Intramolecular Hydrogen Bonding Between the Carboxyl O–H Group and Nitrogen

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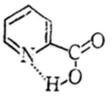
A series of previous investigations in the laboratories of the present authors[1] confirmed the existence of the intramolecular COOH···O hydrogen bond. The rather rare occurence of the hydrogen bond was explained in terms of the stability of the *cis* conformer.

The investigation is now extended to the hydrogen bond including nitrogen as a hydrogen acceptor. The infrared ν_{OH} and the $\nu_{C=O}$ absorptions of pyridine-2-carboxylic (I) and quinoline-2-carboxylic (II) acids were determined as examples of the five-membered hydrogen chelates, and the existence of the intramolecular hydrogen bond was indicated by the appearance of the ν_{OH} bands at lower frequencies (as are listed in the table). The higher $\nu_{C=O}$ frequencies of the acids, I and II, than the acids without intramolecular hydrogen bonds may be attributable to the trans conformation, which is a natural consequence of the formation of the hydrogen bonds, as has been discussed earlier in connection with the oxygen analogs.

The enthalpies of hydrogen bond formation were obtained from the temperature dependence of the relative intensities of the two ν_{OH} absorptions. From a comparison of the data with those for α-alkoxy- and α-keto-carboxylic acids, it has been shown that the COOH···N hydrogen bonds in I and II are by far more favorable in spite of the smaller ΔH values. These results may be explained as follows. The hydrogen bonded conformer should have a planar *s-trans* conformation such as 1, which is one of the stable conformations from the viewpoint of the maximal conjugation between the aromatic heterocycles and the carboxyl group. In other words, the carboxyl groups of the molecules are so arranged as to be likely to form hydrogen bonds. Consequently, it is not the enthalpy but the entropy factor which controls the formation of the hydrogen bonds. The absence of the COOH···N hydrogen bond in *N*-methylanilinoacetic acid lends support to this conclusion; the COOH—N system is not planar in this molecule.



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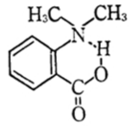

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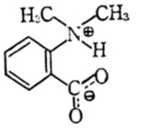

2_a

The hydrogen bond shifts of the ν_{OH} frequencies for *o*-dimethylaminobenzoic (III) and quinoline-8-carboxylic acids are extraordinarily large. The only ν_{OH} absorption observed is a broad band, distributed at from 2200 to 2750 cm^{-1}; it can be assigned to a hydrogen-bonded form such as 2. Intramolecular salt (2_a) formation seems to be improbable, since the carboxylic $\nu_{C=O}$ absorption appears at 1711 cm^{-1}* in both III and IV; this is too high for the antisymmetric stretching absorptions of the carboxylate anion. Ebullioscopic measurement also provides evidence for the strong hydrogen bond. Thus, no dimerization is observed over the concentration range in which benzoic acid dimerizes considerably; it can be explained that the strong intramolecular hydrogen bond prevents these acids from dimerization. Though no comparison of their thermodynamic quantities has been carried out, the larger $\Delta\nu$ value and the disappearance of the free ν_{OH} absorprtion in III and IV implies that a stronger hydrogen chelate is formed when a six-membered ring is to be made.

TABLE I. INFRARED SPECTRA AND HEAT OF HYDROGEN BOND FORMATIONIN DILUTE CCl_4 SOLUTION

Acid	ν_{OH} Absorption, cm^{-1} (Molar extinction coefficient)			$\nu_{C=O}$ Absorption, cm^{-1} (Molar extinction coefficient)	ΔH of H-bond formation (kcal./mol.)
	cis	trans	A_t/A_c		
Pyridine-2-carboxylic	3535 (9.1)	3328 (73.4)	17.8	1783 (657), 1772 (688)	0.2
Quinoline-2-carboxylic	3535 (13.0)	3333 (73.8)	12.8	1776 (1002)	0.8
N-Methylanilinoacetic	3535 (143)	—	—	1768 (822)	—

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

* This absorption lies at abnormally low wave numbers, compared with the ordinary *s-trans* carboxylic acid (ca. 1750 cm^{-1}). This may imply that there is some contribution of 2_a.