been calculated. A Urey-Bradley type of potential was used, extended by the inclusion of hydrogen bond stretching terms where appropriate. In the one instance where a valid comparison with experimental data can be made, *viz*, α-keratin, the calculations indicate that the matrix component, rather than being amorphous, probably contains an ordered structure of higher modulus than the α-helix.

INTRODUCTION

Several calculations of the elastic moduli of synthetic high polymers have been given in the past (1–5). These have all been done using a simple valence force field, that is, taking only bond-stretching and angle-bending forces into account. Recently it has been shown (6) how to calculate the modulus of a polymer molecule using a Urey-Bradley internal force field. This method, which includes bond torsions and interactions between non-bonded atoms, has been applied successfully to the calculation of the moduli of some synthetic high polymers (6–8). In the present paper we consider the application of this technique to the calculation of the elastic moduli of helical polypeptide chain structures. The method has been extended by the inclusion of hydrogen bond stretching terms where appropriate. Comparison of the computed moduli with those observed for some fibrous proteins will be discussed in terms of the structural information which is indicated.

THEORY

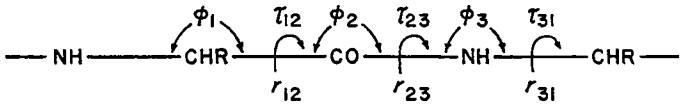
The elastic modulus is defined by

$$E = \left(\frac{F}{A}\right) \Big/ \left(\frac{\Delta d}{d}\right) \tag{1}$$

where F is the applied tensile force, A is the cross-sectional area over which it acts, Δd is the increase in length produced by the force F, and d is the original length. In a helical polypeptide chain structure d could be the axial projection of one amino

acid residue and Δd the increase in axial projection resulting from application of the stress F/A.

Consider a polypeptide chain whose conformation is determined by the set of bond lengths, r, bond angles, ϕ, and torsional angles, τ, shown schematically below. For



helical chain conformations, the α-helix (9), polyglycine II (10), and the parallel-chain and antiparallel-chain pleated sheets (11), the structural parameters of the helix are determined by those of a single peptide residue and by the translation-rotation symmetry of the helix. The external force on such a structure is balanced, at equilibrium, by internal forces which arise from changes in potential energy upon deformation. We may divide these changes into three types: first, alterations in chain parameters such as bond lengths, bond angles, and torsional angles; second, variations in hydrogen bond lengths; third, variations in interactions between side chains along the polypeptide chain. Of the first type it has been shown (7) that the major contribution to the potential in the case of helical structures arises from changes in the torsional angles. This is the case because such deformations require much less energy than distortions of bond lengths and bond angles, and they will therefore contribute most when the structure is displaced from equilibrium. Of the second type, only those hydrogen bonds which are parallel to the axis of elongation (as in the α-helix) will be expected to contribute. To first approximation, hydrogen bonds which are perpendicular to the axis will not be deformed by a longitudinal stress. Of the third type, which comprise primarily van der Waals and electrostatic interactions, little is known in detail with respect to helical protein structures. We feel that these interactions are in general weak in comparison with the potential energy changes considered above, but in certain special cases they may be important. In any event, we have neglected them in the calculations which follow. We may therefore write the total force as

$$F = F_\tau + F_H \tag{2}$$

where

$$F_\tau = \left(\frac{\partial V}{\partial \Delta d}\right)_\tau \tag{3}$$

and

$$F_H = \left(\frac{\partial V}{\partial \Delta d}\right)_H \tag{4}$$

Since we can write the potential energy as

$$V = \tfrac{1}{2} K_{12} r_{31} r_{23} \Delta\tau_{12}^2 + \tfrac{1}{2} K_{23} r_{12} r_{31} \Delta\tau_{23}^2 + \tfrac{1}{2} K_{31} r_{23} r_{12} \Delta\tau_{31}^2 + \tfrac{1}{2} K_H \Delta d^2 \tag{5}$$

where the K's are force constants, we have that

$$\frac{\partial V}{\partial \Delta\tau_{12}} = K_{12}r_{31}r_{23}\,\Delta\tau_{12} = \left(\frac{\partial V}{\partial \Delta d}\right)_{\tau}\cdot\left(\frac{\partial d}{\partial\tau_{12}}\right) = F_{\tau}\cdot T_{12} \tag{6}$$

and similar terms for the other torsional angles, as well as

$$\left(\frac{\partial V}{\partial \Delta d}\right)_{\mathrm{H}} = K_{\mathrm{H}}\,\Delta d = F_{\mathrm{H}} \tag{7}$$

