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Intramolecular Hydrogen Bonding in α-Keto- and α-Alkoxy-carboxylic Acids. VII. Ultraviolet Spectra of Phenylglyoxylic Acid in Various Solvents

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The ultraviolet spectra of phenylglyoxylic acid were determined in various solvents as well as in the mixtures of solvents. A very remarkable hypsochromic shift with increase in intensity was observed when the solvent participates in the formation of hydrogen bond as a hydrogen acceptor. The measurement of the spectra in binary mixtures of the solvents shows that the hypsochromic shift is due to the formation of a 1 : 1 complex of $C_6H_5COCOOH\cdots$solvent type. This hypsochromic shift is interpreted by the destruction of the chelate ring formed by the intramolecular hydrogen bond which enforces the acid molecule to the planar conformation. This view is supported by the simple LCAO-MO calculation on this molecule.

It has been shown that the intramolecular hydrogen bonding between the carboxylic hydroxyl group and the α-oxygen containing functional groups plays an important role in the appearance of the *trans*-conformation[*2] of the carboxyl group.[2–5] Thus, the α-alkoxy and α-oxo-carboxylic acids can exist as *trans*-conformers while the usual carboxylic acids take the *cis*-conformation exclusively. Phenylglyoxylic acid is an α-oxo-carboxylic acid which is capable of forming an intramolecular hydrogen bond as exemplified by Ib. We have studied it by means of infrared spectroscopy.[2] It has been also studied more extensively by Oehme *et al.*[6]

It seems certain that the acid takes a nearly planar conformation when it exists as an intramolecularly hydrogen bonded *trans*-conformer (Ib), in which both carbonyl groups are kept at a *trans* position to each other by hydrogen bond formation. The *cis* conformation of the usual carboxyl group is assumed to be about 2 kcal/mol more stable than the *trans* one,[7] but the *trans*-conformer of phenylglyoxylic acid is predominant in inert solvents because the O-H···O=C hydrogen bond energy (estimated to be about 4—5 kcal/mol) overcomes the stabilization energy of the *cis*-conformer.[8] From the measurement on the temperature dependence of the intensities of the O-H stretching absorption bands assigned to both conformations, the *trans*-conformer is shown to be more stable, and

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[*2] The *cis* or *trans* implies that the oxo(O=)-group and the hydrogen of the carboxyl group are *cis* or *trans*, respectively, with respect to the C–O bond.[1]

1) C. P. Smyth, "Dielectric Behavior and Structure," McGraw Hill, New York (1955), p. 305—307.

2) M. Ōki and M. Hirota, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 856 (1960).

3) M. Ōki and M. Hirota, This Bulletin, **34**, 374, 378 (1961); *ibid.*, **36**, 290 (1963).

4) M. Ōki and M. Hirota, *Spectrochim. Acta*, **17**, 583 (1961).

5) M. Ōki and M. Hirota, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 115 (1965).

6) G. Oehme, G. Fischer and A. Schnellenberger, *Chem. Ber.*, **100**, 425 (1967).

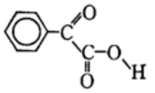
7) T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).

8) M. Hirota, *Kagaku To Kogyo* (*Chem. and Chem. Ind.*), **20**, 12 (1967).

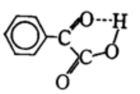
the enthalpy of the conversion was determined to be 1.78 kcal/mol.

In polar solvents, the intramolecular hydrogen bond may be weakened or destroyed both by the usual polar effect and by the intermolecular association. We found a remarkable solvent effect on the ultraviolet spectrum of this acid. The acid has an absorption band at 277.8 mμ (ε, *ca.* 6000) in *n*-hexane, while the absorption in ethanol is at 252.5 mμ (ε, 12100).[9]

In order to interpret this drastic change of absorption spectra in both solvents, the spectra of phenylglyoxylic acid were measured in various solvents and also in binary mixtures of these solvents. The acid is shown to form a 1 : 1 complex with the hydrogen accepting solvent.



Ia



Ib

Experimental

Materials. Phenylglyoxylic acid was prepared from benzoyl chloride and cuprous cyanide by the usual method.[10] Commercial spectro-grade *n*-hexane, methylene chloride and chloroform were used as solvent without further purification. Diethyl ether, ethanol and acetonitrile of commercial special grade were purified by the usual procedures.

Measurement of the Spectra. The ultraviolet spectra were measured by a Hitachi EPS-3T recording spectrophotometer. The molecular orbital calculation of the compound was carried out by a NEAC-2230 digital computer.

