Carboxyl Group as a Proton Donor in the Interaction between Hydroxyl Group and π-Electrons[1]

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Since carboxylic acids form stable dimers due to the strong hydrogen bonding and are generally considered to be stronger proton donors than alcohols and phenols, it is natural to expect that the carboxyl group will also be a proton donor in the interaction with the π-electrons. As to the intramolecular interaction, no example seems to be available in this class, but the report by Suzuki et al.[2] which reveals that *N*-methylphenylacetamide possesses this kind of interaction may be taken as an analogous phenomenon.

In this respect, the authors measured the O–H stretching absorptions (ν_{O-H}) of carboxylic acids which might exhibit the intramolecular interaction due to proximity of the carboxyl group to the aromatic nucleus. The carbonyl stretching absorptions ($\nu_{C=O}$) of the carboxylic acids were also measured, since it was found in this laboratory that the $\nu_{C=O}$ of the free carbonyl group in the " trans " carboxyl group[3] appears at as high as 1790 cm^{-1} [4].

Experimental

The materials used in this work were all known compounds and prepared or purified according to the literature. The physical constants were checked prior to the measurement.

The spectral measurements were carried out with a Perkin Elmer 112G grating infrared spectrometer, the samples being dissolved in carbon tetrachloride unless otherwise specified. The concentration of the solution was made up ca. 0.5 mmol./l. as a compromise between the convenient absorption and the minimum effect of the dimer. A quartz cell of 5 cm. optical length and a sodium chloride cell of 2.45 cm. length were used for the ν_{O-H} region, and the latter and another sodium chloride cell of 0.10 cm. length for the $\nu_{C=O}$ region.

Results and Discussion

The results of the measurements with a series of compounds are listed in Table I.

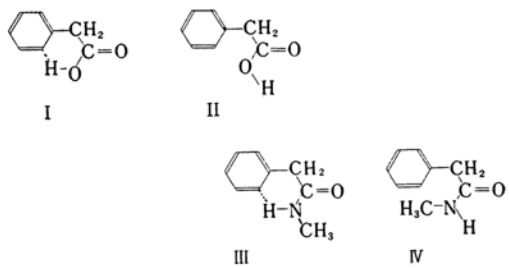


TABLE I. THE ν_{O-H} AND $\nu_{C=O}$ DATA OF SOME CARBOXYLIC ACIDS

Carboxylic acid	ν_{O-H} cm^{-1}	ε^a	$\nu_{C=O}$ cm^{-1}
$PhCH_2CO_2H$	3531.5	61.7	1762.7
Ph_2CHCO_2H	3526.7	68.3	1757.5
Ph_3CCO_2H	3520.9	79.4	1752.2
$PhCH_2CH_2CO_2H$	3532.8	63.8	1758.4
o-$PhC_6H_4CO_2H$	3529.9	81.1	1750.4 1736.9

1) This article is the fifteenth paper pertaining to the intramolecular interaction between hydroxyl group and π-electrons. For the preceding paper see: This Bulletin, **34**, 1395 (1961).

2) I. Suzuki, M. Tsuboi and T. Shimanouchi, *Spectrochim. Acta*, **16**, 467 (1960).

3) The nomenclature, " cis " and " trans " of a carboxyl group, is according to C. P. Smyth, " Dielectric Behavior and Structure ", McGraw-Hill Book Co., Inc., New York (1955), p. 306.

4) M. Ōki and M. Hirota, This Bulletin, **34**, 374 (1961).

In the first place, phenylacetic acid has been considered to be a carboxylic acid which should possess the intramolecular interaction from the structural analogy between the acid I and the methylamide III[2]. Contrary to the expectation, no intramolecular interaction between the carboxyl group and π-electrons is observed. Phenylacetic acid shows single ν_{O-H} and single $\nu_{C=O}$ at the ordinary regions assigned to the monomeric carboxylic acids.

It has been shown that the statistical factors obtained by considering the rotational isomerism about the single bonds play an important role in the intramolecular interaction. For example tribenzylcarbinol has no free hydroxyl group[5], whereas benzyldimethylcarbinol includes ca. 57% free form, provided that the absorption intensities per molecule due to O–H stretching are the same in both free and interacting forms. Triphenylacetic acid must favor the intramolecular interaction as far as the statistical factor is concerned. The results indicate, however, even diphenyl- and triphenylacetic acids possess a single peak for the ν_{O-H} and the $\nu_{C=O}$, respectively. The absorption maxima are in good agreement with those assigned to the monomeric "cis" forms.

Hydrocinnamic acid and *o*-carboxybiphenyl show free carboxyl group only, indicating that the absence of the interaction in phenylacetic acid is not due to the unfavorable ring member. Otherwise, sterically advantageous *o*-carboxybiphenyl should possess the interaction. The doublet $\nu_{C=O}$ of *o*-carboxybiphenyl can not be ascribed to the interaction, but is common for the *o*-substituted benzoic acids[6].