In this formula K_{H} represents the force constant for increase in the O . . . N distance. Since

$$\begin{aligned}\Delta d &= T_{12}\,\Delta\tau_{12} + T_{23}\,\Delta\tau_{23} + T_{31}\,\Delta\tau_{31}\\ &= T_{12}\cdot\frac{F_{\tau}T_{12}}{K_{12}r_{31}r_{23}} + T_{23}\cdot\frac{F_{\tau}T_{23}}{K_{23}r_{12}r_{31}} + T_{31}\cdot\frac{F_{\tau}T_{31}}{K_{31}r_{23}r_{12}}\end{aligned} \tag{8}$$

we have that

$$F_{\tau} = \frac{\Delta d}{\Sigma}\cdot \tag{9}$$

where

$$\Sigma = \frac{T_{12}^2}{K_{12}r_{31}r_{23}} + \frac{T_{23}^2}{K_{23}r_{12}r_{31}} + \frac{T_{31}^2}{K_{31}r_{23}r_{12}} \tag{10}$$

In the case of the α-helix, where the hydrogen bond deformation must be taken into account, we can finally write

$$F = \Delta d\left(\frac{1}{\Sigma} + K_{\mathrm{H}}\right) \tag{11}$$

and

$$E = \frac{d}{A}\cdot\frac{1 + K_{\mathrm{H}}\Sigma}{\Sigma} \tag{12}$$

For the extended chain structures the $K_{\mathrm{H}}\Sigma$ term is not present.

In order to calculate E it is necessary to determine the coefficients T_{ij} which relate the change in length with the changes in torsional angles. If d represents the axial projection along the helix axis per amino acid residue and θ represents the rotational angle per residue about the helix axis, then it has been shown (12) that for a repeating unit consisting of one peptide group

$$\begin{aligned}\cos\left(\frac{\theta}{2}\right) = {} & A_1\cos\left(\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right) - A_2\cos\left(-\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right)\\ & - A_3\cos\left(\frac{\tau_{12}}{2} - \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right) - A_4\cos\left(\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} - \frac{\tau_{31}}{2}\right)\end{aligned} \tag{13}$$

and

$$d\sin\left(\frac{\theta}{2}\right) = A_1B_1\sin\left(\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right) - A_2B_2\sin\left(-\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right)$$

$$- A_3B_3 \sin\left(\frac{\tau_{12}}{2} - \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right) - A_4B_4 \sin\left(\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} - \frac{\tau_{31}}{2}\right) \quad (14)$$

where

$$A_1 = \sin\left(\frac{\phi_1}{2}\right)\sin\left(\frac{\phi_2}{2}\right)\sin\left(\frac{\phi_3}{2}\right)$$

$$A_2 = \cos\left(\frac{\phi_1}{2}\right)\cos\left(\frac{\phi_2}{2}\right)\sin\left(\frac{\phi_3}{2}\right)$$

$$A_3 = \sin\left(\frac{\phi_1}{2}\right)\cos\left(\frac{\phi_2}{2}\right)\cos\left(\frac{\phi_3}{2}\right)$$

$$A_4 = \cos\left(\frac{\phi_1}{2}\right)\sin\left(\frac{\phi_2}{2}\right)\cos\left(\frac{\phi_3}{2}\right)$$

$$B_1 = r_{12} + r_{23} + r_{31}$$

$$B_2 = -r_{12} + r_{23} + r_{31}$$

$$B_3 = r_{12} - r_{23} + r_{31}$$

$$B_4 = r_{12} + r_{23} - r_{31} \quad (15)$$

By differentiating equations (13) and (14) successively with respect to τ_{12}, τ_{23}, and τ_{31} and then substituting the appropriate values of the parameters τ, ϕ, r, and θ, the $\partial d/\partial\tau$ can be computed easily.

CALCULATED ELASTIC MODULI

1. *α-Helix.* The relevant parameters for the the α-helix are (12, 13): $r_{12} = 1.53$ Å, $r_{23} = 1.32$ Å, $r_{31} = 1.47$ Å, $\phi_1 = 110°$, $\phi_2 = 114°$, $\phi_3 = 123°$, $\tau_{12} = -47°$, $\tau_{23} = 180°$, $\tau_{31} = -58°$, $d = 1.50$ Å, and $\theta = 100°$. Using these values we obtain from equation (15) the following values of the coefficients in equations (13) and (14): $A_1 = 0.6038$, $A_2 = 0.2745$, $A_3 = 0.2129$, $A_4 = 0.2296$, $B_1 = 4.32$, $B_2 = 1.26$, $B_3 = 1.68$, and $B_4 = 1.38$.

