INFRARED SPECTRA OF CYCLIC HEXAPEPTIDES CONSTRUCTED OF L(D)-ALANINE AND GLYCINE RESIDUES

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Among the various physicochemical methods used for studying the conformational states of peptide–protein systems, an important place is occupied by infrared (IR) spectroscopy. In the near IR region (4000-2000 cm^{-1}) there are the frequencies connected with the stretching vibrations of the NH groups and sensitive to their participation in hydrogen bonds [1]. In the middle region (2000-800 cm^{-1}) are located the amide I bands (1630-1700 cm^{-1}, C=O stretching vibrations), the amide II bands (1510-1560 cm^{-1}, mainly N–H planar deformation vibrations), and the amide III bands (1215-1305 cm^{-1}, mainly the C–N stretching vibration interacting with the N–H planar deformation vibration). The amide vibrations in the middle IR region have long been used very successfully for characterizing ordered (α and β forms) random-coil structures in a polypeptide chain [2-8]. After the appearance of Miyazawa's book [9], the method of long-wave IR spectroscopy (800-60 cm^{-1}) corresponding to the amide IV (620-780 cm^{-1}, C=O planar deformation vibration), the amide V (640-800 cm^{-1}, N–H nonplanar deformation vibration), the amide VI (530-610 cm^{-1}, C=O nonplanar deformation vibration), and the amide VII (~200 cm^{-1}, C–N torsional vibration) vibrations also came into use for conformational investigations of polypeptides and proteins. In spite of the fact that the amide IV-VII vibrations relate to definite bonds in the amide group, they are not characteristic and are, therefore, extremely sensitive to a change in the conformation of the molecule [2, 10]. The IR spectra of complex peptide systems constructed of sections differing conformationally are usually analyzed on the basis of their comparison with the thoroughly studied spectra of the regular (antiparallel, parallel, and cross β forms, α-helix) or the random-coil forms of polypeptides. However, the results of a study of lysozyme [11], myoglobin, and other proteins [12, 13] in the solid state shows the difficulties of such an approach, since the IR spectrum is greatly complicated because of the presence of the side chains of the various amino-acid segments and also the presence of peptide segments with conformations considerably differing from those mentioned above.

Consequently, at the present time it has become necessary to investigate the IR spectra of various model peptide systems with known conformational parameters which would permit the finding of spectral assignments characteristic for other types of peptide structures (apart from the α and β forms and the random coil). As an example of such a type of investigations we may give the recently published papers by Koyama, Shimanouchi and their colleagues relating to a detailed study of the IR spectra of a series of methylamides of acetylamino acids [14, 15]. The present paper gives the results of a study of the IR spectra of the simplest cyclic hexapeptides (1)-(15) constructed from L(D)-alanine and glycine residues; the conformational states of these compounds (see below) have been considered previously [16-23].

cyclo-*Gly-Gly-Gly-Gly-Gly-Gly*	(1)
hexa-N-deuterocyclohexaglycyl	(1a)
cyclo-*Gly-Gly-Gly-Gly-Gly-D-Ala*	(2)
cyclo-*Gly-Gly-Glv-Gly-D-Ala-D-Ala*	(3)
cyclo-*Gly-Gly-Gly-L-Ala-Gly-L-Ala*	(4)
cyclo-*Gly-Gly-L-Ala-Gly-Gly-L-Ala*	(5)
cyclo-*Gly-Gly-Gly-D-Ala-D-Ala-D-Ala*	(6)

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cyclo-*Gly-Gly-L-Ala-L-Ala-Gly-L-Ala* (7)
cyclo-*Gly-D-Ala-Gly-D-Ala-Gly-D-Ala* (8)
cyclo-*Gly-L-Ala-Gly-L-Ala-L-Ala-L-Ala* (9)
cyclo-*Gly-D-Ala-D-Ala-D-Ala-D-Ala-D-Ala* (10)
cyclo-*D-Ala-L-Ala-L-Ala-L-Ala-L-Ala-L-Ala* (11)
cyclo-*D-Ala-D-Ala-L-Ala-L-Ala-L-Ala-L-Ala* (12)
cyclo-*D-Ala-D-Ala-D-Ala-L-Ala-L-Ala-L-Ala* (13)
cyclo-*D-Ala-D-Ala-L-Ala-D-Ala-D-Ala-L-Ala* (14)
cyclo-*D-Ala-D-Ala-L-Ala-D-Ala-L-Ala-L-Ala* (15)

