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HYDROGEN BOND STUDIED BY ^{14}N NUCLEAR MAGNETIC RESONANCE I.

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A number of theoretical treatments of the nature of a hydrogen bond have been presented by many authors, and these may be divided mainly into two groups, say electrostatic theory in which electrostatic forces are stressed[1)] and delocalization theory where stabilization due to delocalization is considered to be important.[2), 3)] Although it was pointed out in the delocalization theory that the contribution of a charge transfer structure $Y^{+} - H$ in $X - H \cdots Y$ hydrogen bond system or covalent bond between proton and acceptor in other words, was important, the contribution of such a structure has never been confirmed experimentally.

We observed that the peaks of ^{14}N NMR spectra[*1] of pyridine in methanol solution are shifted to higher field compared with the ^{14}N signal of neat pyridine as shown in Table I.

[*1] The ^{14}N NMR spectra were taken with Varian DP - 60 equipped with a V 4230 variable frequency oscillator at 4.3 Mc and VF 2100 FIELDIAL.

TABLE I ^{14}N CHEMICAL SHIFT OF PYRIDINE IN METHANOL

Mole fraction of pyridine	Chemical shift referred to 28% NH_4OH
1	-4.22 ± 0.02 gauss (-306 ± 1 ppm)
0.7	-4.13 ± 0.04 " (-299 ± 3 ")
0.5	-4.10 ± 0.03 " (-297 ± 2 ")

These shifts can be interpreted in terms of a hydrogen bond between pyridine and methanol. In the case of 0.5 mole fraction ^{14}N hydrogen bond shift is +9 ± 3 ppm from the ^{14}N signal of neat pyridine used as a reference standard. The OH proton shift for the same system, illustrated in Fig. I, shows that the maximum hydrogen bond is realized in 0.5 mole fraction. It is because the hydrogen bond OH ··· N is stronger than that of OH ··· O and the maximum hydrogen bond is formed at this concentration.

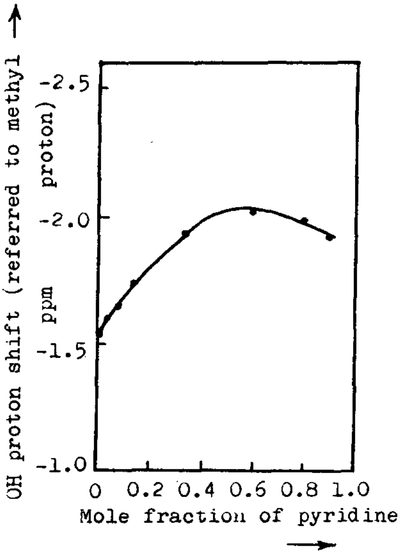

FIG. I OH PROTON SHIFT OF METHANOL IN PYRIDINE

The high field shift of ^{14}N signal in the hydrogen bond formation between OH and N may be interpreted in terms of paramagnetic shielding effect based on the Pople's theory[4)], as was done by Gil and Murrell in the case of the ^{14}N shift of pyridinium ion[5)]. In this report, however, another interpretation based on the valence bond theory describing the hydrogen bond is presented as follows.

According to Coulson and Danielsson[2)], a hydrogen bond system represented as XH $\cdots$ Y is considered to be the superposition of the following structures.

		wave function	contribution
(I)	X — H Y (pure covalent)	χ_I	w_I
(II)	X^- H^+ Y (ionic)	χ_{II}	w_{II}
(III)	X^- H — Y^+ (charge transfer)	χ_{III}	w_{III}

The wave function for the whole system is written as,

$$\Phi = C_I\chi_I + C_{II}\chi_{II} + C_{III}\chi_{III} \qquad (1)$$

and the contribution of each structure

$$w_i = \frac{C_i^2}{C_I^2 + C_{II}^2 + C_{III}^2} \times 100 \; (i = I,\ II,\ III) \qquad (2)$$

The valence bond calculation for OH $\cdots$ N system carried out by the present authors after the Coulson and Danielsson's method is given in Table II. In comparison, the results for OH $\cdots$ O system calculated by Coulson and Danielsson are also cited in Table II. Values used for the calculation are listed in Table III.

We will pick up the terms related to the ^{14}N hydrogen bond shift in each valence bond structure. In the first place, the structure (I) has no relation with ^{14}N hydrogen bond shift, because ^{14}N signal of the structure (I) is the same as that of neat pyridine. In the structure (II), ^{14}N signal may be affected by the electric field due to the neighboring H^+ and O^-.

TABLE II THE CONTRIBUTION OF EACH STRUCTURE

X-H ··· Y	$L_{X\cdots Y}$(Å)[b]	L_{X-H}(Å)[b]	D(kcal/mole)[c]	contribution ω_{I}(%)	ω_{II}(%)	ω_{III}(%)
O-H ··· N	2.80	1.05	12.0	76.7	14.1	9.2
O-H ··· O[a]	2.80	0.986	6.8	85.2	12.0	2.8
O-H ··· O[a]	2.50	0.997	14.4	81.7	12.2	6.1

a) The result by Coulson and Danielsson.[2] b) $L_{X\cdots Y}$ and L_{X-H} denote bond lengths X ··· Y and X-H, respectively.

c) hydrogen bond energy.