The carboxyl group is known to assume "cis" and "trans" structures[3], examples of which are illustrated by I and II, respectively. Establishment of the intramolecular interaction requires the "trans" form of the carboxyl group and this requirement may be the reason why phenylacetic acid does not show the interaction. Namely no matter what configuration is taken, the "cis" structure is disadvantageous.

The "cis" configuration is known to be more stable than the "trans" by several kcal./mol.[7] On the other hand, it is found in this laboratory that a lone pair electrons of a rather highly basic atom is needed to convert the "cis" structure into the "trans"[4], the phenomenon being suggestive of the comparable energies in O–H···O hydrogen bond and in the "cis" structure. π-Electron system, acting as a proton acceptor, is a weak base and can not compensate the required stabilization energy as is suggested by the energy measurement of the O–H···π interactions[8]. The energy of the intramolecular interaction between hydroxyl group and π-electrons has never been higher than 2.5 kcal./mol.[9] and is too low to compete with the stabilization energy of the "cis" structure. In this manner, it is also possible to account for the presence of the intramolecular interaction in *N*-methylphenylacetamide, since the "trans" structure III is more stable than the "cis" IV in the secondary amides[10].

Recently, Nagai and Simamura[11] reported that acetic acid and its halogenated derivatives in carbon tetrachloride show a second ν_{O-H} on addition of benzene and attributed the phenomenon to the intermolecular association between the carboxyl group and the π-electrons of the benzene nucleus. Since the entropy requirement is rather severe in the intermolecular hydrogen bonding[12], it seems unreasonable from this standpoint that the interaction which has not been observed intramolecularly is taking place intermolecularly. The acetic acid-benzene system has therefore been reinvestigated and the results are summarized in Table II together with those of the other aromatic solvents.

TABLE II. ν_{O-H} and $\nu_{C=O}$ OF THE MONOMERIC ACETIC ACID IN SEVERAL SOLVENTS

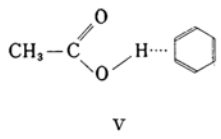
Solvent	ν_{O-H}, cm^{-1}	$\nu_{C=O}$, cm^{-1}
Carbon tetrachloride	3538.2	1769.3
Bromobenzene	3484.8	—
Benzene	3463.1	1763.2
Toluene	3458.8	1762.3
p-Xylene	3447.5	—
Mesitylene	3433.4	—

On dissolution of benzene, monomeric ν_{O-H} of acetic acid in carbon tetrachloride diminishes in its intensity and instead a second ν_{O-H} at ca. 3465 cm^{-1} arises. The intensity of the latter band grows as the concentration of benzene increases and the former disappears when the spectrum was measured in benzene. It can be seen from Table II that ν_{O-H} depends upon the basicity of the benzenoid π-electrons. Thus when the π-electron density in the benzene ring of the solvent molecule is decreased

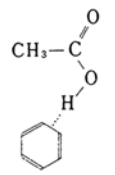
5) M. Ōki and H. Iwamura, ibid., **33**, 1600 (1960).
6) C. I. W. Brooks, G. Eglinton and J. F. Morman, *J. Chem. Soc.*, **1961**, 106.
7) M. M. Davies, *Trans. Faraday Soc.*, **36**, 333 (1940).
8) M. Ōki and H. Iwamura, This Bulletin, **33**, 717 (1960).
9) This highest energy has been obtained for 2-hydroxy-4-nitrobiphenyl. See, M. Ōki, H. Iwamura and Y. Urushibara, ibid., **31**, 769 (1958).
10) I. Suzuki, M. Tsuboi, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **16**, 471 (1960).
11) Y. Nagai and O. Simamura, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961. This Bulletin, **35**, 132 (1962).
12) H. H. Jaffe, *J. Am. Chem. Soc.*, **79**, 2373 (1957).

by halogen substitution, ν_{O-H} of acetic acid appears at higher frequency than in benzene, indicating the weakening of the interaction. On the other hand, when the π-electron density in the benzene ring is raised by substituting with the alkyl group, ν_{O-H} shifts to the lower frequency corresponding to the stronger interaction. The phenomenon is in parallel with those of ν_{N-H} of *N*-methylacetamide[13] and ν_{O-H} of phenol[14] in aromatic solvents, and adds strong support to the notion of the intermolecular interaction between the carboxyl group and π-electrons.

In spite of a rather large shift in ν_{O-H}, $\nu_{C=O}$ shifts little. The wave number (1763 cm^{-1}) is the place where the ordinary monomeric $\nu_{C=O}$ of "cis" configuration appears and too low to be assigned to the "trans" configuration which has the $\nu_{C=O}$ at around 1790 cm^{-1}[4]. Therefore it is tentatively concluded that in the intermolecular interaction between carboxyl group and π-electrons the "cis" configuration is maintained (V and not VI).



V



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13) I. Suzuki, M. Tsuboi and T. Shimanouchi, *J. Chem. Phys.*, **32**, 1263 (1960).
14) R. West, *J. Am. Chem. Soc.*, **81**, 1614 (1959).