The IR spectra of compounds (1) (3), and (8), taken immediately after the preparation of tablets with KBr or of mulls with paraffin oil (Fig. 1) are distinguished by the presence of a large number of bands both in the amide A region and in the amide I-VII regions. A comparison of the spectra of compounds (1)-(15) does not permit any definite relationship whatever between their parameters and the primary structures of the cyclopeptides to be found; taken separately, they likewise do not permit a strict interpretation. Apparently, the complex nature of the spectra is due to the presence in the samples investigated of several conformers each of which makes its own contribution to the observed spectrum. The conformational inhomogeneity of the crystalline samples of the cyclopeptides (1)-(15) is connected with the conditions of their isolation: as a rule, in the last stage they were purified by rapid recrystallization or reprecipitation from aqueous or aqueous ethanolic solutions in which a complex conformational equilibrium is established [21, 22].

In addition to this, we have studied the spectra of the cyclopeptides (1)-(15) after they had been kept at 150-160°C for 1 h. The spectra of compounds (1)-(8) taken after the heating of tablets with KBr (or NaCl) differ sharply from the spectra before heating (Fig. 2); on the other hand, the spectra of compounds (9)-(15) have hardly changed. In the majority of cases, heating free cyclopeptides and their subsequent molding with KBr does not lead to a change in their spectra. On molding with CsBr or CsI and heating to 150-160°C, slight changes are observed only for compound (1). The spectra of compound (1), taken directly after heating with KBr and after 2 weeks do not differ from one another, but the sample obtained after the

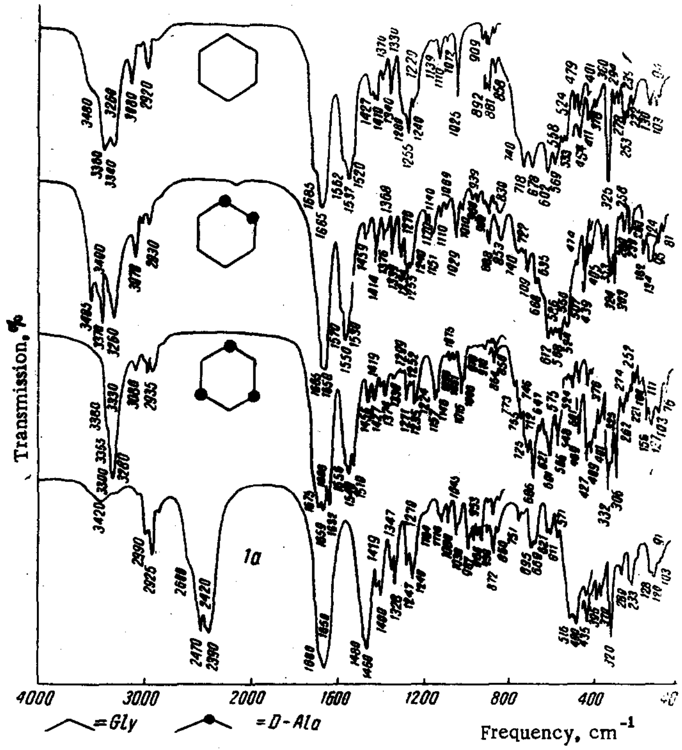


Fig. 1. IR absorption spectra of the cyclohexapeptides (1), (1a), (3) and (8) before heating (tablets with KBr to 400 cm^{-1} and in paraffin oil below 400 cm^{-1}).