We will indicate the calculation of $(\partial d/\partial\tau_{12})$; the other coefficients are obtained in a completely analogous fashion. Differentiation of equations (13) and (14) and substitution of the above parameters gives

$$\sin\left(\frac{\theta}{2}\right)\left(\frac{\partial\theta}{\partial\tau_{12}}\right) = A_1 \sin\left(\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right) + A_2 \sin\left(-\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right)$$

$$- A_3 \sin\left(\frac{\tau_{12}}{2} - \frac{\tau_{23}}{2} + \frac{\tau_{31}}{2}\right) - A_4 \sin\left(\frac{\tau_{12}}{2} + \frac{\tau_{23}}{2} - \frac{\tau_{31}}{2}\right)$$

$$= 0.5419 \quad (16)$$

and

$$\sin\left(\frac{\theta}{2}\right)\left(\frac{\partial d}{\partial\tau_{12}}\right) + \frac{d}{2}\cos\left(\frac{\theta}{2}\right)\left(\frac{\partial\theta}{\partial\tau_{12}}\right)$$

$$= \frac{A_1B_1}{2}\cos\left(\frac{\tau_{12}}{2}+\frac{\tau_{23}}{2}+\frac{\tau_{31}}{2}\right)+\frac{A_2B_2}{2}\cos\left(-\frac{\tau_{12}}{2}+\frac{\tau_{23}}{2}+\frac{\tau_{31}}{2}\right)$$

$$-\frac{A_3B_3}{2}\cos\left(\frac{\tau_{12}}{2}-\frac{\tau_{23}}{2}+\frac{\tau_{31}}{2}\right)-\frac{A_4B_4}{2}\cos\left(\frac{\tau_{12}}{2}+\frac{\tau_{23}}{2}-\frac{\tau_{31}}{2}\right)$$

$$= 1.2052 \tag{17}$$

From equation (16) we find that $(\partial\theta/\partial\tau_{12}) = 0.7074$. Substitution of this value into equation (17) gives $(\partial d/\partial\tau_{12} = T_{12} = 1.1279$. In a similar fashion we find that $T_{23} = 1.3785$ and $T_{31} = 1.1184$.

To complete the calculation we require knowledge of the force constants. By analogy with a comparable value found to be satisfactory for torsions about single bonds in long chain molecules (14), we can choose $K_{12} = K_{31} = 0.05$ millidynes/angstrom. The force constant K_{23} for the peptide bond should be higher, since the planarity of this group in polypeptides (9) is indicative of a partial double bond character. A value of $K_{23} = 0.18$ md/Å is suggested by estimates of the strain energy for twisting about the peptide bond (9, 11), and by normal coordinate calculations on *N*-methyl formamide (15) and *N*-methyl acetamide (16). The hydrogen bond force constant, K_H, is somewhat more difficult to specify accurately since few exact calculations involving this force constant have been done on small molecules. Analysis of the hydrogen bond stretching mode in water (17, 18) suggests a value of about 0.22 md/Å for $K_{O\ldots O}$. In formic acid dimers this force constant is about 0.13 md/Å (19, 20). We have chosen a value of 0.2 md/Å for K_H as being a reasonable one. It may perhaps be somewhat on the high side. Using these values of the force constants, the sum in equation (10) is determined to be 30.31, and the elastic modulus is given by

$$E = \frac{7.06 \times 10^{13}}{20.2A} \text{ dynes/cm}^2 \tag{18}$$

where A is the cross-sectional area in units of square angstroms.

