Proc. Nat. Acad. Sci. USA
Vol. 69, No. 10, pp. 2788–2792, October 1972

Intermolecular Interaction Effects in the Amide I Vibrations of β Polypeptides

(vibrational spectra/perturbation treatment/transition dipole coupling/conformational analysis)

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Communicated by David M. Dennison, July 21, 1972

ABSTRACT **Previous perturbation treatments of the Amide I vibrations of β polypeptides are inconsistent with a detailed normal coordinate analysis of crystalline polyglycine I. This analysis indicates that the D_{10} interaction constant is essentially zero, rather than the large value (about 20 cm^{-1}) required by the earlier application of the perturbation theory. It is suggested that the previously neglected D_{11} term should be included in the perturbation expression, and it is shown that the physical origin of such a term can be accounted for by transition dipole coupling. This mechanism is shown to give a reasonable explanation of splittings of the C=O stretching vibrations in hydrogen-bonded carboxylic acid dimers. Its application to β polypeptides provides a satisfactory interpretation of splittings in the Amide I modes.**

The use of vibrational spectra to identify different polypeptide-chain conformations dates from the work of Elliott and Ambrose (1), who observed that the frequency of the infrared-active Amide I vibration of α polypeptides was about 20 cm^{-1} higher than that of β polypeptides. Further studies on synthetic polypeptides (2) established this observation as a firm empirical rule.

Early attempts (3, 4) to account for this difference were not fruitful. A significant advance in understanding the theoretical basis for the above observation was achieved by Miyazawa (5), who developed a perturbation treatment for the interaction of amide-group vibrations in various polypeptide-chain structures. He also noted that, in addition to the strong Amide I band at about 1630 cm^{-1} in the β polypeptides, a weak band at about 1690 cm^{-1} could be assigned to the antiparallel-chain pleated-sheet structure. This treatment has formed the basis for interpretation of the vibrational spectra of polypeptides and proteins (6, 7).

In the Miyazawa theory, the frequency of an Amide I mode (which is the only one that we will be concerned with in this paper) is given by

$$\nu(\delta,\delta') = \nu_0 + \sum_{s,t} D_{st} \cos(s\delta) \cos(t\delta') \qquad [1]$$

In this equation: ν_0 is the unperturbed peptide group frequency (that is, unperturbed by vibrational interactions with other peptide groups), D_{st} is the constant determining the interactions between peptide groups separated by t chains and s groups along the t^{th} neighboring chain, and δ and δ' are the phase angles between the vibrations in the respective peptide groups. It has been assumed (5) that only the D_{s0} and D_{0t} terms are important, and for the antiparallel-chain pleated-sheet structure only D_{10} and D_{01} [which have been referred to as D_1 and D_1', respectively (5)] have been used (6, 7). Thus, in this case Eq. [1] has been used in the form

$$\nu(\delta,\delta') = \nu_0 + D_{10} \cos\delta + D_{01} \cos\delta' \qquad [2]$$

In applications of Eq. [2] to the antiparallel-chain pleated-sheet structure, $\nu(0,\pi)$ and $\nu(\pi,0)$ were taken from the spectrum of polyglycine I, and the frequency of nylon 66 was assumed to be determined by ν_0 and D_{01} only (6). With the observed values for nylon 66 (2), namely 1640 cm^{-1}, and for polyglycine I (8), namely, $\nu(0,\pi)$ = 1685 and $\nu(\pi,0)$ = 1636 cm^{-1}, the constants in Eq. [2] are found to be ν_0 = 1660.5, D_{10} = 4.0, and D_{01} = −20.5 cm^{-1}. Using these constants, one can predict that $\nu(0,0)$ = 1644 cm^{-1}. [For polyglycine I values of $\nu(0,\pi)$ = 1685 and $\nu(\pi,0)$ = 1632 cm^{-1}, which had been used earlier (6, 7), these constants are determined to be ν_0 = 1658.5, D_{10} = 8.0, and D_{01} = −18.5 cm^{-1}, and $\nu(0,0)$ = 1648 cm^{-1}.]