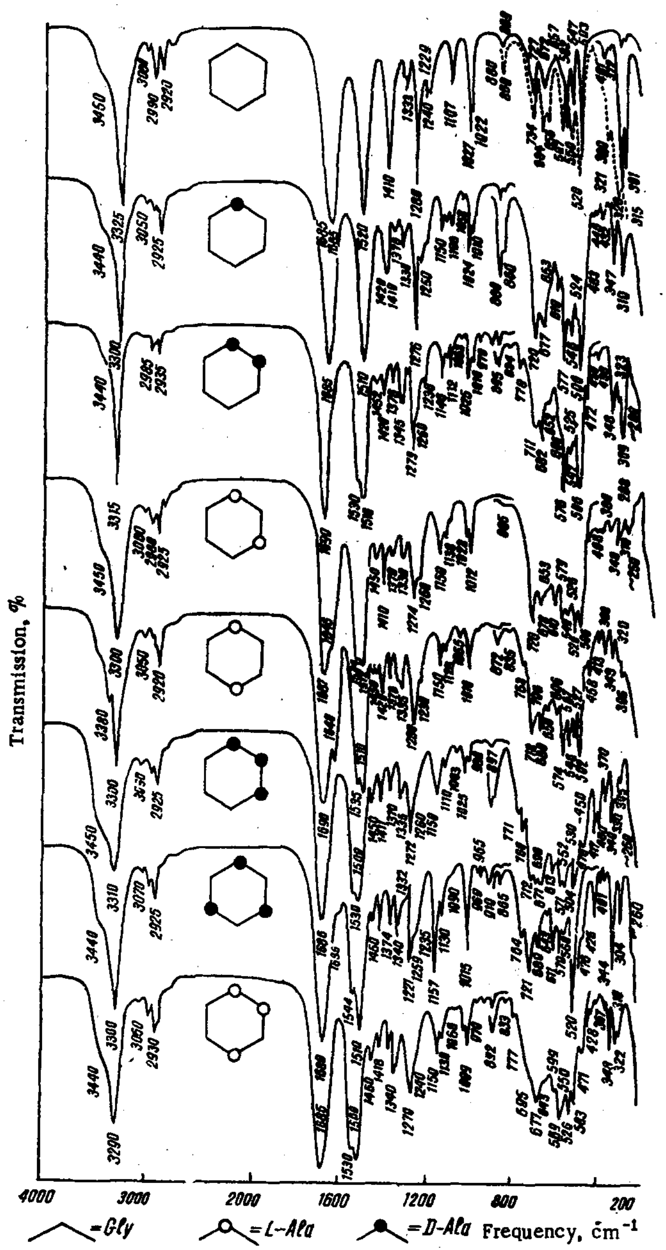


Fig. 2. IR absorption spectra of the cyclohexapeptides (1)-(8) after heating (KBr tablets; the spectrum of form A of Ac-Gly-NHMe is shown dotted).

treatment of the tablet in water, the desalting of the solution on ion-exchange resins, evaporation, and the molding of the residue with KBr gave a spectrum identical with that shown in Fig. 1.

In a consideration of the newly obtained spectra of compounds (1)-(8) (see Fig. 2) it can be seen that they are comparatively simple and monotypical; in the amide A region of each of them there is a band at ~3300 cm^{-1} (NH group participating in the formation of hydrogen bonds) with a characteristic shoulder at ~3440 cm^{-1} (water of hydration or free NH groups), the amide I bands have an unusually high frequency (~1685 cm^{-1}), and in the region most sensitive to changes in conformational states, 800-190 cm^{-1}, the intensity of the bands has increased considerably and the bands or groups of bands common to all the compounds can easily be traced (Table 1).