Results and Discussion

The ultraviolet spectra of phenylglyoxylic acid were determined in six solvents, the results of which are shown Fig. 1. Characteristic data on the absorption maxima are listed in Table 1. As shown in Table 1, the acid has an intense absorption band at about 250 mμ in ethanol, ether and acetonitrile, while it has a weaker absorption band at a longer wavelength in hexane, methylene chloride and chloroform.

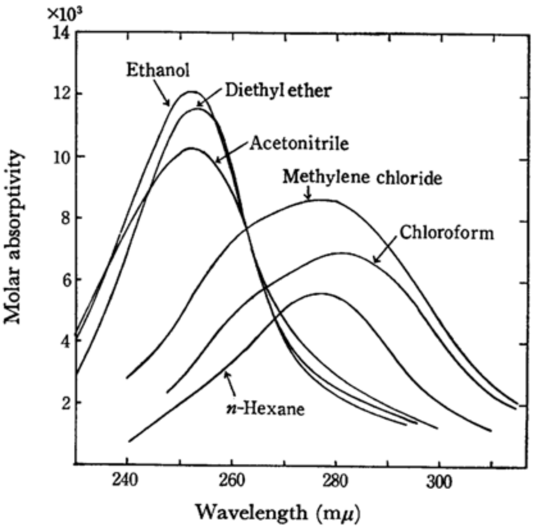


Fig. 1. The ultraviolet spectra of phenylglyoxylic acid in various solvents.

TABLE 1. THE ULTRAVIOLET SPECTRA OF PHENYLGLYOXYLIC ACID IN VARIOUS SOLVENTS

Solvent	Wavelength (mμ)	Intensity (ε_{max})
n-Hexane	277.8	5930
Methylene chloride	278.9	8850
Chloroform	281.5	6900
Acetonitrile	252.8	10300
Diethyl ether	253.8	11500
Ethanol	252.5	12100

The absorption bands at 250 mμ and at 280 mμ can be assigned to the solvated *cis*-conformation (Ia) and intramolecularly hydrogen bonded *trans*-conformation (Ib) of phenylglyoxylic acid, respectively. From the measurement of the O–H stretching and the C=O stretching absorption bands in the infrared region, it was concluded that the acid should take the hydrogen bonded *trans*-conformation in inert solvents which cannot participate in the formation of intermolecular hydrogen bonds to the acid. The similarity of the absorption spectra suggests a similar conformation in chloroform and methylene chloride with that in *n*-hexane. In other words, the intramolecular hydrogen bonding of the acid persists in the solvents of considerable hydrogen donating property. The absorption at about 250 mμ (ε: 12000) in hydrogen accepting solvents may be attributable to the benzoyl chromophore, because it is similar both in the location of the absorption maximum and in intensity. For example, benzaldehyde[11] has an intense absorption maximum at 242 mμ with a shoulder at 248 mμ, their intensities being 14000 and 12500, respectively. This means that the conjugation of the whole molecule is interrupted and the absorption caused by the benzoyl partial chromophore is observed in ethanol, diethyl ether and acetonitrile. These solvents are more or less basic and have hydrogen accepting ability. In these solvents, the intramolecular hydrogen bond of the acid might be destroyed and the intermolecular hydrogen

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[9] M. Hirota, *Kagaku no Ryoiki* (*J. Japan. Chem.*), **18**, 759 (1964).

[10] "Organic Syntheses," Vol. 24, (1944), p. 14.

[11] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

bond between the acidic O–H groups and the solvents might be formed instead. The acid is enforced to take an otherwise unfavorable *trans*-conformation by the intramolecular hydrogen bond, but it can form intermolecular hydrogen bond in the favorable *cis*-conformation. As there is no interaction between the acidic O–H and the ketonic carbonyl groups in the *cis*-form, the carboxyl group is not fixed on the plane of the benzoyl group and the rotation around the C–C bond between the carbonyl and the carboxyl carbons may occur rather freely. This may hinder the conjugation of the whole molecule and results in the appearance of the absorption band of the benzoyl chromophore in ethanol and other hydrogen accepting solvents.

