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Steric Structure of L-Proline Oligopeptides. III. Calculated Absorption Spectra of L-Proline Oligopetides

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The electronic excited states in L-proline oligopeptides were derived from molecular-exciton theory. The dipole-dipole approximation was used in the calculation of transition energies. The calculated absorption spectra related to the conformation of L-proline oligopeptides were compared with observed ones. A satisfactory agreement between the calculated and observed results was obtained.

In previous papers[1,2] the ultraviolet absorption spectra of *N*-tertiary amyloxy carbonyl-L-prolyl oligopeptides synthesized in a stepwise manner were reported. The red shifts of the absorption maxima were related to the conformation. By means of ORD[1] and CD[1] spectra, it was established that the appearance of the helical conformation commences at the tetramer, while the pentamer, hexamer and octamer have the poly-L-proline II-like conformation. Band splitting of the absorption spectra of the dimer was observed. The very broad absorption spectrum of the trimer might be due to three absorption maxima with almost the same intensities. It was also found that the absorption maxima on the longest-wavelength side of the tetramer, pentamer, hexamer and octamer are identical with the shoulder around 200 mμ found in the dimer, but with an increased intensity. Consequently, the absorption band with perpendicular polarization is expected to appear as a shoulder at about 185 mμ (Table 1[1,2] and Fig. 1[1,2]).

Table 1. Wavelengths of UV absorption maxima of L-proline oligopeptides

	In water (mμ)	In acetonitrile (mμ)
Monomer	—	183
Dimer	—	185 198
Trimer	198	185—198*
Tetramer	201	198—200
Pentamer	203	200—201
Hexamer	203	201
Octamer	203	—
Poly-L-Proline II	203	—
Poly-L-Proline I	208	—

* The trimer has a very broad absorption spectrum in the region 185—198 mμ.

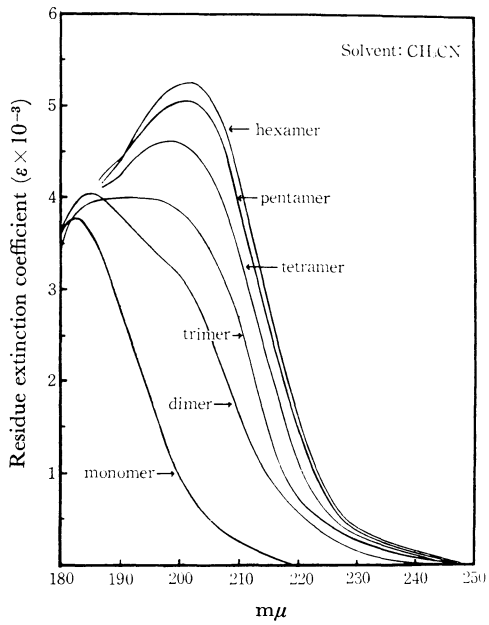

Fig. 1. The ultraviolet absorption spectra of L-proline oligopeptides (see Refs. 1, 2).

According to these results, the absorption maximum around 203 mμ of poly-L-proline II has been identified as the shoulder with an increased intensity around 200 mμ found in the spectra of the dimer.[1,2]

Some investigators[3] have tried to observed band

*1 Presented at Symposium on Molecular Structures of the Chemical Society of Japan (October, 1967).

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1) H. Okabayashi, T. Isemura and S. Sakakibara, *Biopolymers*, **6**, 323 (1968).

2) H. Okabayashi and T. Isemura, Abstract for Symposium on Molecular Structures (October, 1967), p. 17.

3) W. B. Gratzer, W. Rhodes and G. D. Fasman, *Biopolymers*, **1**, 319 (1963).

splitting of the absorption spectra of poly-L-proline I and II without success.

In this study the calculations of the absorption spectra of L-proline oligopeptides were attempted by Tinoco's method[4-6] and compared with the observed absorption spectra. Good agreement between the calculated and the observed absorption spectra was found.

Optical properties of the α-helix and the 3_{10}-helix of polypeptides have been calculated by Tinoco and Woody[5] and the chainlength dependence of the absorbance was thoroughly discussed. Tinoco and Woody[5] have also found that there was satisfactory agreement between experimental absorption spectra and the calculated results. However, the calculated absorption spectra of oligopeptides have not yet been compared with experimental results.

Theory

Following the general expressions used by Tinoco *et al.*;[5,6] the ground state wave function of a oligomer is represented by

$$\Psi = \phi_1\phi_2\phi_3 \cdots \phi_N \tag{1}$$

and a singly excited state, localized at molecule i, by

$$\Psi'_i = \phi_1\phi_2\phi_3 \cdots \phi'_i \cdots \phi_N \tag{2}$$

where ϕ_i and $\phi_{i'}$ are the residue ground- and singly excited state wave functions, respectively, and N is the number of residue.