The above procedure has been criticized (9, 10), primarily on the grounds of the assumed constancy of ν_0. This criticism was based on studies of a series of polyamides (10) that indicated that ν_0 varied by 6 cm^{-1} between nylon 10 and nylon 2. Such variations can give rise to errors in the interaction constants D_{10} and D_{01} that are of the same order as the constants themselves. This objection to taking ν_0 from nylon 66 as applicable to polypeptides has a general validity, since it should not be expected that the unperturbed frequency associated with the peptide group is completely independent of the local chemical environment of this group. This is amply established by detailed normal coordinate analyses of *N*-methyl acetamides and nylons (11), as well as of related molecules (12). It is also confirmed by an extension of these calculations to polyglycines I (13) and II (14). The authors have also stated (10, 15) that their results show that the intrachain interaction between peptide groups (D_{10}) is more important than the interchain interaction (D_{01}).

The need to use the spectrum of nylon 66 in determining the constants in Eq. [2] has been obviated by the recent availability of Raman spectra on the same polypeptides for which infrared spectra are obtainable. Thus, the Raman spectrum of polyglycine I (16) exhibits a single strong band at 1674 cm^{-1}, which can be confidently assigned to the totally symmetric $\nu(0,0)$ mode of the antiparallel-chain pleated-sheet structure. This Raman band plus the $\nu(0,\pi)$ and $\nu(\pi,0)$ infrared bands allow the determination from Eq. [2] of the constants for polyglycine I, which are found to be ν_0 = 1660.5, D_{10} = 19, and D_{01} = −5 cm^{-1}. The interaction constants are quite different from those predicted on the basis of a

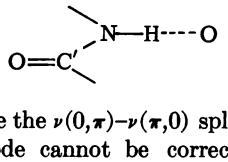
common ν_0 between nylon 66 and polypeptides, and conform to the expectation (10, 15) that the intrachain interaction predominates over the interchain interaction. Similar results are found with the Raman spectra of other polypeptides (17, 18).

Despite the plausibility of the above analysis, it contains grave difficulties. For example, if the splitting of α-nylon 6 frequencies (10) (which occur at 1642 and 1667 cm^{-1}) is indeed due to interaction effects similar to those in polypeptides (15), then, since $D_{10} = 0$ in this case, we find $D_{01} = -12.5$ cm^{-1}. The origin of the large difference from D_{01} for polyglycine is not obvious. Secondly, if the intrachain interaction constant D_{10} is as large as 19 cm^{-1}, then we might anticipate a significant variation of splittings with chain length for short oligomers. The evidence on oligomers of glycine (19) and alanine (20) does not indicate this to be the case, the splittings being essentially independent of chain length. But the most serious problem is that a normal vibration analysis of the exact structure of crystalline polyglycine I (13), based on a detailed general valence force field containing 78 force constants [and refined from a comparably complete force field for the peptide group in nylons and *N*-methylacetamides (11)], fails to reproduce a large value for D_{10}: from such an anaiysis D_{10} is typically of the order of a few cm^{-1}. We feel, therefore, that the representation of Amide I frequencies given by Eq. [2] is incorrect.

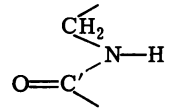
In the following, we show that in the framework of a perturbation treatment for the Amide I vibration of polypeptides, as represented by Eq. [1], the D_{10} term can be taken as effectively zero. On the other hand, it is necessary to include a term that has heretofore been neglected in the perturbation treatment, namely the D_{11} term. It can be shown that there is a reasonable physical basis for including such a term, and that it leads to a more consistent understanding of the spectra of polypeptides and proteins.

Modified perturbation treatment of amide I vibrations

As noted above, a detailed normal vibration analysis of the antiparallel-chain pleated-sheet structure of polyglycine I (13) shows that a value of D_{10} as large as 19 cm^{-1} (as is required by the combined infrared and Raman data) cannot be achieved by a reasonable general valence force field. Such a force field yields the following calculated frequencies (13): $\nu(0,0) = 1663$, $\nu(0,\pi) = 1666$, $\nu(\pi,0) = 1659$, and $\nu(\pi,\pi) = 1662$ cm^{-1}. Even if an intermolecular interaction constant f(C′=O str, H···O str) is introduced (21) for the structure