It is doubtful whether the remarkable solvent dependence of the absorption spectrum is due to the electronic interaction through the hydrogen bond, and the molecule was studied from a molecular orbital theoretical point of view. The HMO calculation was carried out with phenylglyoxylic acid employing the parameters $h_{\dot{O}}=1.0$, $h_{\ddot{O}}=2.0$, $k_{C-O}=0.8$ and $k_{C=O}=1.0$.[12] The π-electronic interaction through the hydrogen bond was considered by assuming the non-zero resonance integral ($\beta_{OH\cdots O}=0.2\beta$) between the oxygen atoms participating in the formation of hydrogen bond, but the lowest $\pi\rightarrow\pi^*$ transition energy does not change remarkably from the result obtained by neglecting the hydrogen bond effect ($\beta_{OH\cdots O}=0$).

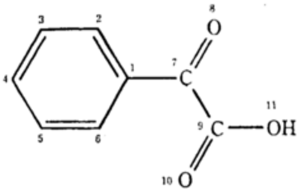

Fig. 2 (1)

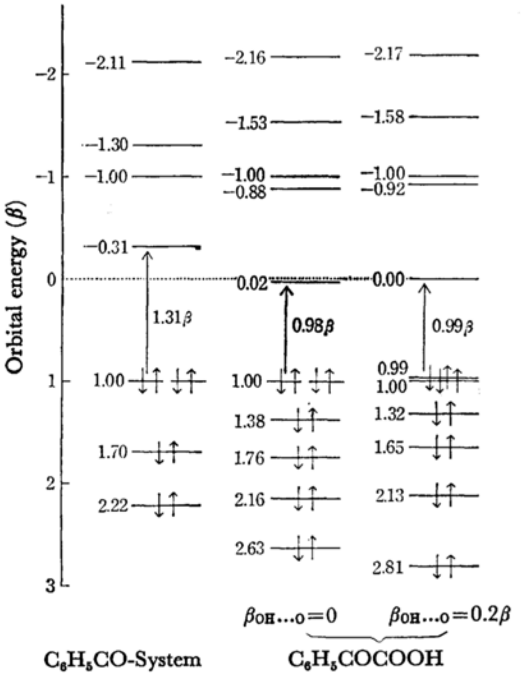

Fig. 2 (2)

Fig. 2. Simple LCAO-MO energy diagrams for phenylglyoxylic acid.

On the other hand, the $\pi\rightarrow\pi^*$ transition energy of the benzoyl system was higher than that of phenylglyoxylic acid, so the solvent effect on its absorption spectrum is explained that the conjugate system is non-planar when the intramolecular hydrogen bond is absent. A very low double bond character of C_7–C_9 bond (bond order $p_{7,9}=0.333$) probably allows to rotate rather freely around this C–C bond. Further study on this problem is in progress, and above interpretation on the absorption spectrum agrees with the result of the Pariser-Parr-Pople MO calculation, details of which will be reported elsewhere.

In short, phenylglyoxylic acid associates with solvents which act as hydrogen acceptors in forming hydrogen bond, while it holds an intramolecularly hydrogen bonded form in the solvent with hydrogen donating ability.

In order to investigate the nature of the interaction between the acid and the solvents, the absorption spectra were measured in a binary mixture of solvents, such as methylene chloride-ethanol, *n*-hexane-diethyl ether, *etc.* The absorption spectra in binary mixture of the solvents are shown in Fig. 3. The isosbestic points were observed in all solvent systems investigated at the concentrations, at most, below 10%, and suggest the formation of only one kind of complexed species of definite composition in these concentration ranges. In order to determine the composition of the complexes, the absorption spectra of the acid in the mixture of the solvents in varying proportions were analysed by a method similar to that reported by Brealey and Kasha.[13] It was assumed that the equilibrium given by Eq. (1) exists between the solvent and solute, where r is constant throughout the range in which the isosbestic point is observed in the spectra.

$$C_6H_5COCOOH + r\cdot \text{Solvent} \rightleftarrows C_6H_5COCOOH\,(\text{Solvent})_r \qquad (1)$$

The stability constant K and the number of solvated molecule r were calculated from the plots of $\log_{10}\{[\text{Complex}]/[C_6H_5COCOOH]\}$ against $\log_{10}$-[Solvent] shown by Fig. 3. From the definition of the formation constant expressed by Eq. (2),

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[12] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961), p. 135.

[13] G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.* **77**, 4462 (1955).