The facts presented above permit the conclusion that the heating of compounds (1)-(8) with KBr (NaCl) is accompanied by conformational rearrangements as a result of which each initial mixture of conformers, on interacting with the ionic crystals of the salt, undergoes a transition into a preferential conformation that

TABLE 1. Frequencies of the Bands in the IR Spectra of the Cyclohexapeptides (1)-(8) Having the "Pleated Sheet" Structure with Two trans-Annular Hydrogen Bonds of the 4 → 1 Type

Frequency, cm^{-1}	Intensity	Assignment	Conformation
3440–3450	m	Water of hydration of free N – H	
3300	s	Amide A	
1680–1690		Amide I	
1510–1530		Amide II	
1440–1450	m	C – CH_3 def.	
1410–1420		CH_2 scissors	
1330–1340		CH_2 fan	
1270–1280	s	Amide III	
1100–800	m.w	Skeletal stretching vibrations CH_2 wagging	
710–730	s	AmideV	$\Phi_{3,6}=(-130°)-(-90°)$, $\psi_{3,6}=0-50°$ (form A of Ac-Gly-NHMe)
670–680		AmideIV?	The same
640–650	w	AmideIV?	$\Phi_{2,5}=(-70°)-(-50°)$, $\psi_{2,5}=(-40°)-(-10°)$, (α-helix)
600–610	m	AmideV?	The same
570–580			$\Phi_{3,6}=(-130°)-(-90°)$, $\psi_{3,6}=0-50$,(form A of Ac-Gly-NHMe)
545–560		Skeletal deformation vibrations	The same
500–520	v.s		The same
370–380	w		
340–350	m		
310–330			$\Phi_{3,6}=(-130°)-(-90°)$, $\psi_{3,6}=0-50$,(form A of Ac-Gly-NHMe)
300–310			

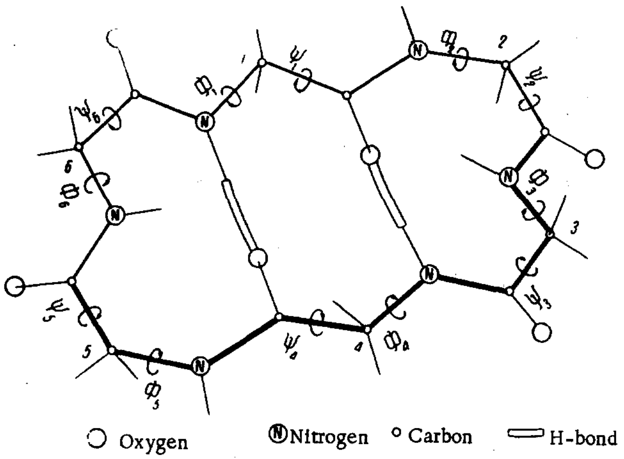


Fig. 3. Model of a molecule of cyclohexaglycyl corresponding to the "pleated sheet" conformation with two intramolecular hydrogen bonds of the 4 → 1 type.

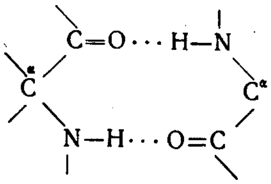
is similar for all the compounds and is the most favorable under the conditions of recording the spectrum. The transition takes place more readily in the case of cyclohexaglycyl (1), and the retention of the form of the spectra of compounds (9)-(15) containing four or more alanine residues is connected with the increase in the energy barriers of the conformational transitions because of the presence of a large number of lateral methyl groups. The role of heating apparently amounts to an acceleration of the process of achieving equilibrium. However, it is not excluded that the observed rearrangement is connected with a change in the nature of the intermolecular interactions in the crystal lattice (for example, as the result of the evaporation of water of crystallization, as has been found for L-propylglycine [24].

