## *Intramolecular Hydrogen Bonding in α-Keto- and α-Alkoxy-carboxylic Acids*[1]

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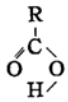
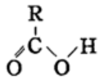
A number of hydroxylic compounds which carry a proton accepting group at a suitable position have been verified to form an intramolecular hydrogen bonding, but only a few examples of intramolecular hydrogen bonding involving the hydroxyl group of a carboxyl group as a proton donor have been known. The structure of a normal carboxyl group has been suggested to be non-planar, the O–H bond being 30° away from *cis*-planar conformation[2]. However, when an acid has a proton accepting group at α- or β-position to the carboxyl group, the *trans*-structure will be stabilized owing to the formation of an intramolecular hydrogen bonding and will be allowed to exist in spite of the otherwise unfavorable conformation.

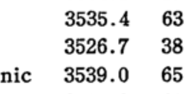

(I) *cis*-Structure


(II) *trans*-Structure

In this regard, the infrared spectra of such compounds including monomethyl oxalate, pyruvic acid, methoxyacetic acid, phenoxyacetic acid, and their homologues were examined with a Perkin Elmer 112G Spectrophotometer in carbon tetrachloride solution[3]. The concentration of the solution was less than 0.002 mol./l. in order to minimize the effect of dimeric association. As summarized in Table I, the results show that a carboxylic acid which carries a proton accepting group at α-position bear two $\nu_{O-H}$ bands. The results may be interpreted as an evidence for the existence of a hydrogen bonding and consequently for structure II. The peaks at higher frequencies appear between 3550 and 3500 cm$^{-1}$ and are assigned to the $\nu_{O-H}$ bands of free monomeric acids. The peaks at lower frequencies can be assigned to the $\nu_{O-H}$ bands of the intramolecularly hydrogen-bonded forms. It may be also pointed out that the intramolecular hydrogen bonding is observed only when a five membered ring is formed (structure III).

TABLE I. $\nu_{O-H}$ ABSORPTION OF THE CARBOXYL GROUP OF VARIOUS CARBOXYLIC ACIDS

| Acid | $\nu_{O-H}$ Absorption frequencies | | | |
|---|---|---|---|---|
| | Free form | | Hydrogen-bonded form | |
| | $\nu_{max}$ | $\varepsilon_{max}$ | $\nu_{max}$ | $\varepsilon_{max}$ |
| Monomethyl oxalate | 3516.3 | 34 | 3461.1 | 72 |
| Monomethyl malonate | 3529.9 | 58 | | |
| Pyruvic | 3528.9 | 16 | 3430.7 | 69 |
| Acetoacetic | 3530.7 | 60 | | |
| Benzoylformic | 3504.2 | 22 | 3397.2 | 69 |
| Benzoylacetic | 3535.4 | 63 | | |
| Methoxyacetic | 3526.7 | 38 | 3395.8 | 31 |
| β-Methoxypropionic | 3539.0 | 65 | | |
| Phenoxyacetic | 3527.9 | 60 | 3484.7 | 34 |
| β-Phenoxypropionic | 3531.7 | 68 | | |


(III)

Since the proton accepting power of an atom is largely influenced by the electron density, the authors expected some electronic effects to be exerted on the hydrogen bonding ability; the spectra of various substituted phenoxyacetic acids were thus measured. The results are in accordance with the expectation, as shown in Table II, where apparent integrated absorption intensities of the two bands

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[1] Part I: *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), in press.

[2] C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill Book Co., Inc., New York (1955), p. 306.

[3] M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

TABLE II. $\nu_{O-H}$ ABSORPTION OF *p*-SUBSTITUTED PHENOXYACETIC ACIDS

| Substituents | Free form | | Hydrogen-bonded form | | Intensity ratio* |
|---|---|---|---|---|---|
| | $\nu_{max}$ | $B_f$ | $\nu_{max}$ | $B_h$ | $B_h/B_f$ |
| $CH_3O$ | 3527.7 | 1.28 | 3481.3 | 1.02 | 0.80 |
| $CH_3$ | 3528.8 | 1.21 | 3484.5 | 0.96 | 0.79 |
| H | 3526.9 | 1.54 | 3487.5 | 0.75 | 0.49 |
| Cl | 3524.3 | 2.32 | 3492.9 | 0.74 | 0.32 |
| $C_6H_5CO$ | 3525.6 | 2.5 | 3495.6 | 0.25 | 0.10 |
| $NO_2$ | 3521.8 | | Not found. | | 0 |

* The ratio is a more important factor than the individual integrated intensity in discussing the properties of the bands, since the effect of the dimeric form can not be completely neglected.

were obtained graphically instead of taking the absorption coefficient because of the closeness of the two bands.

Another evidence for the existence of the hydrogen bonding may be obtained from the measurement of the carbonyl region. The measurement revealed that two bands are also found for the monomeric acid when it carries a proton accepting group at the $\alpha$-position and that the higher frequency absorption disappears when no hydrogen bonding is observed in the O–H stretching region. Thus, the peak at about $1790\,cm^{-1}$ is assigned to the $\nu_{C=O}$ band of structure II and that between 1735 and $1730\,cm^{-1}$ to structure I.

The details will be reported in the near future.

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