# *The Electronic Effect of the Substituents on the Intramolecular Hydrogen Bonding of o-Aryloxybenzoic Acids**

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As early as 1955, Davies[1,2] reported the intramolecular hydrogen bonding of *o*-methoxybenzoic acid (II: $R=CH_3$); the enthalpy of the hydrogen bonding was then estimated to be 3.3 kcal./mol. It is also known that *o*-alkoxy- and *o*-aryloxybenzoic acids show some anomalous properties which may be attributed to intramolecular interaction.[3-5] In spite of this early discovery, however, systematic studies of this phenomenon are lacking and little is known about its nature. Since the authors are interested in the intramolecular hydrogen bonding of carboxylic acids, this work was undertaken as an extension of their earlier work.

An earlier study disclosed that the intramolecular hydrogen bonding of the alkoxy- and aryloxy-alkanoic acids is observed only when the alkoxyl or aryloxyl group is placed at the $\alpha$-position of the carboxyl group to form five-membered rings by means of the hydrogen bond (III: $n=1$).[6] Therefore, we have to face a very interesting problem; "Why does the six-membered hydrogen bond system exist very stably in *o*-alkoxybenzoic acid, but not in $\beta$-phenoxy- or $\beta$-methoxy-propionic acid (III: $n=2$)?" In order to clarify the situation, various effects on the interaction must be studied. Thus, the electronic effect exerted by the substituent in the aryl group of *o*-aryloxybenzoic acid was investigated as a first step, the effect of the configuration being also discussed.

## Experimental

**The Preparation of Materials.** — All the *o*-aryloxybenzoic acids were prepared from *o*-chlorobenzoic acid and the corresponding phenols by modifying Fritzsche's method[7] as described below.

Into a methanol solution (70 ml.) of sodium methoxide prepared from 4.6 g. (0.2 g. atom) of sodium, a mixture of phenol (9.4 g., 0.1 mol.) and *o*-chlorobenzoic acid (15.7 g., 0.1 mol.) was added with efficient stirring. As soon as the addition was over, about 0.5 g. of copper powder was added, and then the solvent was distilled off to dryness by immersing the flask in an oil bath kept at 150°C. The reaction mixture was heated up to 190~220°C in the oil bath, whereupon the abrupt initiation of the condensation was observed. After an hour, the reaction mixture was cooled and the entire mixture dissolved in water. After filtration, the filtrate was acidified to give crude *o*-phenoxybenzoic acid. Recrystallization from xylene-ligroin yielded 18.0 g. (84%) of the pure compound. Similarly, the following compounds were prepared (Table I):

TABLE I. ANALYTICAL DATA AND PHYSICAL CONSTANTS OF 2-(*p*-SUBSTITUTED PHENOXY)-BENZOIC ACIDS

| *p*-Substituent | Analytical data: Calcd., % | | | | M. p. °C |
|---|---|---|---|---|---|
| | C | H | Found, % C | H | |
| Acetyl | 70.30 | 4.72 | 70.34 | 4.83 | 182 |
| Chloro | 62.70 | 3.63 | 62.93 | 3.78 | 112 |
| Methoxy | 68.84 | 4.95 | 68.86 | 4.96 | 144 |

**Measurement of the Spectra.** — The infrared spectra were recorded with a Perkin Elmer 112G grating infrared spectrophotometer; the spectral slit widths were 1.0 cm$^{-1}$ and 0.6 cm$^{-1}$ for the O-H and C=O stretching regions respectively. The measurement was carried out in a carbon tetrachloride solution with a concentration of less than

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[*] The preceding paper: M. Ōki and M. Hirota, This Bulletin, **36**, 290 (1963).

1) M. Davies and D. M. F. Griffiths, *J. Chem. Soc.*, **1955**, 132.

2) M. Davies, "Hydrogen Bonding—Papers presented at the Symposium on Hydrogen Bonding held at Ljubljana, 29 July—3 August, 1953" (Pergamon Press, 1959), p. 393.

3) C. J. W. Brooks, G. Eglinton and J. E. Morman, *J. Chem. Soc.*, **1961**, 106.

4) D. Peltier and A. Pichevin, *Bull. soc. chim. France*, **1960**. 1141.