The conformational states of compounds (1)-(15) have been investigated in detail in solution by means of a complex of physicochemical methods (UV [20], IR [19, 23], and NMR spectroscopy [19, 21, 22], CD and ORD curves [18, 20], and dipole moments [18, 23]). The spatial structure of the cyclopeptides (1) and (3) in the crystalline state has been established by x-ray structural analysis [16, 17]. It was shown that the cyclohexapeptides constructed of glycine and alanine residues possess rich conformational possibilities. They are capable of realizing diverse structures differing in symmetry, in the presence of intramolecular hydrogen bonds, and in the mutual orientations of the atoms and groups. However, the most common structure which can be found in all rings under very diverse conditions both in solutions and in the crystalline state is the so-called "pleated sheet" structure (Fig. 3) stabilized by two trans-annular hydrogen bonds of the 4 → 1 type first proposed for cyclohexapeptides by Schwyzer [25, 26]. The results of an investigation of the NMR spectra of other cyclohexapeptides containing, in addition to glycine residues, those of leucine [27], tyrosine [27, 28], histidine [27], and proline [29] lead to a similar conclusion. The results of a calculation of the potential energy of cyclohexaglycyl and of cyclohexa-L-alanyl [30] also indicate a preference for a structure of the "pleated sheet" type.

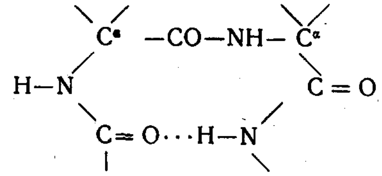
From what has been said it follows that the conformation realized in the cyclopeptides (1)-(8) after heating with KBr must be assigned to the "pleated sheet" type. A comparison of the results of x-ray structural analysis [17], NMR spectra (in particular, the spin–spin coupling constants of the protons in the NH–CH fragments [19, 21, 22]) and theoretical conformational analysis [30] permits the following most probable conformational parameters to be suggested for it (all amide bonds in the trans configuration, $\omega = 0$):*

$$\Phi_{1,4}\ (-170^\circ)-(-110^\circ),\ \Phi_{2,5}\ (-70^\circ)-(-50^\circ);\ \Phi_{3,6}\ (-130^\circ)-(90^\circ)$$
$$\Psi_{1,4}\ (-180^\circ)-(-160^\circ),\ 160-180^\circ;\ \Psi_{2,5}\ (-40^\circ)-(-10^\circ)\ \Psi_{3,6}\ 0-50^\circ$$

For an analysis of the IR spectra of this form it is desirable to compare them with the spectra of other peptide systems constructed of glycine and alanine residues. Since three pairs of amino-acid residues nonequivalent from the conformational point of view located at the "fold of the sheet" (1) and (4) and at its angles (2 and 5; 3 and 6) participate in the "pleated sheet" structure, it is natural to assume that in the 800-200 cm^{-1} region bands corresponding to each of the pairs should appear. In view of the fact that the parameters Φ and Ψ of residues 1 and 4 are close to the parameters of the β structure ($\Phi = -130^\circ$, $\Psi = 140^\circ$), those of residues 2 and 5 to the α-helix ($\Phi = -60^\circ$, $\Psi = -60^\circ$), and those of residues 3 and 6 to form A of N-acetylglycine methylamide (the coordinates $\Phi = -60$, $\Psi = 0$ have been proposed for this [14] [more accurately, apparently, $\Phi = -90^\circ$, $\Psi = 0^\circ$, see below]) we should expect in the spectrum of compounds (1)-(8) the presence of bands corresponding to the characteristic frequencies of the three forms mentioned: ≈ 710 and ≈ 450 cm^{-1} for the β form [32, 33], 650, 610, and 380 cm^{-1} for the α-helix [32], and five strong bands for the A form of Ac-Gly-NHMe (see the spectrum shown dotted in Fig. 2). In actual fact, the bands mentioned above are present in the majority of the spectra given in Fig. 2, and we have made their provisional assignment on this basis (see Table 1). In addition to this, for compound (1) the bands characteristic of β sections are practically absent, which possibly shows the planar structure of sections of the type of



(bounded by one and four residues and by intramolecular hydrogen bonds), i.e. the closeness of the parameters $\Phi_{1,4}$ and $\Psi_{1,4}$ (−180°). In this case, the antisymmetrical vibrations in the section considered prove to be weak, probably because of the absence of a center and plane of symmetry and do not appear in the spectrum. Thus, the spectrum of compound (1) after heating with KBr practically reflects the properties of a ten-membered ring stabilized by 4 → 1 hydrogen bonds



and it may serve as a basis for spectral assignments in a number of compounds containing such sections. However, in compounds (3)-(8) the symmetry of the central part of the cyclopeptide delimited by 4 → 1 hydrogen bonds is somewhat distorted as a result of the complexity of the side chain and bands appear corresponding to the β form in the 470-420 cm^{-1} region although they are of low intensity (see Fig. 2). It is difficult to record the appearance of bands at 720-710 cm^{-1} because of overlapping with the amide V band for residues with other conformational parameters.

