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CIRCULAR DICHROISM OF D-PHENYLGLYCINE

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The vibrational structure in circular dichroism spectrum of D-phenylglycine in the wavelength region corresponding to the α-band of the phenyl chromophore was observed at room temperature and at liquid nitrogen temperature. We analyzed this vibrational structure in comparison with that of L-phenylalanine.

Many authors have studied near ultraviolet Cotton effects of optically active aromatic compounds such as α- and β-phenylalkylamine and L-phenylalanine with their special regard to vibrational structures in circular dichroism (CD) spectra.[1-6] Horwitz et al.[1] reported that L-phenylalanine and its derivatives show vibrational structures in their near ultraviolet CD spectra, and they analyzed the vibronic bands assuming these compounds to have a C_{2v} symmetry. They concluded that the totally symmetric vibration affects neither the signs nor the magnitudes of the CD bands of such compounds and the non-totally symmetric vibration can often alter the magnitude and even the sign of the vibronic CD bands. They also mentioned that the CD band corresponding to the 0-0 transition of the phenyl chromophore can be detected with the substituted L-phenylalanines both at room temperature and at liquid nitrogen temperature nevertheless in the case of non-substituted L-phenylalanine it appears only at room temperature.

We observed the vibrational structure in the near ultraviolet CD and the absorption (AB) spectra at room temperature and at liquid nitrogen temperature in the wavelength region corresponding to the α-band of the phenyl chromophore for D-phenylglycine, which was prepared according to Steiger's method[7] and resolved by Betti's method[8]. Figure 1 shows the CD and the AB spectra of D-phenylglycine recorded by a JASCO J-20A polarimeter and a Hitachi EPS-3T spectrometer, respectively. These spectra resemble those of α- and β-phenylalkylamine, L-phenylalanine and its derivatives reported by Horwitz and Willis[1,2].

The absolute value of the optical anisotropy factor, $|\Delta\varepsilon/\varepsilon|$, of D-phenylglycine

in this wavelength region is about eight times as large as that of L-phenylalanine at room temperature. Therefore, the dissymmetric perturbation to the phenyl chromophore in D-phenylglycine can be regarded more effective than in L-phenylalanine, since we can naturally assume that the $|\Delta\varepsilon/\varepsilon|$ value is directly proportional to the effective strength of the perturbation by the dissymmetric field caused by the optically active moiety. This probably reflects the fact that the distance between the phenyl chromophore and the chiral carbon atom in D-phenylglycine is shorter than that in L-phenylalanine and/or the fact that the phenyl chromophore in D-phenylglycine rotates less freely than that in L-phenylalanine.

The rotational freedom of the phenyl chromophores both of D-phenylglycine and L-phenylalanine will be reduced at low temperature while the distances between the phenyl chromophore and the chiral carbon atom of these compounds are not altered by the temperature dropping. The $|\Delta\varepsilon/\varepsilon|$ values for D-phenylglycine and L-phenylalanine are observed to be much enhanced at liquid nitrogen temperature compared to those at room temperature. From these, we can say that the effective dissymmetric perturbations by the optically active residues of these compounds are strengthened at low temperature as a result of the reduction of the rotational freedom of the phenyl chromophores. The ratio of the $|\Delta\varepsilon/\varepsilon|$ value of D-phenylglycine to that of L-phenylalanine, on the other hand, decreases from 8 to 2 by the temperature dropping from room temperature to liquid nitrogen temperature. From the fact that such a sharp decrease in the ratio is caused only by the loss of the rotational freedom of the phenyl chromophore accompanying the temperature dropping, it is concluded that the difference between the $\Delta\varepsilon/\varepsilon$ values of D-phenylglycine and L-phenylalanine at room temperature is mainly attributed to the difference in the rotational freedom of the phenyl chromophore between D-phenylglycine and L-phenylalanine. The distance between the chiral carbon atom and the phenyl chromophore can be regarded to have little significance for the magnitude of the dissymmetric perturbation exerted on the phenyl chromophore.

The CD and the AB spectral features of D-phenylglycine at lower temperatures are quite similar to those at room temperature, but they are more highly resolved with a definite shoulder at the longest wavelength side which could not be detected at room temperature. We take this shoulder band as the 0-0 transition band for this compound in the following discussions. The vibrational analysis of the CD and the AB spectra for the α-band of the phenyl chromophore of D-phenylglycine is shown in Table 1 along with those of L-phenylalanine and L-α-phenylethylamine. In analogy to the vibration-

al analysis of the CD spectrum of L-phenylalanine[1], D-phenylglycine was considered as a mono-substituted benzene with a C_{2v} symmetry, where the electronic transition in this region has the character of $A_1 \rightarrow B_2$. We determined symmetries of vibrations on the basis of the Ginsburg's treatment[9] for the AB spectrum of toluene vapor.

