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The Solvent and Concentration Dependences of the Nuclear Magnetic Resonance Spectra of 8-Quinolinol

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The solvent and concentration dependences of proton magnetic resonance spectra of 8-quinolinol are investigated. The resonance lines of each proton indicate the selective and specific dilution shifts in various solvents. These shifts can be successfully accounted for by assuming the specific solute-solute interactions. It can therefore be presumed that there are both a self-collision complex and a dimerized hydrogen bond formed between solutes in this system.

Keywords——NMR; 8-quinolinol; solvent; complex; hydrogen; bond; crystal; structure; collision

Introduction

One of the interesting problems in the studies of intermolecular interactions is a chemical association formed between molecules. A number of investigations have been carried out in various field, the stacking between base pairs of deoxyribonucleic acid, charge transfer complexes, inclusion compounds, collision complexes and hydrogen bonds. Our attention to the collision complex and the hydrogen bond has been developed during investigations on the solvent and concentration effects of 8-quinolinol by proton magnetic resonance spectroscopy.[2] The resonance signals of this compound show the selective and specific dilution shifts in various solvents. The origin of the dilution shifts can be successfully accounted for by assuming the specific steric arrangement formed between solute molecules. This strongly suggests specific solute–solute interactions, a self-collision complex and a self-hydrogen bond formed between solute molecules regardless of the species of solvents. And the possibility of these interactions is further examined by other methods of infrared and crystallographycal analysis. On the other hand, solvent effects on each ring proton of this compound are discussed in detail by examining the correlations between dilution coefficients ($\Delta\delta/\Delta c$) which are defined from the slopes of the dilution curves well reflecting the solvent effects. A part of the discussion had been already proposed by us.[3]

In this present paper, we chiefiy discuss the origins of the specific dilution shifts and its solvent effects in detail, and refer to the possibility of the self-collision complex and the self-hydrogen bond.

Experimental

8-Quinolinol is supplied for this study with refining by sublimation in high vacuum after recrystalized several times. The solvents (carbon tetrachloride, carbon disulfide, chloroform-d_1, acetone-d_6, acetonitrile-d_3, dioxane-d_8, dimethyl-d_6 sulfoxide, pyridine-d_5) used are all dehydrated on the molecular sieves 3A (1/16 meshes) previously dried by heating. The samples are all degassed by freezing and thawing several times under high vacuum (*ca.* 10^{-5} mmHg). On account of the solubility limitation of this compound in various solvents, the concentration range used in this experiment is from *ca.* 0.1 M to *ca.* 5 M.

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[1] Location: *2-2-1, Ozika, Shizuoka.*
[2] S. Katayama, Y. Akahori, and H. Mori, *Chem. Pharm. Bull.* (Tokyo), **21**, 2622 (1973).
[3] S. Katayama and Y. Akahori, *Chem. Lett.*, **1977**, 503.

The ^{1}H nuclear magnetic resonance (NMR) spectra are measured by chiefly using JNM-C-60-H spectrometer, occasionally using FX-100 spectrometer at a room temperature (23°). Tetramethylsilane is used as the internal standard and all chemical shifts are given in Hz down-field from this origin. The spectra are all calibrated by interpolation from side bands generated by an audio oscillator. The audio oscillator is monitored by a frequency counter. The chemical shifts and the coupling constants are accurated to less than 0.3 Hz unless otherwise specified.

The analysis of the spin systems are carried out by simulation and iterative method using NEAC 2200-400 and HITAC 8700. The calculations are done until the values of parameters, the differences between theoretical and observed values are reduced by *ca.* 1/100 Hz in an error.