It can be seen from Fig. 2 that the spectra of compounds (1)-(8) in the 730-500 cm^{-1} region are extremely similar, as a whole, to the spectrum of form A of Ac-Gly-NHMe.

Consequently, the cyclopeptides must contain sections with the same conformational parameters as form A. As was shown above, these sections are amino-acid residues in positions 3 and 6 with the coor-

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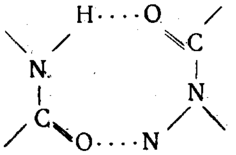
*To describe the conformational states of cyclopeptides, we have used the nomenclature proposed by the IUPAC Commission in 1969 [31].

dinates $\Phi=-130^\circ$ to -90° and $\Psi=0$ to 50°, which permits some refinement in the parameters proposed previously for form A, $\Phi=-60^\circ$, $\Psi=0^\circ$ with the proposal of the new figures: $\Phi=-90^\circ$, $\Psi=0^\circ$.*

In conclusion, it is desirable to consider the question of the possibility of studying the cis-trans isomerism of the amide bonds in peptides by means of IR spectra. After investigating the spectra of a large series of model cis-amides (piperazine-2,5-diones and 4- to 7-membered lactams), Blaha et al. [38] came to the conclusion that the distinguishing features of cis-amide bonds are a low frequency of the amide A band (≈ 3200 cm^{-1}) due to stable intermolecular hydrogen bonds of the  type, a high frequency of the amide I band (1670-1690 cm^{-1}), the location of the amide II band at ≈ 1440 cm^{-1} (instead of 1540 cm^{-1} as for the trans-amides) and its displacement on N-deuteration to the ≈ 1235 cm^{-1} region, and the position of the amide III band at 1305-1345 cm^{-1} and the absence of its displacement on deuteration (the trans-amide III band, generally located at ~ 1250 cm^{-1}, is shifted on deuteration to ~ 980 cm^{-1}). In the opinion of these authors, any of the characteristics mentioned can be used to answer the question of the presence of cis-amide bonds in compounds containing amide groups in the same configuration, but it is extremely difficult to detect cis-amide bonds in the presence of trans bonds. Blaha et al. [38] came to the conclusion of the presence of cis bonds in some diastereomers of cyclo-Gly-Phe-Leu-Gly-Phe-Leu on the basis of the presence of a band at ~ 1340 cm^{-1} and the appearance after deuteration of a band at ~ 1235 cm^{-1}. In our opinion, because of the conformational nonhomogeneity of the crystalline samples and the possibility of diverse interactions of the vibrational frequencies, all the spectral features mentioned are characteristic not only of cis-amides but also of compounds with trans-amide bonds.† In particular, this is shown by the results of the present work. In spite of the absence of cis bonds in compounds (1)-(15) [16, 17, 19], their IR spectra frequently show bands at 3200 cm^{-1}; as a rule, the amide I band is characterized by a high frequency, and bands appear in all the spectra at 1310-1345 cm^{-1}. Finally, the N-deuteration of cyclohexaglycyl (1) appreciably increases the intensity of the band at ~ 1240 cm^{-1} (see Fig. 1). Thus, the question of the presence of cis-amide bonds in cyclopeptides investigated by the Czechoslovak authors must be considered as open, and the use of other methods is necessary for its solution.