5) O. H. Wheeler, *Can. J. Chem.*, **39**, 2603 (1961).

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

7) P. Fritzsche, *J. prakt. Chem. N. F.*, **20**, 269 (1879).

0.002 mol./l. in the $\nu_{O-H}$ region and less than 0.0005 mol./l. in the $\nu_{C=O}$ region at 20∼25°C. Each absorption curve was assumed to be a Lorentzian curve, and the integrated intensity was calculated from the equantion :[8,9]

$$A=2.30\times\frac{\pi}{2}\cdot\frac{1}{cl}\log\left(\frac{T_0}{T}\right)_{max}\times\Delta\nu_{1/2}$$

Since the spectral measurements were carried out under conditions which gave spectral slit widths less than one-tenth of the half-band width, the application of the equation is permissible.

TABLE II. THE INFRARED ABSORPTION SPECTRA OF *o*-(*p*-SUBSTITUTED PHENOXY)BENZOIC ACIDS ($p$-$XC_6H_4OC_6H_4COOH$-$o$)

The $\nu_{O-H}$ absorption data

| X | | $\nu_{max}$ cm$^{-1}$ | $\varepsilon_{max}$ | $\Delta\nu_{1/2}$ | $A\cdot10^{-2}$ | $A_t/A_c$ |
|---|---|---|---|---|---|---|
| $CH_3O$ | cis | 3528.2 | 22.9 | 29.7 | 2.46 | 13.7 |
| | trans | 3391.0 | 130 | 53.2 | 24.98 | |
| | | 3350.4 | 44.0 | 54.5 | 8.65 | |
| $CH_3$ | cis | 3528.4 | 33.5 | 30.9 | 3.75 | 8.12 |
| | trans | 3393.8 | 125 | 54.0 | 24.38 | |
| | | 3350.1 | 30.9 | 53.6 | 5.98 | |
| H | cis | 3527.8 | 40.4 | 29.8 | 4.35 | 6.70 |
| | trans | 3399.5 | 120 | 50.6 | 21.92 | |
| | | 3357.9 | 34.1 | 58.4 | 7.20 | |
| Cl | cis | 3527.6 | 59.6 | 30.1 | 6.49 | 2.86 |
| | trans | 3411.7 | 74.7 | 54.5 | 14.70 | |
| | | 3374.8 | 17.4 | 61.6 | 3.86 | |
| $CH_3CO$ | cis | 3528.6 | 66.8 | 42.2 | 10.19 | 0.903 |
| | trans | 3421.5 | 36.1 | 53.3 | 6.95 | |
| | | 3387.6 | 11.3 | 55 | 0.98 | |

TABLE III

The $\nu_{C=O}$ absorption data

| X | | $\nu_{max}$ cm$^{-1}$ | $\varepsilon_{max}$ | $\Delta\nu_{1/2}$ | $A\cdot10^{-3}$ | $A_t/A_c$ |
|---|---|---|---|---|---|---|
| $CH_3O$ | cis | 1730 | 74.0 | 15.5 | 4.14 | 8.58 |
| | trans | 1752.4 | 863 | 11.4 | 35.54 | |
| | | 1762 | 73.0 | 12.3 | 3.24 | |
| $CH_3$ | cis | 1730.7 | 102 | 15.9 | 5.86 | 6.76 |
| | trans | 1750.9 | 838 | 13.1 | 39.65 | |
| | | 1759 | 138 | 10.6 | 5.28 | |
| H | cis | 1731 | 157 | 14.8 | 8.40 | 3.88 |
| | trans | 1752.1 | 785 | 11.5 | 32.59 | |
| | | 1762 | 155 | 10.4 | 5.82 | |
| Cl | cis | 1733 | 188 | 18.0 | 12.21 | 2.21 |
| | trans | 1752.1 | 646 | 11.6 | 27.05 | |
| | | 1763 | 135 | 10.6 | 5.17 | |
| $CH_3CO$ | cis | 1733.9 | 154 | 17.2 | 9.56 | 1.13 |
| | trans | 1752.0 | 268 | 11.2 | 10.84 | |
| | | 1761 | 53.5 | 14.0 | 2.70 | |

## Results and Discussion

The O–H stretching and the C=O stretching absorptions were determined with various *o*-(*p*-substituted phenoxy)benzoic acids; the results are summarized in Tables II and III.