The value of E now depends on the specification of A. For an isolated α-helix of radius 5Å (21), the value of E is found to be 4.46×10^{10} dynes/cm^2. From data on the cross-sectional areas of the unit cells of synthetic polypeptides (21) we can compute the expected elastic moduli. Two of these are given in Table I. No experimental observations are available for these materials which would serve to check the calculations. Experimental data are, however, available for α-keratin, so it is desirable to consider the modulus to be expected for this fibrous protein. Several studies (22–26) have led to the suggestion that the α-helices in α-keratin are in the form of coiled coils, probably aggregated to give 3-strand ropes (25, 26). No detailed structure has been given for the α-helix in such a coiled coil, but the deformation from an ordinary α-helix is small (24) and we are probably justified in using equation (18) as a first approximation in the calculation of the modulus. In any

case, such a calculation is likely to give an upper limit to the modulus because it is to be expected that the initial straightening of a coiled coil will require less energy than the extension of the α-helix. The modulus of a single 3-strand rope, based on a radius of 10.3 Å for the over-all unit (25), is found to be 3.15×10^{10} dynes/cm^2. In α-keratin such ropes do not occur in long-range hexagonal close-packing, but rather are localized in microfibrils which are embedded in a sulfur-rich matrix (27, 28). In hair and wool these microfibrils appear both from electron microscopy (27) and from x-ray diffraction (29) to be about 70 Å in diameter and to have a center-to-center separation of about 100 Å (although slightly smaller values are also quoted (28)). Prevailing opinion (27–31) considers that the matrix is largely amorphous. The contribution of this component to the modulus is therefore difficult to estimate since its structure is not known. If it is neglected, and we assume that the microfibril accommodates fifteen 3-strand ropes (26), then the modulus for the over-all structure is 1.82×10^{10} dynes /cm^2. The modulus of an individual microfibril is 4.10×10^{10} dynes /cm^2. We will consider later the conclusions concerning the nature of the matrix which are suggested by comparison of observed and calculated values of the modulus of α-keratin.

2. *Polyglycine II.* The structure of polyglycine II has been shown to be based on a threefold helix (10). The relevant parameters are (12): $\tau_{12} = -144°$, $\tau_{23} = 180°$, $\tau_{31} = 76°$, $d = 3.1$ Å, and $\theta = 120°$ (the values of the r's and the ϕ's are the same as for the α-helix). Using the method described in the previous section, we compute $T_{12} = -0.0887$, $T_{23} = 0.2308$, and $T_{31} = 0.5992$. Recalling that the hydrogen bonds make no contribution to the modulus since they are essentially perpendicular to the fiber axis, and using the unit cell dimensions which have been given (10), we calculate E to be 41.0×10^{10} dynes/cm^2.

TABLE I
CALCULATED ELASTIC MODULI OF POLYPEPTIDE CHAIN STRUCTURES

Structure	Calculated modulus
α-Helical structures	
Single α-helix	4.46×10^{10} dynes/cm^2
Poly-L-alanine	5.52
Poly-γ-methyl-L-glutamate	2.83
Three-strand rope	3.15
α-Keratin microfibril	4.10
α-Keratin microfibril lattice	1.82
Polyglycine II	41.0
Extended chain structures	
Antiparallel-chain pleated sheet	
Bombyx mori silk	198
Tussah silk	172
Parallel-chain pleated sheet	36.6

3. *Antiparallel-Chain Pleated Sheet.* The relevant parameters for this polypeptide chain structure are (12): $\tau_{12} = 145°$, $\tau_{23} = 180°$, $\tau_{31} = -142°$, $d = 3.5$ Å, and $\theta = 180°$. Calculations similar to the above give $T_{12} = 0.1585$, $T_{23} = -0.0395$, $T_{31} = -0.2361$, and

$$E = \frac{4.29 \times 10^{13}}{A} \text{ dynes/cm}^2 \tag{19}$$

Two fibrous protein structures are thought to be based on the antiparallel-chain pleated sheet, Bombyx mori silk (32) and Tussah silk (33). Using the cross-sectional areas computed from the unit cell dimensions, the elastic moduli are found to be 198×10^{10} dynes/cm^2 and 172×10^{10} dynes/cm^2, respectively.

4. *Parallel-Chain Pleated Sheet.* The necessary parameters of the parallel-chain pleated sheet are (12): $\tau_{12} = 112°$, $\tau_{23} = 180°$, $\tau_{31} = -118°$, $d = 3.25$ Å, and $\theta = 180°$. The calculated values of the coefficients are $T_{12} = 0.3780$, $T_{23} = 0.0434$, and $T_{31} = -0.2232$. The modulus is given by

$$E = \frac{1.65 \times 10^{13}}{A} \text{ dynes/cm}^2 \tag{20}$$

It is thought that the structure of β-keratin (obtained, for example, by the mechanical elongation of α-keratin) is based on the parallel-chain pleated sheet (11). Recent infrared studies (34, 35) give support to this proposal. If we accept the chain packing indicated by x-ray diffraction studies (36), then the modulus determined from equation (20) is 36.6×10^{10} dynes/cm^2.