EXPERIMENTAL

The synthesis of compounds (1)-(15) has been described previously [40-43]. Compound (1) was N-deuterated by dissolution in D_2O and evaporation to dryness three times. The degree of deuteration was checked from the intensity of the amide A band (~ 3300 cm^{-1}). The IR spectra in the 4000-625 cm^{-1} region were taken on a Perkin-Elmer 257 instrument with diffraction gratings. The 700-400 cm^{-1} region was studied on a Hilger H-800 instrument with a KBr prism. A Hitachi FIS-21 instrument with diffraction gratings was used to obtain the spectra in the 500-450 cm^{-1} region. The accuracy of the frequency measurements was ± 2 cm^{-1} for the Perkin-Elmer 257 and Hilger H-800 instruments and ± 1 cm^{-1} for the FIS-21 spectrometer, the calibration of which was performed with the spectra of H_2O vapor. All the samples were examined at room temperature in the solid phase (tablets with KBr down to 250 cm^{-1}, tablets with CsBr down to 190 cm^{-1}, and mull with paraffin oil between polyethylene windows down to 40 cm^{-1}).

The deuteration of the cyclohexaglycyl was performed by A. I. Miroshnikov.

SUMMARY

By IR spectroscopy in the middle and far regions of the spectrum it has been found that on being heated with KBr a number of cyclic hexapeptides with L(D)-alanine and glycine residues undergo a transition from a mixture of various conformers into a monotypical conformational state corresponding to the "pleated sheet" structure with two trans-annular hydrogen bonds of the 4 → 1 type.

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*Although the probabilities of the realization of the conformations with $\Phi=-60^\circ$, $\Psi=0^\circ$ and with $\Phi=-90^\circ$, $\Psi=0^\circ$ are approximately the same according to quantum-mechanical calculations [34], on the conformational charts obtained by the semiempirical method the first conformation is represented by a region with a higher energy [35-37].

† The only exception is the amide II band: several authors have shown that in nondeuterated trans-amides it is always located at ~ 1540 cm^{-1}, and in cis-amides at 1440 cm^{-1}, being superposed on the deformation vibrations of the CH_2 groups (see, for example, [39]).