in order to reproduce the $\nu(0,\pi)$–$\nu(\pi,0)$ splitting (13), we find that the $\nu(0,0)$ mode cannot be correctly predicted: for f(C′=O, H···O) = 0.45 mdyn/Å, we calculate $\nu(0,0) = 1645$, $\nu(0,\pi) = 1686$, $\nu(\pi,0) = 1641$, and $\nu(\pi,\pi) = 1682$ cm^{-1}. This result does not depend sensitively on variations in force constants. Thus, the eigenvector elements of the four Amide I modes show that the manner of coupling of the C′=O stretching coordinate with other coordinates that are geometrically close to it is almost the same for the four modes. Therefore, interaction terms between these coordinates do not change the splittings significantly. This is also apparent from an examination of the Jacobian matrix elements for D_{10}, namely, $\partial D_{10}/\partial f_i$, which are all small. Introduction of other intramolecular interaction constants does not improve the situation. Thus, in the structure below, introduction of a



force constant f(C′=O str, N—C str) has very little effect on D_{10}. In the above structure the eigenvector elements show that the coupling of the C′=O stretching coordinate with the deformation coordinates of the CH_2 group differs considerably for the four Amide I modes, and therefore introduction of such interaction force constants would give rise to a large D_{10}. However, no physical bases for large interaction terms of this nature are apparent. (The coupling of the C′=O stretching coordinate with the deformation coordinates of the neighboring CH_2 group is almost the same for the four Amide I modes, so no differential splittings are possible through these interactions.)

Nor does the value of D_{10} depend significantly on the details of the structure. Calculations were done (13) for peptide repeat distances of 3.35 Å, 3.45 Å, 3.55 Å, and 3.62 Å, as well as for crystal structures in which neighboring chains were displaced by +0.5 Å and −0.5 Å with respect to the standard structure. None of these variations gave rise to a large positive value of D_{10}. It is clear that other mechanisms must be invoked in order to account for the splittings of the Amide I modes.

If the D_{10} term is indeed close to zero, as is indicated by the normal vibration calculations on polyglycine I (13), then it becomes necessary to consider the inclusion of additional terms in Eq. [1] beyond those represented by Eq. [2]. The one that initially deserves examination is the D_{11} term, since this interaction, which is shown in Fig. 1, represents the next nearest Amide group perturbation. It is clear that such a term will be large in this new formalism, that is for $\nu(\delta,\delta')$ given by

$$\nu(\delta,\delta') = \nu_0 + D_{10}\cos\delta + D_{01}\cos\delta' + D_{11}\cos\delta\cos\delta' \quad [3]$$

For example, using the polyglycine I frequencies and setting $D_{10} = 5$ cm^{-1} (which is the largest value given by any of our trial calculations), we find that $\nu_0 = 1674.5$, $D_{01} = -19.5$, and $D_{11} = 14$ cm^{-1}. This value of D_{11} means that the frequency of the symmetric C′=O stretching vibration involving the indicated groups in Fig. 1 is 28 cm^{-1} higher than the antisymmetric stretching vibration. Such a direct coupling between the C′=O groups involved in the D_{11} interaction would not be part of an ordinary valence force field (since the groups are not directly connected, either by chemical

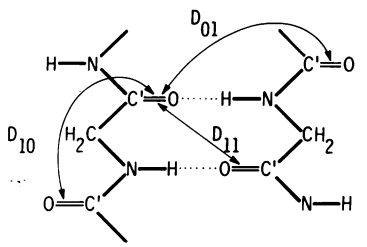


FIG. 1. Interaction constants in the perturbation treatment of the Amide I modes of the antiparallel-chain pleated-sheet structure of polypeptides.

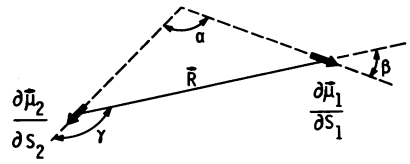
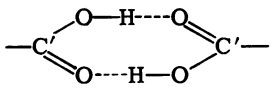


FIG. 2. Coupling of transition dipoles.

bonds or by hydrogen bonds), and we must, therefore, inquire into the possible physical basis for this interaction.