The perturbed, singly excited states of the oligopeptides are written as follows:

$$\Psi'_K = \sum_{i=1}^{N} C_{iK}\Psi'_i \qquad K = 1, 2, 3, \cdots N \tag{3}$$

The Hamiltonian of the oligomer is represented by

$$\boldsymbol{H} = \sum_{i}^{N} H_i + \sum_{i<j}^{N} \boldsymbol{V}_{ij} \tag{4}$$

where $\boldsymbol{V}_{ij}$ is the interaction operator between residue i and j.

The coefficients, C_{ik}, and the eigenvalues, E_k, are obtained by solving the secular equation

$$D_N = |\, V_{ij} - \delta_{ij}E \,| = 0 \tag{5}$$

The secular determinant D_H has the form,

$$D_N = \begin{vmatrix} V_{11}-E & V_{12} & V_{13} & \cdots & V_{1N} \\ V_{21} & V_{22}-E & V_{23} & \cdots & V_{2N} \\ V_{31} & V_{32} & V_{33}-E & \cdots & V_{3N} \\ V_{41} & V_{42} & V_{43} & \cdots & V_{4N} \\ \vdots & \vdots & \vdots & & \vdots \\ V_{N1} & V_{N2} & V_{N3} & \cdots & V_{NN}-E \end{vmatrix} \tag{6}$$

where $\underset{(i\neq j)}{V_{ij}} = \langle\phi_i|\boldsymbol{H}|\phi'_i\rangle$ and $V_{ij} = \langle\phi_i|\boldsymbol{H}|\phi'_i\rangle$

Calculation and Results

Figure 2 shows the coorodinate system[7] for the calculation of the absorption spectra of L-proline oligopeptides. The three fold axis of the oligopeptides is identical with the z axis perpendicular to the plane of the paper. Each residue of the oligomers is located around the three fold axis on the assumption that the tetramer, pentamer, hexamer and octamer exist entirely in a poly-L-proline II-like structure and the dimer and trimer assume the same conformation as found in the helical structure of poly-L-proline II.

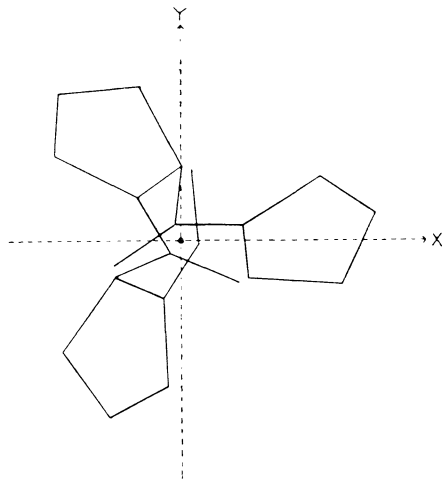

Fig. 2. Schematic representation of the poly-L-proline II-like structures of L-proline oligopeptides. Cowan and McGavin's coordinate system[7] is used.

It is assumed that the magnitude and direction of the π-π^* transition moment μ in the peptide groups of L-proline oligomers are the same as those of π-π^* transition moment (μ=3.05D) for the absorption at 190 mμ in myristamide.[8] This assumption seems to be the most reasonable approximation at the present time. In the calculations the

4) I. Tinoco, Jr., *J. Chem. Phys.*, **33**, 1332 (1960).
5) I. Tinoco, Jr., and R. W. Woody, *ibid.*, **38**, 1317 (1963).
6) D. F. Bradley, I. Tinoco, Jr., and R. W. Woody, *Biopolymers*, **1**, 239 (1963).
7) P. Cowan and S. McGavin, *Nature*, **176**, 501 (1955).
8) D. L. Peterson and W. T. Simpson, *J. Amer. Chem. Soc.*, **79**, 2375 (1957).

dipole-dipole approximation for the interaction potential was used:

$$V_{ij} = \frac{(\mu_i \cdot \mu_j)}{R_{ij}^3} - 3\frac{(\mu_i \cdot \boldsymbol{R}_{ij})(\mu_i \cdot \boldsymbol{R}_{ij})}{R_{ij}^5} \qquad (7)$$

where μ_i is the π-π^* transition dipole moment of the ith peptide group with $\mu_i = \mu$ and R_{ij} the distance between the $\pi = \pi^*$ transition dipole moment of the ith peptide group and that of the jth peptide group, and moreover the nearest neighbor interaction and all neighboring interaction were considered.

The calculated values of the absorption maxima and the dipole strengths of L-proline oligopeptides are shown in Fig. 3.

The absorption band maxima with parallel polarization at the longest-wavelength side apparently are displaced to red with increasing chain length. Moreover, the calculated absorption maxima also are convergent as are the observed ones. Naturally the perpendicular band maxima should converge. In these calculations the maxima of the calculated perpendicular bands tend to converge at about 186 mμ.