Table 1. Vibrational analysis of AB and CD spectra of D-phenylglycine in comparison with L-phenylalanine and L-phenylethylamine

Symmetry of vibronic state	Symmetry of vibration	D-phenylglycine AB-max ($\times10^3$cm^{-1})	D-phenylglycine CD-max ($\times10^3$cm^{-1})	L-phenylalanine AB-max* ($\times10^3$cm^{-1})	L-phenylalanine CD-max* ($\times10^3$cm^{-1})	L-phenylethylamine AB-max** ($\times10^3$cm^{-1})	L-phenylethylamine CD-max** ($\times10^3$cm^{-1})
B_2	A_1	37.36	37.36	37.36	(37.31)##	37.5	37.6
	#		37.52		37.54		
A_1	B_2	37.88	37.88	37.88	37.88	38.0	
B_2	A_1		38.29	38.30		38.5	38.5
	#		38.46		38.43		
A_1	B_2	38.74	38.75	38.80	38.80	38.9	
B_2	A_1		39.21				39.4
A_1	B_2	39.56	39.57			40.0	

* From reference 1 at liquid nitrogen temperature.

** From reference 2 at room temperature.

\# The symmetry of this vibration is pending in reference 1.

\## From room temperature measurement.

In Ginsburg's study, the band at 37,477 cm^{-1} in the vapor phase spectrum of toluene is assigned to the 0-0 transition, and to this transition the totally symmetric vibration of 932 cm^{-1} and the non-totally symmetric vibration of 528 cm^{-1} are combined. The A_1 progression (excitations to the vibronic states A_1) and the B_2 progression (excitations to the vibronic states B_2) follow the 0-0 transition by the spacings of 528, (528+932) and (528+2×932) cm^{-1} and by the spacings of 932, 2×932 and 3×932 cm^{-1}, respectively. As is seen in Table 1, the CD spectrum of D-phenylglycine is composed of three progressions of different vibronic symmetries, i.e. progressions of unclarified symmetry, A_1 symmetry and B_2 symmetry. It is interesting to see that the symmetrical property of the CD spectrum of D-phenylglycine is similar to that of