As we have observed (13), coupling between the transition dipoles associated with the C′=O stretching vibrations provides a physical basis for understanding the origin of the D_{11} interaction. This is not only because it can account reasonably for the splittings of the Amide I modes, but it also explains similar splittings in dimers of carboxylic acids. Since this case is relevant to that of the polypeptides, we first turn to a consideration of it.

It has been observed (22–24) that the C′=O stretching vibrations in hydrogen-bonded dimers of carboxylic acids that have the structure below are split. For example, the splitting in acetic acid (22) is 56 cm^{-1} and in adipic acid (24) it is 49 cm^{-1}. In all cases, the symmetric stretching vibration is at a *lower* frequency than the antisymmetric stretching vibration, just opposite to the case of the polypeptides (i.e., $D_{11} < 0$). Explanations of this splitting have been related to tautomerism (22), and to some form of direct interaction between the two C′=O stretching vibrations (24), although no specific model was given. We wish to show that transition dipole coupling provides a plausible explanation for at least some part of this effect.



The potential energy between two transition dipoles oriented with respect to each other as shown in Fig. 2 is given by

$$V = \frac{1}{\epsilon} \cdot \frac{|\partial\mu_1/\partial S_1| \cdot |\partial\mu_2/\partial S_2|}{|R|^3} \cdot (\cos\alpha \cdot 3\cos\beta\cos\gamma) \cdot S_1 \cdot S_2 \qquad [4]$$

where ϵ is the dielectric constant (taken here to be 1), $\partial\mu_i/\partial S_i$ is a transition dipole moment, and S_i is a stretching coordinate (V is in ergs for quantities in [4] in cgs units). The interaction force constant between the two transition dipoles is, therefore,

$$F_{12} = |\partial\mu_1/\partial S_1| \cdot |\partial\mu_2/\partial S_2| \cdot \frac{\cos\alpha - 3\cos\beta\cos\gamma}{|R|^3} \left(\frac{\text{dyne}}{\text{cm}}\right) \qquad [5]$$

When R is given in Å and $\partial\mu_i/\partial S_i$ is given in Debye/Å = 10^{-10} esu, Eq. [5] becomes

$$F_{12} = 0.1 \cdot |\partial\mu_1/\partial S_1| \cdot |\partial\mu_2/\partial S_2| \cdot \frac{\cos\alpha - 3\cos\beta\cos\gamma}{|R|^3} \left(\frac{\text{mdyn}}{\text{Å}}\right) \qquad [6]$$

If both transition dipoles are associated with C′=O stretching, this becomes

$$F = 0.1 \left(\frac{\partial\mu}{\partial r_{C'=O}}\right)^2 \cdot X \qquad [7]$$

where

$$X = \frac{\cos\alpha - 3\cos\beta\cos\gamma}{R^3} \qquad [8]$$

is the geometrical factor. The interaction constant is given by

$$D = \left(\frac{\partial\nu}{\partial F}\right) \cdot F \qquad [9]$$

and the total splitting between components is

$$\Delta\nu = 2D \qquad [10]$$

A normal vibration calculation of the system below, using the force constants of Suzuki and Shimanouchi (24), with and without a F(C′=O str, C′=O str) term, shows that

$$\Delta\nu \cong 130 \cdot F(\text{C′=O str, C′=O str}) \qquad [11]$$

For a $\Delta\nu \cong -50$ cm^{-1} (as noted earlier) we find that F(C′=O str, C′=O str) $\cong -0.38$ mdyn/Å, and D $\cong -25$ cm^{-1} with $(\partial\nu/\partial F) \cong 65$. If we use eq. [7] and [8] to calculate F from a transition dipole coupling mechanism, then we find that for a C′···C′ distance of 3.94 Å and a transition dipole centered at the mid-point of the C′=O bond, the interaction force constant is given by $F = -0.0020(\partial\mu/\partial r_{C'=O})^2$. The transition dipole moment is, of course, unknown, but values of the order of 10 may be reasonable (25). This would give $F = -0.20$ mdyn/Å (whereas $(\partial\mu/\partial r_{C'=O}) = 13$ would give $F = -0.34$ mdyn/Å). Although we are not prepared to claim unique agreement, it is clear that the transition dipole coupling mechanism gives the correct sign of F and a value that is of the appropriate order of magnitude.