**Assignment of the Infrared Spectra.**—Before the intramolecular hydrogen bonding is discussed, the assignment of the absorption bands should be carried out. The O–H and the C=O stretching absorption spectra of *o*-phenoxybenzoic acid are illustrated in Figs. 1 and 2 respectively. In the O–H stretching region, three absorption bands were found; the one at 3527.8 cm$^{-1}$ is no doubt the absorption caused by the monomeric cis-configuration (IIa), while the others may arise from the monomeric trans forms and/or the dimeric forms.

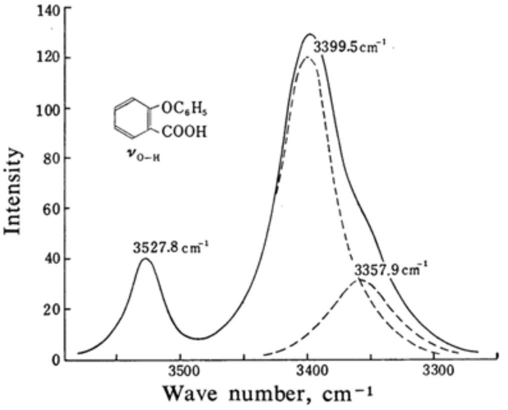


Fig. 1

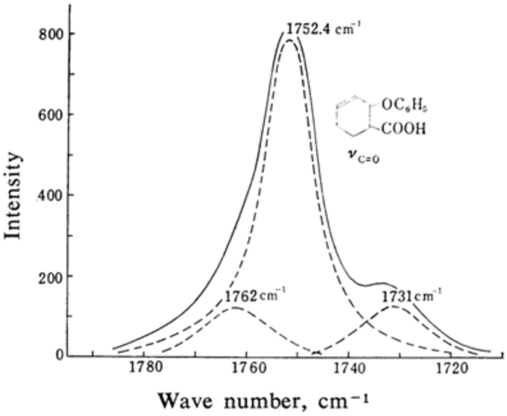
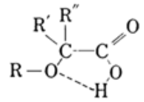


Fig. 2



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$R=CH_3$, $C_2H_5$, $CH(CH_3)_2$ or $XC_6H_4$
$R'$ and $R''=H$ or $CH_3$

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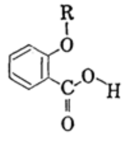
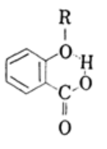
[8] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[9] K. Kuratani et al., *J. Japanese Chem.* (*Kagaku-no-ryôiki*), Suppl. Ed., No. 31, 1 (1958).



IIa



IIb

$RO(CH_2)_nCOOH$
III

The results obtained at various concentrations, however, exclude the latter possibility, and so the two absorption bands at 3399.5 cm$^{-1}$ and 3357.9 cm$^{-1}$ are both attributed to the hydrogen-bonded trans-configuration.

Then the measurement was carried out at various temperatures, with both the O–H and the C=O stretching absorptions (Table IV),

TABLE IV. THE TEMPERATURE DEPENDENCE OF THE INTENSITY RATIO ($A_t/A_c$) OF *o*-PHENOXYBENZOIC ACID

$\nu_{O-H}$ Region

| $T$, °K | 1000/$T$ | Absorption intensity | | Intensity ratio |
|---|---|---|---|---|
| | | $\varepsilon_{cis}$ | $\varepsilon_{trans}$ | $\varepsilon_t/\varepsilon_c$ |
| 296.7 | 3.37 | 43.0 | 122 | 2.83 |
| 307.0 | 3.26 | 47.2 | 125 | 2.65 |
| 317.2 | 3.15 | 53.5 | 125 | 2.32 |
| 325.5 | 3.07 | 62.8 | 129 | 2.09 |
| 339.2 | 2.95 | 64.4 | 124 | 1.93 |

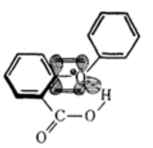
$\Delta H$=1.89 kcal./mol.

