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Analysis on NMR Spectra of 8-Hydroxyquinoline and Its Solvent Effects

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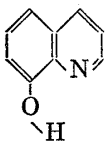
Analysis of nuclear magnetic resonance spectra of 8-hydroxyquinoline precisely have been carried out in various solvents, and the values of chemical shifts and coupling constants of the ring protons are extraporated in infinite dilution. These extraporated values indicate the characteristic and functional natures of solvents interacting with the solute molecule. The concentration and the solvent dependences are discussed in detail.

8-Hydroxyquinoline (**1**) is a very familiar, simple and well-known compound. A considerable number of studies on the metal chelations, fluorescences, MO calculations and the various spectroscopic approaches of this compound have been carried out.



(1)

The proton magnetic resonance spectrum of this compound has been recorded and analyzed previously by Reeves.[2] But these reported spectra were not sufficiently resolved to permit a detail analysis, and we have accordingly obtained more highly resolved recordings. The chemical shifts and the coupling constants of ring protons in various solvents (carbon tetrachloride, chloroform, acetone, acetonitrile, carbon disulfide, dimethyl sulfoxide, dioxane and pyridine) have been obtained and the values were extrapolated to infinite dilution in each solvent. In addition, the detailed discussions on solvent effects and concentration dependences are performed.

Moreover, the present paper will be referred on the existence of long range coupling in this compound, inter- and intra-molecular hydrogen bondings and the effect of a quadrupole moment of ^{14}N. First, it is interesting that the long range coupling can be found between C-4 proton and C-5 proton. Secondly, the presence of intermolecular hydrogen bonding is of notable. Previously Reeves[2] assumed from the interatomic distance that the intramolecular hydrogen bonding almost did not existed, while Aramaki[3] reported on the presence of intramolecular hydrogen bonding which was evidenced with infrared (IR) spectra measured in carbon tetrachloride. From our nuclear magnetic resonance (NMR) study, it comes to the conclusion that an intramolecular hydrogen bonding is not found remarkably. And lastly, the electric quadrupole effect of ^{14}N is made manifest in NMR signals of C-2 proton. Owing to this effect, the line width of C-2 proton displays the temperature dependence.

Experimental

Materials——8-Hydroxyquinoline and solvents are commercial products (reagent grade and spectra grade, respectively).

Preparation of Sample——8-Hydroxyquinoline is supplied for this study with refining by sublimation in high vacuum after recrystalized several times. Deutero solvents are dehydrated on the molecular sieves 3A (1/16 meshes) previously dried by heating. The solutions of this compound are degassed by freezing and thowing several times under high vacuum (10^{-5} mmHg). Owing to the solubility limitation of this compound in various solvents, the concentration range used in this experiment is from *ca.* 0.1M to *ca.* 5M.

Recording of Spectra——The proton magnetic resonance spectra were taken with a JNM-C-60-H high resolution NMR spectrometer operating at 60 MHz and with the external lock system, sweep rate 0.9 Hz/sec

1) Location: *2-2-1, Ozika, Shizuoka.*
2) L.W. Reeves and K.O. Stroemme, *Can. J. Chem.*, 39, 2318 (1961).
3) K. Aramaki and S. Fujii, *Boshoku Gijutsu*, 14, 350 (1965).

at a room temperature (23°). Tetramethylsilane was used as the internal standard and all chemical shifts were given in Hz down-field from this origin. The spectra were calibrated by interporation from side bands generated by an audio oscillator. The audio oscillator was continuously monitored by a frequency counter. The chemical shifts and the coupling constants are accurate to less than ±0.3 Hz unless otherwise specified.

Analysis——Simulation and the iterative method used the least square are applied to a variety of the spin systems. The computations are done until the value of parameters, the differences between calculated value and observed values, are reduced by about 1/100 Hz in an error using the iterative method,[4] which is the most available method to estimate the magnetic parameters. The computations are carried out by NEAC 2200—400 and HITAC 5020 with Fortran Language, using in part the library program "H-DIAG" of Tokyo University.

Result and Discussion

The nuclear magnetic resonance spectra of 8-hydroxyquinoline are consisted of the resonance lines of the AMX three spin system arising from C-2, C-3 and C-4 protons and the complicated ABC three spin system arising from C-5, C-6 and C-7 protons and a single broad line arising from OH proton, as is shown in Fig. 1. Then the C-3 resonance lines are overlapped with those of the complicated ABC spin system described above.