Similar results are obtained for the polypeptides. Thus, for the polyglycine I structure (see Fig. 1), if we assume that the transition dipole moment is located at the center of the C′=O bond, that this moment is tilted 20° from the C′=O bond direction toward the N → C direction (26), and that $(\partial\mu/\partial r_{C'=O}) = 8$ Debye/Å, then we calculate $F_{10} = -0.03$, $F_{01} = -0.12$, and $F_{11} = 0.26$ mdyn/Å. Since for the polypeptides we also find $(\partial\nu/\partial F) \cong 65$, this corresponds to contributions to the interaction constants D_{10}, D_{01}, and D_{11} of -2, -8, and $+17$ cm^{-1}, respectively. If the above values of the F's are incorporated in a normal vibration analysis, and the values of f(C′=O) and f(C′=O, H···O) are adjusted slightly (to 9.71 and 0.35 mdyn/Å, respectively) in order to give an optimum fit (13), then the following values are calculated for the Amide I modes: $\nu(0,0) = 1674$, $\nu(0,\pi) = 1688$, $\nu(\pi,0) = 1639$, and $\nu(\pi,\pi) = 1721$ cm^{-1}. The first three frequencies are in excellent agreement with experiment. Putting the above values into Eq. [3] gives: $\nu_0 = 1680.5$, $D_{10} = 0.5$, $D_{01} = -24$, and $D_{11} = 17$ cm^{-1}. We see, therefore, that transition dipole interactions provide a reasonable physical mechanism for predicting a large positive D_{11} term, as well as a vanishing D_{10} term.

Based on the complete intermolecular contributions of the force field to the above four quantities, we find that

$$\begin{aligned} \nu_0 &\cong 1673.5 + 20 \cdot f(C'{=}O, H\cdots O) \\ D_{10} &\cong 2.5 + 65F_{10} \\ D_{01} &\cong -46 \cdot f(C'{=}O, H\cdots O) + 65F_{01} \\ D_{11} &\cong 65F_{11} \end{aligned} \qquad [12]$$

It will be seen from these relations that ν_0 depends on the force constant $f(C'{=}O, H\cdots O)$. We also find that the coefficient of $f(C'{=}O, H\cdots O)$ in this equation (but not in that for D_{01}) is sensitive to the crystal structure. For example, if the right-hand chain in Fig. 1 is lowered by 0.5 Å with respect to the left-hand chain, the coefficient is 10 rather than 20; if it is raised by 0.5 Å, the coefficient is predicted to be 38. It is also clear that the above treatment gives rise to a significantly different value of ν_0 than that predicted from Eq. [2]. Finally, it should be noted that, since $F_{10} < 0$, the combined effects of the general valence force field and the transition dipole coupling are to reduce D_{10} to essentially zero.

We have also done a normal vibration analysis of a parallel-chain pleated-sheet structure of polyglycine that incorporates the same transition dipole coupling as used above. The peptide repeat distance along the chain axis was taken as 3.35 Å and the interchain spacing as 4.7 Å. For this structure, we find that $F_{10} = -0.03$, $F_{01} = -0.16$, and $F_{11} = 0.0$ cm^{-1}. Using the above values of $f(C'{=}O)$ and $f(C'{=}O, H\cdots O)$, we calculate the following Amide I modes: $\nu(0,0) = 1652$, $\nu(0,\pi) = 1703$, $\nu(\pi,0) = 1650$, and $\nu(\pi,\pi) = 1701$ cm^{-1}, corresponding to $\nu_0 = 1676.5$, $D_{10} = 1$, $D_{01} = -25.5$, and $D_{11} = 0.0$ cm^{-1} [only the $\nu(0,0)$ and $\nu(\pi,0)$ modes are optically active]. From this calculation we also obtain

$$\begin{aligned} \nu_0 &\cong 1671 + 16 \cdot f(C'{=}O, H\cdots O) \\ D_{10} &\cong 3 + 65F_{10} \\ D_{01} &\cong -43 \cdot f(C'{=}O, H\cdots O) + 65F_{01} \\ D_{11} &= 0 \end{aligned} \qquad [13]$$

These relations are seen to be similar to those for the antiparallel-chain structure.