DISCUSSION

In order to compare the experimental measurements of elastic moduli with the calculated values it is necessary that the modulus of the crystalline regions be obtained. It has been shown (37) how this may be accomplished for a polymer fiber in which crystalline regions alternate with non-crystalline regions along the fiber axis. What is required is to measure by x-ray diffraction the relative elongation of the crystalline regions, $\Delta d/d$, for a given macroscopic relative elongation, $\Delta l/l$. If the observed modulus is E_0, then the modulus of the crystalline component is given by

$$E = E_0 \cdot \frac{\Delta l/l}{\Delta d/d} \tag{21}$$

If in addition there is a component with a modulus E' in parallel with the above system, then E_0 in equation (21) must be replaced by $(E_0 - E')$.

Among the fibrous proteins an adequate determination of E is available at present only for α-keratin. In this case it has been observed, for wool, that in the range of up to 2 per cent extension, which corresponds to the Hooke's law region of the load-extension curve (38), the 5.1 Å and 1.5 Å meridian spacings characteristic of the

x-ray diffraction pattern of the α-helix can both be increased reversibly by about 2% (39). This indicates that the factor $(\Delta l/l) / (\Delta d/d)$ in equation (21) is essentially unity, and therefore if there is no parallel component the measured modulus E_0 should correspond to that of the α-helical structure. Several values of E_0 have been given. In one set of measurements (38) E_0 is given as 5.6×10^{10} dynes/cm^2 for dry keratin at 20°C, with a value of 10.9×10^{10} dynes/cm^2 when extrapolated to absolute zero. Another measurement (40) gives a value of 4.3×10^{10} dynes/cm^2 for dry horsehair in extension and 9.5×10^{10} dynes/cm^2 in compression.

Comparison of these values with the calculated moduli (see Table I) reveals several interesting points. Even if we accept the smaller values of the observed modulus, it is clear that the microfibril lattice alone cannot account for the results, since, as can be seen from Table I, it predicts a modulus 2 to 3 times lower than the observed value. It should be noted that of course no high modulus component in series with the α-helical component can give a structure of higher modulus. The only way to obtain this is to put another structure in parallel with the α-helix. This function is most likely served by the matrix component of α-keratin. We would conclude therefore that the matrix component should not be thought of as an independent non-rigid structure. It is probably intimately linked with the microfibrillar component, and elongates with it when a tensile stress is applied to the fiber. Nor can the matrix consist of an amorphous elastic protein, such for example as resilin (41). The latter, with a modulus of about 0.7×10^{10} dynes/cm^2, would only raise the calculated modulus of the overall lattice to about 2.2×10^{10} dynes/cm^2. In fact, if the observed modulus of α-keratin can be as high as about 10×10^{10} dynes/cm^2, as seems likely from the presently available data, this implies that the matrix component must have an intrinsic modulus higher than that of the α-helix, since hexagonally close-packed microfibrils of modulus 4.1×10^{10} dynes/cm^2 give a modulus for the over-all structure of only 3.71×10^{10} dynes/cm^2. It should be noted that the situation here is in marked contrast to that usually found for synthetic polymers (3–8), where the observed elastic moduli are *lower* than the calculated moduli. Since it is not likely that an unordered network, even if cross-linked by, say, cystine bonds, would have a modulus as high as that of the α-helix, we believe that these results point to the presence in the matrix of some fairly ordered high-modulus structure. It is not possible to specify this structure from the present analysis, but it is interesting to note that independent arguments (42) suggest the presence of an extended chain type of structure in the matrix of α-keratin. The present results would be entirely consistent with this suggestion.

As noted before, reliable elastic moduli are not available for other fibrous proteins. Thus, the measured modulus of silk is of the order of 14×10^{10} dynes/cm^2, (43) but information is not available which would permit from this result a determination of the modulus of the crystalline regions. Experimental results of this kind are clearly desirable. They would not only serve to check the above calcula-

tions, but might also permit more accurate determination of the hydrogen bond stretching force constant.