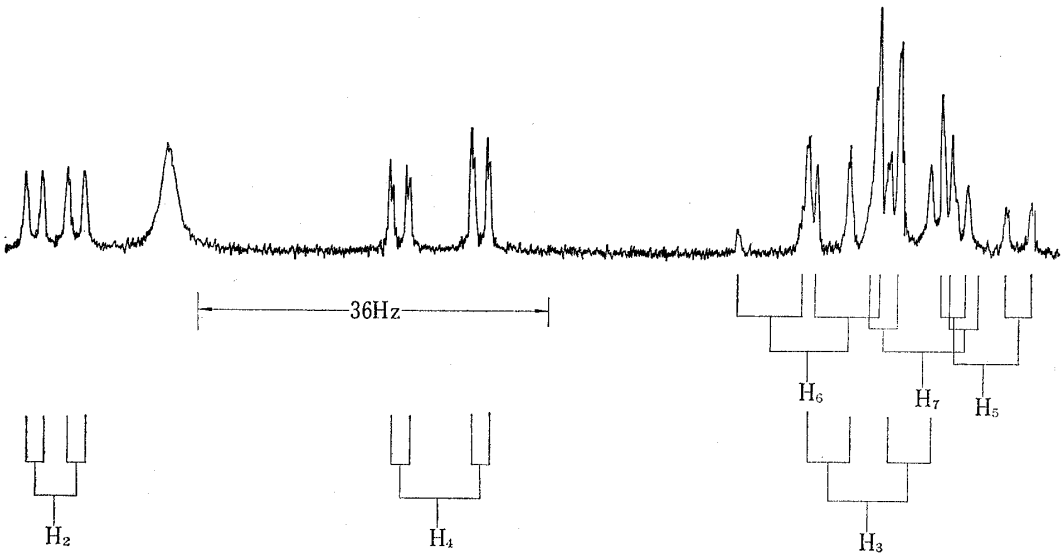


Fig. 1. The NMR Spectrum of 8-Hydroxyquinoline in Carbon Tetrachrolide and Its First Order Analysis

Each of the quartet resonance lines of C-4 proton showed a further fine splitting because of a long range spin-spin interaction with C-5 proton. In general, a weak spin-spin interaction observed with quinolinoid ring compounds may be expected to be the one between C-5 proton and C-8 proton as is known as the cross ring long range coupling,[5] but such a long range coupling can not exist because of replacement C-8 proton with OH substituent.

The C-2 proton resonance lines becomes broadened with an increase in temperature as shown in Fig. 2. This broadening is responsible for the quadrupole moment of nitrogen atom coupled with C-2 proton. In general, the broadened resonance lines must be removed by the irradiation to nitrogen atom, for example, the case of N-methylformamide.[6] The irradiation to nitrogen atom changed the slightly broadened C-2 resonance lines to sharper

4) J.W. Emsley, J. Feeney and L.H. Sutcliffe, "Progress in Nuclear Magnetic Resonance Spectroscopy, "Vol. 1, Chap. 3, Pergamon press, Oxford, 1966, p. 205.
5) M. Martin-Smith, S.T. Reid and S. Sternhell, *Tetrahedron Letters*, **1965**, 2393.
6) J.W. Emsley, J. Feeney and L.H. Sutcliffe, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 6, Chap. 3, Pergamon Press, Oxford, 1971, p. 127.

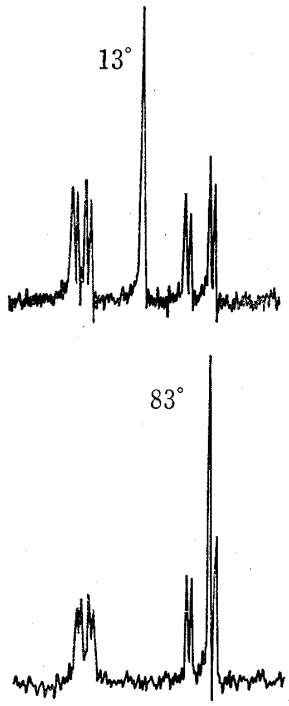


Fig. 2. The Temperature Dependence of the Quadrupole Moment of the Nitrogen Atom on C-2 Proton

The resonance lines on down-field side (quartet) come to be broadening with an increase in temperature.

