Intramolecular Hydrogen Bonding in o-Aryloxybenzoic Acids

By Michinori Ōki and Minoru Hirota

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Although many investigators[1-4] reported the infrared spectra of benzoic acids, most of the measurements were restricted to the O–H stretching absorptions. A report by Brooks, Eglintion and Morman[2] is an exception which reports both ν_{O-H} and $\nu_{C=O}$ absorptions and the higher $\nu_{C=O}$ frequencies with the *ortho* substituted acids are mentioned. In the light of the recent observation[5] of the intramolecular hydrogen bonding in aryloxy- and alkoxy-acetic acids, it will be interesting to interprete the data of the ν_{O-H} and $\nu_{C=O}$ absorptions with *o*-aryloxybenzoic acids from the stand point of the cis and trans isomerism (Ia, Ib and II) of the carboxyl group.

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[1] M. M. Davies, "Hydrogen Bonding .... Papers presented at the Symposium on Hydrogen Bonding held at Ljubljana, 29 July-3 August, 1957" (Pergamon Press, 1959) and *J. Chem. Soc.*, **1955**, 132.

[2] C. J. W. Brooks, G. Eglinton and J. E. Morman, ibid., **1961**, 106.

[3] D. Peltier and A. Pichevin, *Bull. soc. chim. France*, **1960**, 1141.

[4] O. H. Wheeler, *Can. J. Chem.*, **39**, 2603 (1961).

[5] M. Ōki and M. Hirota, This Bulletin, **34**, 374, 378 (1961).

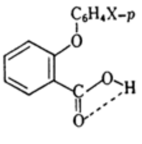
TABLE I. ν_{O-H} ABSORPTION DATA OF p-$XC_6H_4OC_6H_4COOH$-o

X		ν_{max}(cm^{-1})	ε_{max}	$\Delta\nu_{1/2}$(cm^{-1})	$A\times10^{-3}$ (l./mol. cm^2)	A_t/A_c
CH_3O	cis	3528.2	22.9	29.7	1.07	13.7
	trans	3391.0	130	53.2	10.86	
		3350.4	44.0	54.5	3.76	
H	cis	3527.8	40.4	29.8	1.89	6.70
	trans	3399.5	120	50.6	9.53	
		3357.9	34.1	58.4	3.13	
Cl	cis	3527.6	59.6	30.1	2.82	2.86
	trans	3411.7	74.7	54.5	6.39	
		3374.8	17.4	61.6	1.68	

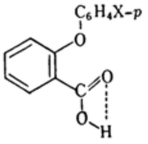
TABLE II. $\nu_{C=O}$ ABSORPTION DATA OF p-$XC_6H_4OC_6H_4COOH$-o

X		ν_{max}(cm^{-1})	ε_{max}	$\Delta\nu_{1/2}$(cm^{-1})	$A\times10^{-3}$ (l./mol. cm^2)	A_t/A_c
CH_3O	cis	1730	138	15.5	3.36	4.60
	trans	1752.4	863	11.4	15.45	
H	cis	1731	157	14.8	3.65	3.88
	trans	1752.1	785	11.5	14.17	
Cl	cis	1733	188	18.0	5.31	2.21
	trans	1752.1	646	11.6	11.76	

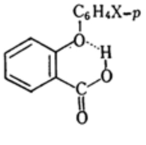
The infrared spectral data* are summarized in Tables I and II. It will be seen that the electronic effect of thes ubstituent is operative to the hydrogen bonding. An electron repelling group at the *para*-position enhances the hydrogen bond formation and causes a larger A_t/A_c ratio, where A_t and A_c represent the integrated intensities due to trans and cis isomers, respectively.



Ia



Ib



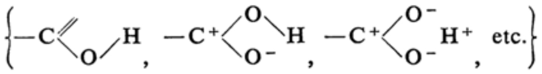
II

In the ν_{O-H} region, the band at the lower frequency (3411~3350 cm^{-1}) is undoubtedly assigned to the trans hydrogen-bonded isomer (II). On the other hand, the assignment of the $\nu_{C=O}$ absorption band is not clearly established and the lower $\nu_{C=O}$ band has been assigned to the trans isomer by several investigators. Quite contrary to the previous assignment, the present authors attribute the higher $\nu_{C=O}$ band (ca. 1752 cm^{-1}) for aryloxybenzoic acids) to the trans isomer from the following reasons.

i) The ratio A_t/A_c increases as the Hammett's σ-constant of the substituent decreases, and this tendency is consistent with the A_t/A_c ratio in the ν_{O-H} region.

ii) Through the intensity measurement at various temperatures with the ν_{O-H} and the $\nu_{C=O}$ bands of o-phenoxybenzoic acid, nearly equal energy difference (ΔH) values (1.90 kcal./mol. with the ν_{O-H} bands and 1.87 kcal./mol. with the $\nu_{C=O}$ bands) for the equilibrium between the cis and the trans isomers were obtained by assuming the assignment in Table II.

iii) Since the resonance forms of the cis isomer illustrated below are possible and the ionic character of the C=O bond may cause the lower C–O bond order, the lower $\nu_{C=O}$ frequency than the trans isomer is expected.



The ultraviolet spectra of these acids were

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* The infrared measurement was carried out with a Perkin Elmer 112G spectrophotometer under the condition in which the spectral slit width was less than 1.0 cm^{-1} for the ν_{OH} region and less than 0.7 cm^{-1} for the $\nu_{C=O}$ region. (See Refs. 5 and 6) The samples were dissolved in carbon tetrachloride to make up ca. 0.001 mol./l. solution.

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

also measured and an outstanding hypsochromic shift of B-band[7] was observed when the solvent was changed from heptane to ethanol. (For example, the bands at 287 and 293 mμ of *o*-phenoxybenzoic acid in heptane shift to 274 and 279 mμ.) This phenomenon can be interpreted as support for the existence of an intramolecular hydrogen bonding.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

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[7] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy", Edward Arnold Ltd., London (1954), p. 124.