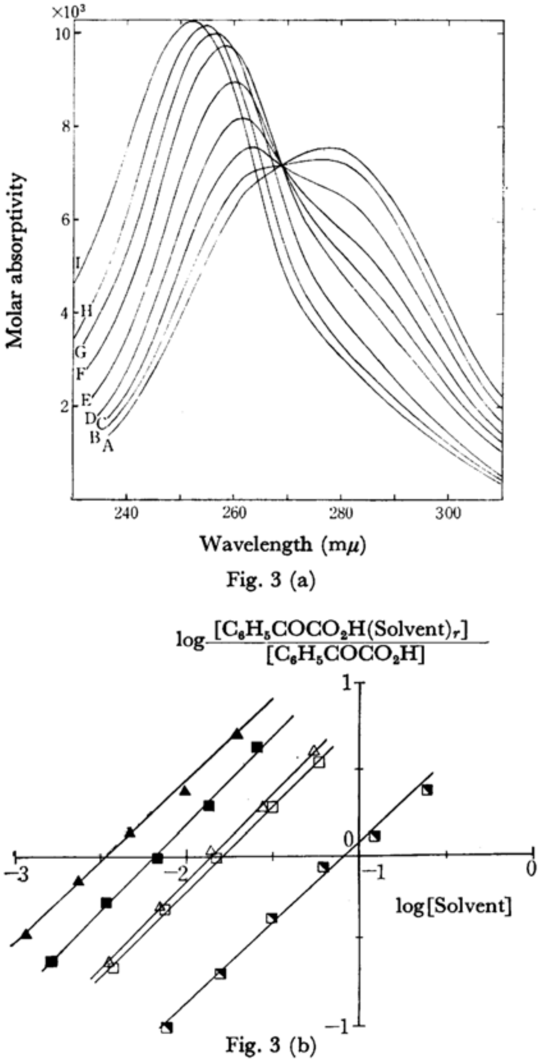

Fig. 3 (a)

Fig. 3 (b)

Fig. 3. The ultraviolet spectra of phenylglyoxylic acid in the binary mixtures of the solvents.
(a) An example of the spectra in the binary mixtures of the hydrogen accepting solvent (ethanol) and the inert solvent (methylene chloride).
A: pure CH_2Cl_2, B: 0.4% ethanol, C: 1.6% ethanol, D: 3.2% ethanol, E: 6.4% ethanol, F: 12.8% ethanol, G: 50% ethanol, H; 80% ethanol and I: pure ethanol.
(b) Logarithm of the concentration of the hydrogen accepting solvent *versus* log $\{[C_6H_5COCOOH\cdot(Solvent)_r]/[C_6H_5COCOOH]\}$.

Eq. (3) is easily derived by taking logarithm.

$$K = [C_6H_5COCOOH\cdot(Solvent)_r]/[C_6H_5COCOOH][Solvent]^r \qquad (2)$$

$$\log K = \log\{[Complex]/[C_6H_5COCOOH]\} - r\cdot\log[Solvent] \qquad (3)$$

This indicates that the tangent of the log{[Complex]/[$C_6H_5COCOOH$]} *vs.* log[Solvent] plot will give the *r*-value and the intercept of the log[Solvent] axis will give the log*K* value multiplied by *r*. The formation constants and the number of associated solvent molecule of some hydrogen bond complexes of phenylglyoxylic acid are tabulated in Table 2.

TABLE 2. THE ASSOCIATION CONSTANTS *K* AND THE MOLE RATIOS *r* OF THE PHENYLGLYOXYLIC ACID-SOLVENT COMPLEXES

Solvent system	*K*	*r*
C_6H_{14}–C_2H_5OH	219	0.95
C_6H_{14}–$(C_2H_5)_2O$	77.6	1.02
CH_2Cl_2–C_2H_5OH	178	1.03
CH_2Cl_2–$(C_2H_5)_2O$	61.7	0.98
CH_2Cl_2–CH_3CN	9.73	0.92

Formation of the 1 : 1 complex of phenylglyoxylic acid with ethanol as well as with ether and with acetonitrile, was thus confirmed from the *r*-values presented in the table. On the other hand, the acid does not form hydrogen bond with chloroform or methylene chloride, which can act as hydrogen donor in hydrogen bond formation. The results are in accordance with the fact that the carboxyl group is acidic and has a tendency to donate hydrogen to other molecules, while the basicity of the acid is rather low in comparison with other carbonyl compounds. The stronger hydrogen bond complex is formed when the hydrogen acceptor(solvent) has a stronger hydrogen accepting power and when the inert solvent is less polar.

In summary, the remarkable solvent shift observed in the ultraviolet spectrum of the acid is due to the 1 : 1 complex formation with hydrogen accepting solvents, which destroys the intramolecular hydrogen bonding present in inert solvents and allows the non-planar conformation of the acid.

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