The above analysis thus leads to the conclusion that a perturbation treatment of the Amide I vibrations of β polypeptides and proteins should be based on the following relationship:

$$\nu(\delta,\delta') = \nu_0 + D_{01}\cos\delta' + D_{11}\cos\delta\cos\delta' \qquad [14]$$

Therefore, it is apparent that intermolecular interactions play the predominant role in the Amide I splittings, contrary to previous beliefs (10, 15).

DISCUSSION

In order to account for the splittings of Amide I modes in β polypeptides, we have seen that it is necessary to use the more general perturbation expression of Eq. [3]. A detailed normal vibration analysis, which includes transition dipole coupling, now shows (*a*) that we can set $D_{10} = 0$ to a good approximation, and (*b*) that the D_{11} term is sensitive to structure, since it depends on the relative orientations of the dipoles. Thus, the transition dipole orientations for the antiparallel-chain pleated sheet are such as to give a relatively large positive F_{11}, while for the parallel-chain pleated sheet the orientations are such that F_{11} is essentially zero.

The above considerations emphasize the fact that the equations differ for the two types of β structures. For the antiparallel-chain pleated-sheet structure of polyglycine I, the following relations hold:

$$\begin{aligned} \nu(0,0)_A &= 1674 = \nu_0 + D_{01} + D_{11} \\ \nu_{\|}(0,\pi)_A &= 1685 = \nu_0 - D_{01} - D_{11} \\ \nu_{\perp}(\pi,0)_A &= 1636 = \nu_0 + D_{01} - D_{11} \\ \nu_{\perp}(\pi,\pi)_A &= [1723] = \nu_0 - D_{01} + D_{11} \end{aligned} \qquad [15]$$

The first three relations give rise to $\nu_0 = 1679.5$, $D_{01} = -24.5$, and $D_{11} = 19$ cm^{-1}, from which the value of $\nu_{\perp}(\pi,\pi)_A$ can be predicted. For a parallel-chain pleated-sheet structure, we expect for the optically active modes

$$\begin{aligned} \nu_{\|}(0,0)_P &= \nu_0 + D_{01} \\ \nu_{\perp}(\pi,0)_P &= \nu_0 + D_{01} \end{aligned} \qquad [16]$$

Thus, the two frequencies should be almost identical. If ν_0 and D_{01} have values close to those for the antiparallel-chain structure (which is indicated by the normal vibration analyses), then we expect $\nu_{\|}(0,0)_P \cong \nu_{\perp}(\pi,0)_P \cong 1655$ cm^{-1}.

It is to be noted that our analysis gives some results that are significantly different from those of previous studies (5–7, 9, 10, 15, 21). For example, we predict the weak $\nu_{\perp}(\pi,\pi)_A$ mode to occur near 1720 cm^{-1} rather than near 1670 cm^{-1}, as previously suggested. Also we find $\nu_0 \cong 1680$ cm^{-1}, whereas earlier analyses gave $\nu_0 \cong 1660$ cm^{-1}. In this connection, our results indicate that it would be unrealistic to associate ν_0 with the frequencies of "unordered" portions of polypeptides and proteins: since intrachain interactions are very small, and since interchain interactions always exist (peptide groups being generally hydrogen bonded to each other), the unperturbed frequency should not be observed. Thus, the observation (27, 28) of a band at 1656 cm^{-1} in silk (in addition to bands at 1632 and 1701 cm^{-1} due to the antiparallel-chain structure) is not to be attributed to a "random" component, but is more likely to be due to a parallel-chain structure. Such "defects" in the hydrogen-bonding pattern may well occur in predominantly ordered regions of antiparallel chains, since neighboring sheets contain chains with parallel orientation. This points up another difference between our and previous analyses: we assign the strong $\nu_{\perp}(\pi,0)_P$ mode to a band near 1655 cm^{-1} rather than near 1630 cm^{-1}, as has been done. As a consequence, it is no longer clear that, as claimed (10, 29), the structure of β-keratin can be based so uniquely on the antiparallel-chain pleated-sheet structure. Finally, it should be noted that, whereas in earlier treatments the strong infrared bands of both β structures were at nearly identical frequencies, but were distinguishable from that of the α-helix at ~1652 cm^{-1}, a consequence of our analysis is that the frequencies of the parallel-chain sheet overlap those of the α-helix and are distinct from those of the antiparallel-chain sheet. While a normal vibration analysis that incorporates transition dipole coupling has yet to be done for the α-helix, it is understandable at this stage why the α-helix frequency is close to that of the parallel-chain sheet: both structures have similar parallel arrangements of peptide groups.