$\nu_{C=O}$ Region

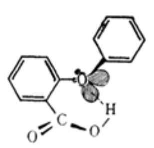
| $T$, °K | 1000/$T$ | Absorption intensity | | Intensity ratio |
|---|---|---|---|---|
| | | $\varepsilon_{cis}$ | $\varepsilon_{trans}$ | $\varepsilon_t/\varepsilon_c$ |
| 296.7 | 3.37 | 135 | 852 | 6.31 |
| 312.7 | 3.19 | 149 | 845 | 5.77 |
| 322.8 | 3.10 | 154 | 792 | 5.14 |
| 336.0 | 2.98 | 169 | 794 | 4.70 |
| 345.2 | 2.90 | 208 | 864 | 4.16 |

$\Delta H$=1.78 kcal./mol.

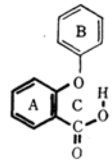
and the enthalpy difference, $\Delta H$, for IIa → IIb was determined to be 1.89 kcal./mol. from the results obtained in the O–H stretching region by assuming the above assignment. Here the 3357.9 cm$^{-1}$ band is disregarded for the sake of simplicity. From the $\nu_{C=O}$ spectrum, the enthalpy difference is determined to be 1.78 kcal./mol. by assigning the band at 1731 cm$^{-1}$ to the cis configuration and the band at 1752.4 cm$^{-1}$ to the trans. The agreement of the two $\Delta H$ values supports the above assignment and also the reliabilty of the enthalpy difference value for this equilibrium. The much smaller $\Delta H$ value than that of *o*-methoxybenzoic acid indicates a weaker hydrogen bonding; this will be discussed later. The fact that the carbonyl absorption of the trans isomer appears at a higher frequency had already been interpreted as arising from the absence of intramolecular interaction between the hydroxyl and the carbonyl group in the same carboxyl group.[6,10]



IVa



IVb



IVa'

The carbonyl band at 1762 cm$^{-1}$ is assigned to the trans-configuration which causes the 3357.9 cm$^{-1}$ band in the O–H stretching region, from the parallel change in intensity.* On the other hand, the higher C=O stretching band should be assigned to the structure which makes the less contribution to the resonance between the benzene nucleus and the carboxylic C=O group. Thus, the trans $\nu_{O-H}$ absorption at the higher frequency and the $\nu_{C=O}$ absorption at the lower frequency are attributed to the system IVa (The thick lines in IVa' indicate the planar conjugated system.), while the trans $\nu_{O-H}$ absorption at the lower frequency and the trans $\nu_{C=O}$ absorption at the higher frequency are attributed to the less probable conjugate system, IVb. In the IVa system, the hydrogen bond is formed by the lone pair electrons conjugating with the B ring (in IVa'), and the hydrogen-bonded ring system C is on the same plane with the ring system A, a pseudo-aromatic nature being expected. On the other hand, the hydrogen bond is formed by the participation of the lone pair electrons conjugating with the A ring in the IVb system, and the conjugated six-membered hydrogen bond system existing in IVa is partly destroyed.

The diphenyl ether system is concluded to be non-planar, and the two stable rotational isomers are assumed by some authors.[11] It is obvious, in accordance with the postulation, that the existence of the two rotational isomers is also probable in this diphenyl ether system, that of *o*-aryloxybenzoic acids.

In the case of *o*-aryloxybenzoic acids, the shift of the $\nu_{O-H}$ absorption maxima caused

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[10] M. Ōki and M. Hirota, *Spectrochim. Acta*, **17**, 583 (1961).

* The following may be added as another proof for this assignment. The introduction of a 3-alkyl group to 2-methoxybenzoic acid causes a $\nu_{O-H}$ shift to a lower frequency. It is assumed that the steric interference between 3-alkyl and 2-methoxyl groups causes the rotation of the $C_{Ph}$-O bond, leaving the $CH_3O$ group intact; therefore, the hydrogen bonding may be strengthened because of the richer electron density of the oxygen atom. Therefore, a higher $\nu_{O-H}$ absorption corresponds to a more planar structure.