TABLE III VALUES USED FOR THE CALCULATIONS

	unit	N[e]	O[f]
R_e(X-H)[a]	Å	1.01	0.97
$\underline{a}$[b]	$Å^{-1}$	1.78 [8]	2.23
D_{GM}(X-H)[b]	kcal/mol	63.5 [9]	60.6
D(X-H)[c]	kcal/mol	87.7 [9]	110.2
ionization potential	kcal/mol	319 [11]	312.5
electron affinity	kcal/mol	17 [11]	50.7
α X-H[d]	cc	0.924×10^{-24} [10]	0.81×10^{-24}

a) R_e means X-H equilibrium bond length.

b) Values $\underline{a}$ and D_{GM} are constants in Morse function $D_{GM}[\exp(-2\underline{a}(R-R_e))-2\exp(-\underline{a}(R-R_e))]$ and D_{GM} means X-H covalent bond energy.

c) D(X-H) means dissociation energy of X-H bond.

d) A polarizability of X-H bond.

e) We assumed that hybridization of nitrogen is of sp^2 type.

f) The values are given by Coulson and Danielsson[2].

This effect, evaluated by the Marshall-Pople's formula[6), *2],

$$\sigma = - \frac{881}{216} \frac{a_0^3 E^2}{mC^2} \qquad (3)$$

makes the signal shift to lower field by about 0.2 ppm. This value is negligible considering the accuracy of experiment. Finally it is expected that the ^{14}N chemical shift of the structure (III) is almost the same as that of pyridinium ion, in which ^{14}N signal is shifted to high field by 123 ± 11 ppm as compared with that of neat pyridine according to the result of Baldeschwieler and Randall[7)]. In the latter cases lone pair electrons of nitrogen atom which are most effective to the paramagnetic shielding in ^{14}N resonance are eliminated. The $N^+ - H$ bond length in the present hydrogen bond system is greater than that of pyridinium ion[*3] and the excitation energy in the theoretical treatment of the paramagnetic shielding for nitrogen atom[4), 5)] $\sigma(N^+ - H) \rightarrow \pi^*$ is then expected to be smaller than that of pyridinium ion. However, considering that the mean excitation energy in the structure (III) is almost the same as that of pyridinium ion, and that lone pair electrons are eliminated in both structures, we may expect that ^{14}N signal of the structure (III) and that of the pyridinium ion are almost the same. If the actual electronic structure is the superposition

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[*2] Although this formula presents shielding constant for 1 s electron, it may be expected that there is not so much difference in nitrogen shielding. This point will be checked in future publication.

[*3] We adopted the O ··· N and H ··· N bond length are 2.80 Å and 1.75 Å, respectively[1)], and $N^+ - H$ bond length is cited as 1.034 Å in the case of ammonium chloride[12)]

of structures (I), (II) and (III),the apparent chemical shift δ_{obs} is expressed as,

$$\delta_{obs.} = \omega_{I}\delta_{I} + \omega_{II}\delta_{II} + \omega_{III}\delta_{III} \qquad (4)$$

where chemical shifts for each site are δ_I, δ_{II}, and δ_{III}, and population probabilities are ω_I, ω_{II}, and ω_{III}, respectively. By applying this formula to the above hydrogen bond system, the relation

$$\delta_{obs.} = \omega_{III}\delta_{III} \qquad (5)$$

is obtained, where δ_I and δ_{II} are zero from the reasons mentioned above. Then $\omega_{III} = 7 \pm 3\%$ is obtained using the observed values, $\delta_{obs.} = 9 \pm 3$ ppm and $\delta_{III} = 123 \pm 11$ ppm (^{14}N shift of pyridinium ion).

The coincidence between the observed and calculated values of ω_{III}, the latter being shown in Table II, is satisfactory.

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REFERENCES

1) see G. C. Pimentel and A. L. McClellan, "The Hydrogen bond", pp. 227 - 254. W. H. Freeman and Company (San Fransisco) 1960.

2) C. A. Coulson and U. Danielsson, Arkiv Fysik, 8, 239, 245 (1954).

3) H. Tsubomura, Bull. Chem, Soc. Japan, 27, 415 (1954).

4) J. A. Pople, J. Chem. Phys., 37, 53 (1962).

5) V. M. S. Gil and J. N. M. Murrell, Trans. Faraday Soc., 60, 248 (1964).

6) T. W. Marshall and J. A. Pople, Mol. Phys. 1, 199 (1958).

7) J. D. Baldeschwieler and E. W. Randall, Proc. Chem. Soc., 1961, 303.

8) G. Herzberg, "Molecular Spectra and Molecular Structure (I)",

D. Van Norstand Co. (1950).

9) L. Pauling, "The Nature of Chemical Bond" Third Edition, Cornell Univ. Press. (1960).

10) J. O. Hirshfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids" John Wiley and Sons. Inc. (1954).

11) H. O. Pritchard and H. A. Skinner, Chem. Revs., 55, 745 (1955).

12) "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London (1958).