Our modification of the perturbation treatment of Amide I modes has important implications for the analysis of peptide conformations in proteins by vibrational spectroscopy, as will be treated in greater detail in a later publication.

This research was supported by Grants GB-15682 and GP-10922 from the National Science Foundation. A postdoctoral fellowship from the Macromolecular Research Center at the University of Michigan to Y. A. is gratefully acknowledged.

1. Elliott, A. & Ambrose, E. J. (1950) *Nature* **165**, 921–922.
2. Bamford, C. H., Elliott, A. & Hanby, W. E. (1956) *Synthetic Polypeptides* (Academic Press, New York).
3. Krimm, S. (1955) *J. Chem. Phys.* **23**, 1371–1372.
4. Cannon, C. G. (1956) *J. Chem. Phys.* **24**, 491–492.
5. Miyazawa, T. (1960) *J. Chem. Phys.* **32**, 1647–1652.
6. Miyazawa, T. & Blout, E. R. (1961) *J. Amer. Chem. Soc.* **83**, 712–719.
7. Krimm, S. (1962) *J. Mol. Biol.* **4**, 528–540.
8. Suzuki, S., Iwashita, Y., Shimanouchi, T. & Tsuboi, M. (1966) *Biopolymers* **4**, 337–350.
9. Elliott, A. & Bradbury, E. M. (1962) *J. Mol. Biol.* **5**, 574–576.
10. Bradbury, E. M. & Elliott, A. (1963) *Polymer* **4**, 47–59.
11. Jakeš, J. & Krimm, S. (1971) *Spectrochim. Acta Part A* **27**, 19–34.
12. Jakeš, J. & Krimm, S. (1971) *Spectrochim. Acta Part A* **27**, 35–63.
13. Abe, Y. & Krimm, S., *Biopolymers*, in press.
14. Abe, Y. & Krimm, S., *Biopolymers*, in press.
15. Elliott, A., Bradbury, E. M., Downie, A. R. & Hanby, W. E. (1962) in *Polyamino Acid, Polypeptides, and Proteins*, ed. Stahman, M.A. (University of Wisconsin Press, Madison), pp. 255–269.
16. Small, E. W., Fanconi, B. & Peticolas, W. L. (1970) *J. Chem. Phys.* **52**, 4369–4379.
17. Wallach, D. F. H., Graham, J. M. & Oserhoff, A. R. (1970) *FEBS Lett.* **7**, 330–334.
18. Koenig, J. L. & Sutton, P. J. (1971) *Biopolymers* **10**, 89–106.
19. Smith, M., Walton, A. G. & Koenig, J. L. (1969) *Biopolymers* **8**, 29–43.
20. Sutton, P. & Koenig, J. L. (1970) *Biopolymers* **9**, 615–634.
21. Miyazawa, T. (1967) in *Poly-α-Amino Acids*, ed. Fasman, G. D. (Marcel Dekker, Inc., New York).
22. Kishida, S. & Nakamoto, K. (1964) *J. Chem. Phys.* **41**, 1558–1563.
23. Suzuki, M. & Shimanouchi, T. (1968) *J. Mol. Spectrosc.* **28**, 394–410.
24. Suzuki, M. & Shimanouchi, T. (1969) *J. Mol. Spectrosc.* **29**, 415–425.
25. Segal, G. A. & Klein, M. L. (1967) *J. Chem. Phys.* **47**, 4236–4240.
26. Sandeman, I. (1955) *Proc. Roy. Soc. Ser. A* **232**, 105–113.
27. Suzuki, E. (1967) *Spectrochim. Acta Part A*, **23**, 2303–2308.
28. Fraser, R. D. B., MacRae, T. P., Stewart, F. H. C. & Suzuki, E. (1965) *J. Mol. Biol.* **11**, 706–712.
29. Fraser, R. D. B., MacRae, T. P., Parry, D. A. D. & Suzuki, E. (1969) *Polymer* **10**, 810–826.