[11] One of the latest reports on this problem is that of S. Fujiwara H. Shimizu, and Y. Morimo, *J. Chem. Phys.*, **34**, 1467 (1961). See also K. Higashi and S. Uyeo, This Bulletin, 14, 87 (1939).

by the hydrogen bonding ($\Delta\nu_{max}$) is much larger than in the case of 2-aryloxyalkanoic acids, but the assignment established to the latter is qualitatively applicable.

**The Substituent Effect on the Absorption Intensity.**—The data in Tables II and III show the variation of the ratio ($A_t/A_c$) of the absorption intensity due to the trans isomer to that due to the cis isomer with the change in the electronic nature of the substituents; this result is illustrated by the $\log(A_t/A_c)$ vs. $\sigma$ relation presented in Fig. 3. Table V also gives numerical values.

In general, the hydrogen bonding is favorable when the electron density of the hydrogen-accepting atom (the ether oxygen atom in this case) is large; therefore, the larger $A_t/A_c$ ratio is expected for the bases with electron-repelling substituents.

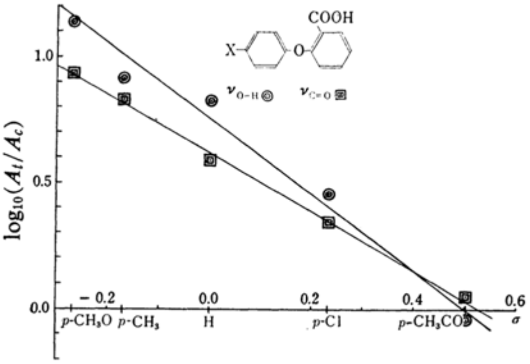

Fig. 3

TABLE V. THE RELATION BETWEEN THE $\sigma$-CONSTANT AND $\log(A_t/A_c)$ OF $o$-($p$-SUBSTITUTED PHENOXY)BENZOIC ACIDS

| Substituent | $\sigma$-Constant | $\log(A_t/A_c)$ | |
|---|---|---|---|
| | | O–H Region | C=O Region |
| CH$_3$O | −0.268 | 1.137 | 0.933 |
| CH$_3$ | −0.170 | 0.910 | 0.830 |
| H | 0.000 | 0.826 | 0.589 |
| Cl | 0.227 | 0.456 | 0.344 |
| CH$_3$CO | 0.502 | −0.044 | 0.053 |

This tendency is observed in many hydrogen bond systems, and the same is observed with the spectra of $o$-aryloxybenzoic acids, in both the O–H and C=O absorption bands. This finding also supports the assignment of the $\nu_{C=O}$ absorptions, since the opposite inclination of the $\log(A_t/A_c)$ vs. $\sigma$ plot would be expected from a wrong assignment.

**Conclusions on the Nature of the Hydrogen Bonding.**—The hydrogen bonding in $o$-aryloxybenzoic acid causes a much larger $\nu_{O-H}$ shift and enthalpy gain, and the hydrogen-bonded species are much more favorable than are $\alpha$-aryloxyacetic acids and their homologs. This cannot be explained by the steric factor only. The pseudo-aromatic nature of the hydrogen bond system (the C ring in IVa′) could explain the unusual stability of this hydrogen bonding. The pseudo-aromatic nature of the hydrogen bond system will be established in the following paper.[12]

## Summary

The infrared hydroxyl and carbonyl absorptions of $o$-aryloxybenzoic acids have been reported and the assignment of each absorption band in these regions made. The higher carbonyl-stretching absorptin at about 1752 cm$^{-1}$ has been attributed to the intramolecular hydrogen-bonded trans isomer from the following reasons: i) The $A_i/A_c$ intensity ratio in the hydroxyl-stretching region increases as the Hammett $\sigma$-constant of the substituent decreases, and the same tendency is observed by assigning the carbonyl band at a higher frequency to the trans isomer; ii) From the measurement of the absorption intensity of 2-phenoxybenzoic acid at various temperatures, in both the hydroxyl and carbonyl regions, the authors have obtained nearly equal enthalpy difference values (1.89 and 1.78 kcal./mol. respectively) between the cis and trans isomers by assuming the above assignment.

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[12] M. Ōki and M. Hirota, This Bulletin, 37, 213 (1964).