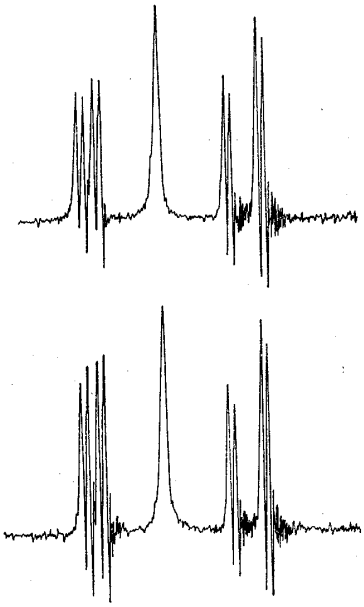


Fig. 3. The Effect of the Quadrupole Moment on C-2 Proton

The irradiation to ^{14}N disappears the effect of the quadrupole moment and makes the C-2 resonance lines more sharp one.

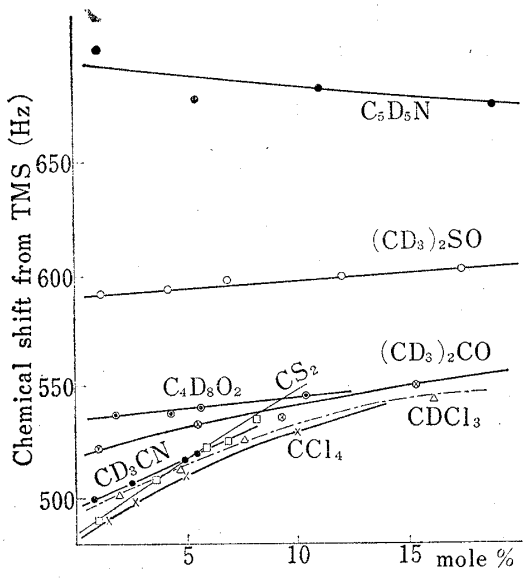


Fig. 4. Dilution Shifts of -OH Proton of 8-Hydroxyquinoline in Various Solvents

ones as shown in Fig. 3. This were confirmed the assignment of the resonance lines of C-2 proton. On the other hand, OH resonance line progressively moved to higher field with dilution, as shown in Fig. 4, and also with an increase in temperature. This phenomenon is illustrated by assuming the existence of intermolecular hydrogen bonding. The dilution effect generally correlates with the intermolecular hydrogen bonding but not with the intra molecular hydrogen bonding, and that it is in proportion to the amount of the intermolecular hydrogen bonding.

When the chemical shift differences are not suficiently large in comparison with the values of its coupling constants, the chemical shifts and the coupling constants which are directly obtained from observed spectra, in general, are not necessarily to display the original values. Accordingly the theoretical treatment was carried out and the calculated values of the chemical shifts and the coupling constants were extrapolated to infinite dilution. They are summerized in Table I and II.

The proton chemical shifts of aromatic compounds are found to be strongly dependent on the concentration as well as the temperature. Dilution of an aromatic compound with various solvents gives rise to the movement of the proton resonance lines, that is, results

Table I. The Chemical Shifts and the Coupling Constants of 8-Hydroxyquinoline on Infinite Dilution with Various Solvents

(Hz)	H_5	H_6	H_7	J_{56}	J_{57}	J_{67}
CCl_4	425.9	444.1	434.2	7.51	1.19	8.17
$CDCl_3$	432.1	448.2	441.1	7.51	1.22	8.25
$(CD_3)_2CO$	428.2	449.2	445.3	7.32	1.52	8.22
$C_4D_8O_2$	426.8	445.8	438.3	7.50	1.25	8.17
CD_3CN	428.4	448.6	444.3	7.38	1.61	8.16
CS_2	419.8	441.7	433.2	7.52	1.22	8.17
$(CD_3)_2SO$	426.2	447.8	444.3	7.24	1.65	8.09
C_5D_5N	441.3	450.6	445.0	8.14	1.80	7.10

Table II. The Chemical Shifts and the Coupling Constants of 8-Hydroxyquinoline on Infinite Dilution with Various Solvents