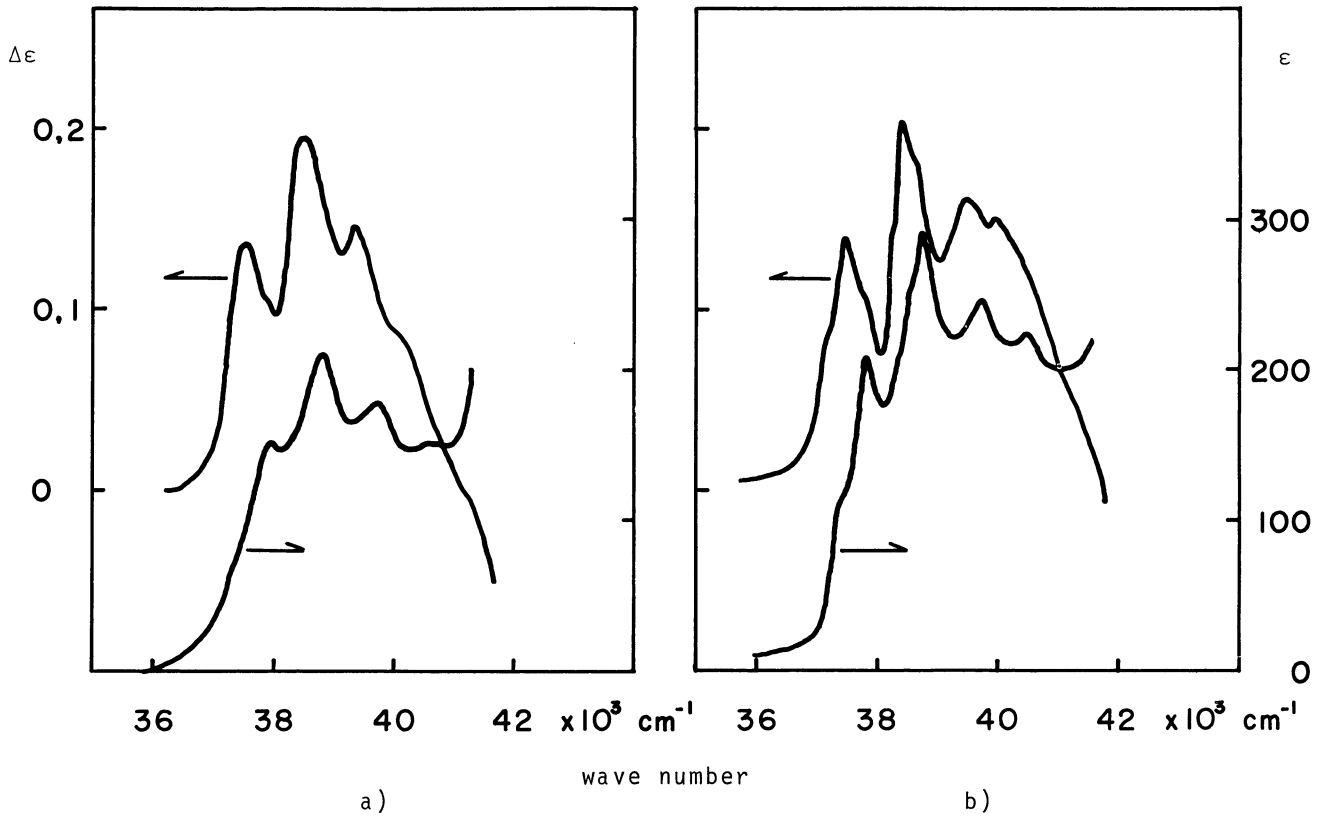

Figure 1. AB and CD spectra of D-phenylglycine in methanol glycerol (1 : 1 in Vol.) with small amount of 0.1 N NaOH added; a) at room temperature, b) at liquid nitrogen temperature

L-phenylalanine while it is quite different from the symmetrical property of the CD spectrum of L-α-phenylethylamine. That is, for D-phenylglycine (L-phenylalanine) the sign and the magnitude of the CD band are mainly determined by the vibrations of 160 (180) cm^{-1} and 510 (540) cm^{-1} and not affected by the totally symmetric vibration of 930 (940) cm^{-1}, in contrast to the case of L-α-phenylethylamine where the main feature of the CD curve is determined by the totally symmetric vibration of 900 cm^{-1} and the CD band assigned to the 0-0 transition has a large magnitude.

The circular dichroism induced in the wavelength region of the absorption band of the symmetric phenyl chromophore suggests the existence of the magnetic transition moment which couples with the electric transition moment of the phenyl chromophore giving rise to this circular dichroism. No transition having such a magnetic moment is allowed for the phenyl chromophore as long as it has a C_{2v} symmetry, so we must

invoke the following mechanisms for the explanation of the circular dichroism; i) the intrinsic magnetic transition moment in the phenyl chromophore (which is naturally perpendicular to the electric transition moment as far as the phenyl chromophore has a C_{2v} symmetry) loses its orthogonality with the electric transition moment through the reduction of the symmetry of the phenyl chromophore by the perturbation from the dissymmetric field and/or ii) the magnetic transition moment of the dissymmetric amino acid moiety attached to the phenyl chromophore has the parallel component with the electric transition moment of the phenyl chromophore.

The magnetic transition moment can be closely correlated to the optical anisotropy factor $\Delta\varepsilon/\varepsilon$. The $|\Delta\varepsilon/\varepsilon|$ value of L-α-phenylethylamine, which has a methyl group in the place of the carboxyl group attached to the chiral carbon atom of D-phenylglycine, is nearly equal in magnitude to that of D-phenylglycine, so it can be safely said that the n-π* transition of the carboxyl group has no significance for the induction of the magnetic transition moment and that the carboxyl group contributes only to form the dissymmetric environment around the chiral carbon atom of these optically active phenyl compounds.

There are some transitions which have a magnetic transition moment in the phenyl chromophore, such as σ-π* transitions. These transitions, in general, have much higher energies than the π-π* transition for which the circular dichroism is observed in this paper. Therefore, even if the mixing occurs between the magnetic transition moment and the electric transition moment within the phenyl chromophore, we can expect that this mixing is too weak to lead to the observable optical rotation.

References

1) J.Horwitz, E.H.Strickland, and C.Billups, J.Am.Chem.Soc., 91, 184 (1969).

2) H.E.Smith and T.C.Willis, J.Am.Chem.Soc., 93, 2282 (1971).

3) A.Moscowitz, A.Rosenberg, and A.E.Hansen, J.Am.Chem.Soc., 87, 1813 (1965).

4) M.Legrand and R.Viennet, Bull.Soc.Chim.France, 2798 (1966).

5) J.C.Craig, R.P.K.Chan, and S.K.Roy, Tetrahedron, 23, 3573 (1967).

6) N.Sakota, K.Okita, and Y.Matsui, Bull.Chem.Soc.Japan, 43, 1138 (1970).

7) R.E.Steiger, Org.Syn., Coll.Vol.3, 84 (1955).

8) M.Betti and M.Mayer, Ber., 41, 2071 (1908).

9) N.Ginsburg, W.W.Robertson, and F.A.Matsen, J.Chem.Phys., 14, 511 (1946).

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