LITERATURE CITED

1. S. Mizushima, The Structure of Molecules and Internal Rotation, Academic Press, New York (1954).
2. H. Susi, in: Structure and Stability of Biological Macromolecules, Vol. 2, S. N. Timasheff and G. Fasman (editors), Marcel Dekker, New York (1969).
3. A. Elliott and E. I. Ambrose, Nature, 165, 921 (1950).
4. A. Elliott, Proc. Roy. Soc. (London), A221, 104 (1954).
5. T. Miyazawa and E. R. Blout, J. Amer. Chem. Soc., 83, 712 (1961).
6. G. Fasman and E. Blout, J. Amer. Chem. Soc., 82, 2262 (1960).
7. Y. Masuda and T. Miyazawa, Bull. Chem. Soc., Japan, 42, 570 (1969).
8. W. B. Rippon, I. M. Anderson, and A. G. Walton, J. Mol. Biol., 56, 507 (1971).
9. T. Miyazawa, K. Fukushima, S. Sugano, and Y. Masuda, Conformation of Biopolymers, Vol. 2, Academic Press, New York (1967), p. 557.
10. A. M. Dwivedi and V. D. Gupta, Chem. Phys. Lett., 8, No. 2 (1971).
11. K. Fukushima and T. Miyazawa, Annual Meeting of the Chemical Society of Japan, Tokyo (1964).
12. M. Beer, G. B. Sutherland, K. N. Tanner, and D. L. Wood, Proc. Roy. Soc. (London), A 249, 147 (1959).
13. Yu. N. Chirgadze and A. M. Ovsepyan, Dokl. Akad. Nauk SSSR, Ser. Biol., 201, 744 (1971).
14. Y. Koyama and T. Shimanouchi, Biopolym., 6, 1037 (1968).
15. Y. Koyama, T. Shimanouchi, M. Sato, and T. Tatsuno, Biopolym., 10, 1059 (1971).
16. I. L. Karle and J. Karle, Acta Cryst., 16, 969 (1963).
17. I. L. Karle, J. W. Gibson, and J. Karle, J. Amer. Chem. Soc., 92, 3755 (1970).
18. V. T. Ivanov, V. V. Shilin, G. A. Kogan, E. N. Meshcheryakova, L. B. Senyavina, E. S. Efremov, and Yu. A. Ovchinnikov, Tetrahedron Lett., 1971, 2841.
19. S. L. Portnova, V. V. Shilin, T. A. Balashova, J. Biernat, V. F. Bystrov, V. T. Ivanov, and Yu. A. Ovchinnikov, Tetrahedron Lett., 1971, 3085.
20. V. T. Ivanov, G. A. Kogan, E. A. Meshcheryakova, V. V. Shilin, and Yu. A. Ovchinnikov, Khim. Prirodn. Soedin., 309 (1971).
21. S. L. Portnova, T. A. Balashova, V. F. Bystrov, V. V. Shilin, J. Biernat, V. T. Ivanov, and Yu. A. Ovchinnikov, Khim. Prirodn. Soedin., 323 (1971).
22. V. T. Ivanov, S. L. Portnova, T. A. Balashova, V. F. Bystrov, V. V. Shilin, J. Biernat, and Yu. A. Ovchinnikov, Khim. Prirodn. Soedin., 339 (1971).
23. V. T. Ivanov, L. B. Senyavina, E. S. Efremov, V. V. Shilin, and Yu. A. Ovchinnikov, Khim. Prirodn. Soedin., 347 (1971).
24. Yu. N. Chirgadze, Infrared Spectra and the Structure of Polypeptides and Proteins [in Russian] Moscow (1965).
25. R. Schwyzer, P. Sieber, and B. Gorup, Chimia, 12, 90 (1958).
26. R. Schwyzer, Record Chem. Progr., 20, 147 (1959).
27. K. D. Kopple, M. Ohnishi, and A. Go, Biochem., 8, 4087 (1969).
28. K. D. Kopple, M. Ohnishi, and A. Go, J. Amer. Chem. Soc., 91, 4264 (1969).
29. R. Schwyzer and U. Ludescher, Helv. Chim. Acta, 52, 2033 (1969).
30. C. Ramakrishnan and K. P. Sarathy, Int. J. Prot. Res., 1, 103 (1969).
31. Biokhim. Biofiz. Acta, 229, 1 (1971).
32. K. Itoh and T. Shimanouchi, Biopolym., 7, 649 (1969).
33. V. M. Tul'chinskii and G. A. Kogan, Proceedings of an All-Union Conference on the Study of the Structure of Organic Compounds by Physical Methods [in Russian], Kazan' (1971), p. 140.
34. B. Maigret, B. Pullman, and D. Perahia, J. Theor. Biol., 31, 269 (1971).
35. E. M. Popov, G. M. Lipkind, S. F. Arkhipova, and V. G. Dishevskii, Mol. Biol., 2, 622 (1968).
36. G. M. Lipkind, S. F. Arkhipova, and E. M. Popov, Zh. Strukt. Khim., 11, 121 (1970).
37. G. M. Grippen and H. A. Scheraga, Proc. Nat. Acad. Sci. U. S., 64, 42 (1969).
38. K. Blaha, I. Smolikova, and A. Vitek, Collection Czech. Chem. Commun., 11, 4296 (1966).
39. L. Bellamy, Advances in Infrared Group Frequencies, Methuen, London (1968).
40. H. Gerlach, J. A. Owtschinnikov [Yu. A. Ovchinnikov], and V. Prelog, Helv. Chim. Acta, 47, 2294 (1964).
41. H. Gerlach, G. Haas, and V. Prelog, Helv. Chim. Acta, 49, 603 (1966).
42. V. T. Ivanov, V. V. Shilin, and Yu. A. Ovchinnikov, Zh. Obshch. Khim., 40, 924 (1970).
43. V. T. Ivanov, V. V. Shilin, J. Biernat, and Yu. A. Ovchinnikov, Zh. Obshch. Khim., 41, No. 10 (1971).