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REFERENCES

1. MEYER, K. H., and LOTMAR, W., *Helv. Chim. Acta,* 1936, **19,** 68.
2. LYONS, W. J., *Appl. Physics,* 1958, **29,** 1429.
3. TRELOAR, L. R. G., *Polymer,* 1960, **1,** 95.
4. TRELOAR, L. R. G., *Polymer,* 1960, **1,** 279.
5. TRELOAR, L. R. G., *Polymer,* 1960, **1,** 290.
6. SHIMANOUCHI, T., ASAHINA, M., and ENOMOTO, S., *J. Polymer Sc.,* in press.
7. ASAHINA, M., and ENOMOTO, S., *J. Polymer Sc.,* in press.
8. ENOMOTO, S., and ASAHINA, M., *J. Polymer Sc.,* in press.
9. PAULING, L., COREY, R. B., and BRANSON, H. R., *Proc. Nat. Acad. Sc.,* 1951, **37,** 205.
10. CRICK, F. H. C., and RICH, A., *Nature,* 1955, **176,** 780.
11. PAULING, L., and COREY, R. B., *Proc. Nat. Acad. Sc.,* 1951, **37,** 251; 1953, **39,** 253.
12. MIYAZAWA, T., *J. Polymer Sc.,* 1961, **55,** 215.
13. PAULING, L., and COREY, R. B., *Proc. Roy. Soc. London, Series B,* 1953, **141,** 10.
14. MIYAZAWA, T., *J. Chem. Physics,* 1961, **35,** 693.
15. DEGRAAF, D. E., Abstracts, Biophysical Society, February, 1959.
16. MIYAZAWA, T., *Bull. Chem. Soc. Japan,* 1961, **34,** 691.
17. LIPPINCOTT, E. R., and SCHROEDER, R., *J. Chem. Physics,* 1955, **23,** 1099.
18. PIMENTEL, G. C., and MCCLELLAN, A. L., The Hydrogen Bond, San Francisco, W. H. Freeman and Co., 1960, 132ff.
19. SLUTSKY, L. and BAUER, S. H., *J. Am. Chem. Soc.,* 1954, **76,** 270.
20. MIYAZAWA, T., and PITZER, K. S., *J. Am. Chem. Soc.,* 1959, **81,** 74.
21. BAMFORD, C. H., ELLIOTT, A. and HANBY, W. E., Synthetic Polypeptides, New York, Academic Press Inc., 1956.
22. CRICK, F. H. C., *Nature,* 1952, **170,** 882.
23. PAULING, L., and COREY, R. B., *Nature,* 1953, **171,** 59.
24. CRICK, F. H. C., *Acta Cryst.,* 1953, **6,** 689.
25. LANG, A. R., *Acta Cryst.,* 1956, **9,** 436.
26. FRASER, R. D. B., and MACRAE, T. P., *J. Mol. Biol.,* 1961, **3,** 640.
27. ROGERS, G. E., *Ann. New York Acad. Sc.,* 1959, **83,** 738.
28. ROGERS, G. E., *J. Ultrastruct. Research,* 1959, **2,** 309.
29. FRASER, R. D. B., and MACRAE, T. P., *Biochim. et Biophysica Acta,* 1958, **29,** 229.
30. BIRBECK, M. S. C., and MERCER, E. H., *J. Biophysic. and Biochem. Cytol.,* 1957, **3,** 203.
31. FRASER, R. D. B., MACRAE, T. P., and ROGERS, G. E., *Nature,* 1959, **183,** 592.
32. MARSH, R. E., COREY, R. B., and PAULING, L., *Biochim. et Biophysica Acta,* 1955, **16,** 1.
33. MARSH, R. E., COREY, R. B., and PAULING, L., *Acta Cryst.,* 1955, **8,** 710.
34. MIYAZAWA, T., and BLOUT, E. R., *J. Am. Chem. Soc.,* 1961, **83,** 712.
35. KRIMM, S., *J. Mol. Biol.,* in press.
36. ASTBURY, W. T., and Woods, H. J., *Phil. Trs. Roy. Soc. London Series A,* 1933, **232,** 333.
37. DULMAGE, W. J., and CONTOIS, L. E., *J. Polymer Sc.,* 1958, **28,** 275.
38. MEREDITH, R., The Mechanical Properties of Textile Fibers, New York, Interscience Publishers, Inc., 1956.
39. ASTBURY, W. T., and HAGGITH, J. W., *Biochim. et Biophysica Acta,* 1953, **10,** 483.
40. DENBY, E. F., *Textile Research J.,* 1961, **31,** 69.

41. WEIS-FOGH, T., *J. Mol. Biol.*, 1961, **3**, 520.
42. KRIMM, S., *Nature*, 1961, **192**, 810.
43. HARRIS, M., Handbook of Textile Fibers, Washington, D. C., Harris Research Laboratories, Inc., 1954.