(Hz)	H_2	H_3	H_4	J_{23}	J_{24}	J_{34}
CCl_4	522.5	442.9	485.6	4.2	1.6	8.1
$CDCl_3$	527.0	445.5	489.5	4.2	1.6	8.1
$(CD_3)_2CO$	528.8	453.0	490.5	4.2	1.6	8.1
$C_4D_8O_2$	524.3	445.5	490.5	4.2	1.6	8.1
CD_3CN	528.7	449.9	496.4	4.2	1.6	8.1
CS_2	524.0	441.7	484.0	4.2	1.6	8.1
$(CD_3)_2SO$	531.3	453.5	500.3	4.2	1.6	8.1
C_5D_5N	534.0	441.5	490.0	4.2	1.6	8.1

in changes of the spectrum pattern. Further, it is necessary to discuss the phenomena described above from the viewpoint of the inter- and/or intra-molecular interactions. The proton chemical shifts for perturbation arise from the solute-solute and solute-solvent interactions. In the solvents which cause the specific interaction with the solute molecule, the shift arising from solute-solute interaction gradually decreases with dilution. On the contrary, that from solute-solvent interaction progressively increases and this shift comes to be exclusively predominant with infinite dilution. Then, in the solvents which do not cause the specific interaction with the solute molecule, the shift arising from solute-solute interaction gradually diminishes with dilution. In this case, this shift is obviously accounted for one from the "isolated" solute molecule.

Figure 5 shows the solvent shifts ($\Delta = \nu_0\delta_{\text{solv.}} - \nu_0\delta_{CCl_4}$) of the ring protons, *i.e.*, deviations from the chemical shifts measured in CCl_4. The used chemical shifts are quoted from Table I and II. Of course, if the specific solute-solvent interaction is taken as being absent in carbon tetrachloride, the solvent shift values seem to be in proportion to the strength of intermolecular interaction between a solute and a solvent. The more a graph is away from the horizontal line of carbon tetrachloride, the more a solvent peculiarly comes to interact with the solute molecule. Then, the tendencies of the solvent shifts can be classified into the four groups, 1) acetonitrile, dimethylsulfoxide and dioxane, 2) chloroform and pyridine, 3) carbondisulfide and 4) acetone. It is of interest that chloroform and pyridine belong to the same group on a function of the solvent. And also, especially it is noteworthy that the values of the solvent shifts on C-5 proton are most sensitive for the species of solvent.

The proton shilding constant generally depends upon the carbon π-electron density.[7] In present paper, each value of the proton chemical shift is qualitatively in accord with the corresponding carbon π-electron density on the nutral molecule of 8-hydroxyquinoline, except

7) M.R. Chakrabarty, E.S. Hanrahan and A.R. Leply, *Tetrahedron*, 23, 2879 (1967).

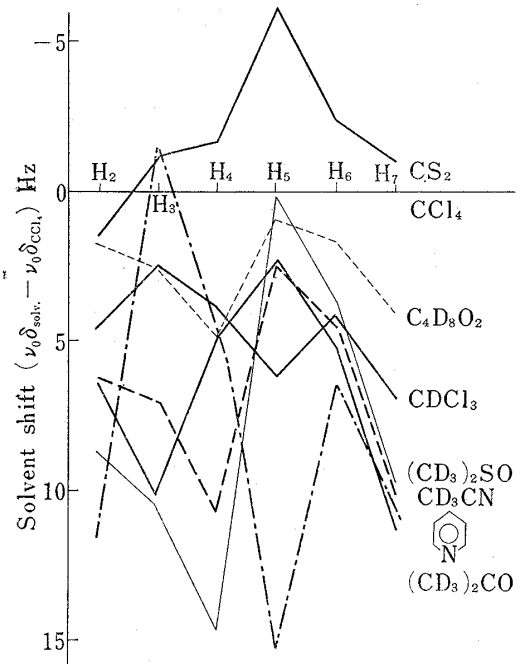


Fig. 5. Solvent Shifts ($\nu_0\delta$solv.$-\nu_0\delta_{CCl_4}$) of Ring Proton of 8-Hydroxyquinoline

TABLE III. The Correlation between π-Electron Densities on the Neutral Molecule of 8-Hydroxyquinoline and Its Proton Chemical Shifts

	π-Electron density	Chemical shift (Hz)
C-2	0.909	527.6
C-4	0.941	490.9
C-6	0.997	447.0
C-3	1.005	446.7
C-5	1.041	428.6
C-7	1.053	440.7

for C-5 and C-7 as listed in Table III. This inconsistency of C-5 and C-7 may be for the reason described below. The resonance line of C-7 actually appears in lower-field than it is intrinsic because of the effect of the magnetic anisotropy arising from somewhat nature of oxo-form in solution. And also the practical π-electron density of C-7 tends to be over-estimated, since the calculated π-electron densities are not taken account of the effect of the intermolecular interaction.

The results obtained in present paper on the solvent and concentration dependences of 8-hydroxyquinoline will be developed for the studies on the collision complex and the relation between the hydrogen bonding parameters of various solvents and the dilution shifts in forthcoming papers.

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