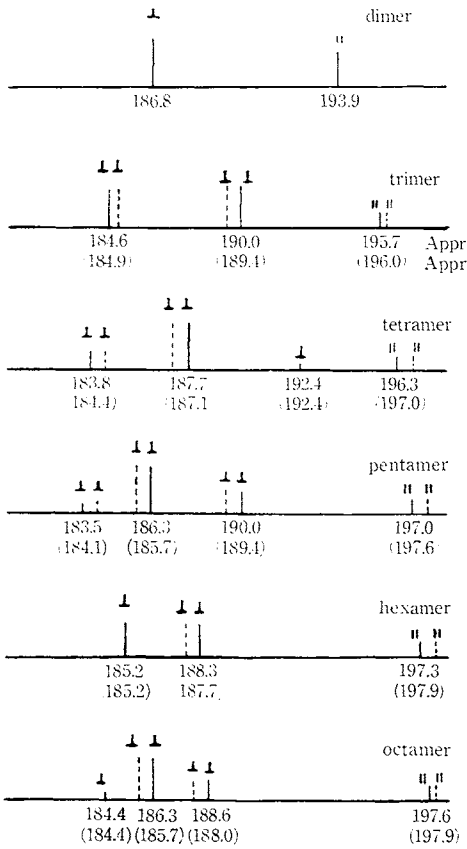

Fig. 3. Calculated absorption spectra and calculated dipole strengths of L-proline oligopeptides. The values and the direction of μ are chosen to coincide with those of the 1900 A transition in myristamide.

* The calculations were carried out by the nearest neighbor approximation.

** All neighboring interactions were considered in this approximation.

The solid lines are obtained by approximation 1 and the broken lines by approximation 2.

The change in the intensity of the observed absorption spectra and the calculated values of the dipole strengths of L-proline oligopeptides should be compared.

In the dimer the calculated dipole strengths are in good accord with the observed intensity of the peak and the shoulder of the dimer.

The present calculations indicate that the absorption spectra of the trimer should have two perpendicular bands and a parallel band. This result should be regarded as the theoretical prediction for the broadening which was observed in the asborption spectra of the trimer.

There is a noteworthy change in the intensity of the band maxima at about 200 mμ of the tetramer, pentamer and hexamer. In particualr, the change of the intensity between the trimer and other three oligomers (tetramer, pentamer and hexamer) is notable and seems to be associated with the helical structure of the oligomers.

However, the present calculations for the change of dipole strengths with increasing chain length do not agree with that of the observed intensities. That is, the calculated dipole strengths of four oligomers (trimer, tetramer, pentamer and hexamer) are almost the same, and moreover there is no increase in the dipole strengths between the trimer and the tetramer.

Disagreement between the calculated dipole

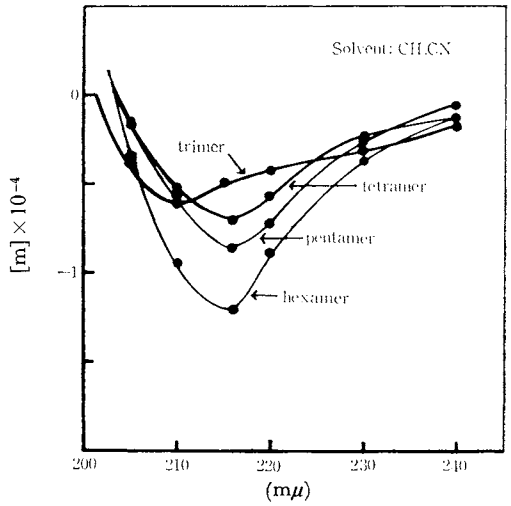

Fig. 4. The ORD curves of L-proline oligopeptides in acetonitrile.
Trimer, concn. = 1.590 mg/20 ml of CH_3CN
Tetramer, concn. = 1.65 mg/20 ml of CH_3CN
Pentamer, concn. = 1.61 mg/20 ml of CH_3CN
Hexamer, concn. = 1.64 mg/20 ml of CH_3CN
Quartz cells of 1 mm path length were employed.

strengths and the observed intensity of these oligomers may depend upon the calculation in which zero-order exciton wave functions were used. For a satisfactory explanation of the intensity the use of first-order exciton[9] wave functions or other developed methods[10,11] may be required.

The ORD curves of the trimer, tetramer, pentamer and hexamer were obtained. The measurements were carried out on a Jasco Model ORD/UV-5 Spectropolarimeter.

The position of the minimum and cross-over point in the ORD curve of the trimer is at about 210 mμ and 201 mμ.

The ORD curves of the three oligomer (tetramer, pentamer and hexamer exhibit the same minimum and cross-over points[2] as does poly-L-proline II (see Fig. 4).

These facts clearly indicate that the helical structure of the poly-L-proline II type as measured by absorption spectra appears at the tetrapeptide and that the pentamer and hexamer have complete poly-L-proline II-like structures. These observations were in aqueous solutions and in methyl alcohol as well as in acetonitrile. Although the absorption spectra of the dimer and trimer differ from that found for the poly-L-proline II-like structure, the calculated and observed results agree sufficiently well to ascertain that these oligomers likewise assume a poly-L-proline II-like conformation.

9) I. Tinoco, Jr., *J. Amer. Chem. Soc.*, **82**, 4785 (1960).
10) W. Rhodes, *ibid.*, **83**, 3609 (1961).
11) S. Yomosa and H. Nakano, *J. Phys. Soc. Jap.*, **21**, 1369 (1966).

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