Results and Discussion

The Origins of the Dilution Shifts

The proton resonance lines of 8-quinolinol show the selective, specific dilution shifts in various solvents. The dilution curves of H-2, H-3 and H-4 ring protons of this compound

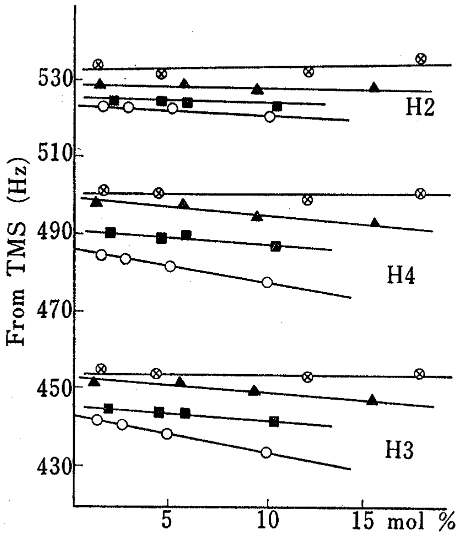

Fig. 1. The Dilution Curves of H-2, H-3 and H-4 Protons of 8-Quinolinol in Various Solvents

○; CCl_4, ▲; $(CD_3)_2CO$, ■; $C_4D_8O_2$, ⊗; $(CD_3)_2SO$.

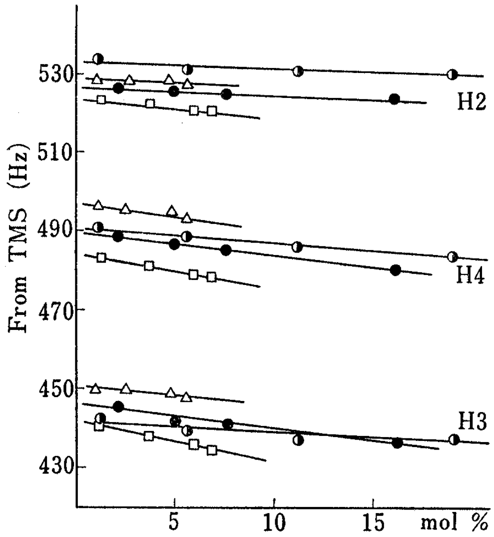

Fig. 2. The Dilution Curves of H-2, H-3 and H-4 Protons of 8-Quinolinol in Various Solvents

◑; C_5D_5N, ●; $CDCl_3$, □; CS_2, △; CD_3CN.

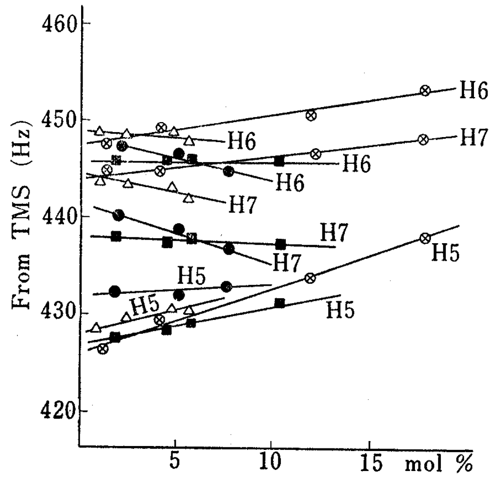

Fig. 3. The Dilution Curves of H-5, H-6 and H-7 Protons of 8-Quinolinol in Various Solvents

⊗; $(CD_3)_2SO$, △; CD_3CN, ■; $C_4D_8O_2$, ●; $CDCl_3$.

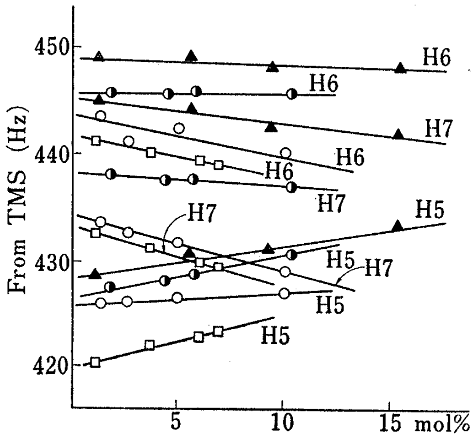

Fig. 4. The Dilution Curves of H-5, H-6 and H-7 Protons of 8-Quinolinol in Various Solvents

◑; C_5D_5N, ○; CCl_4, □; CS_2, ▲; $(CD_3)_2CO$.

in various solvents are shown in Fig. 1 and 2. These resonance lines in most solvents show the low field shifts with dilution except for H-2 in dimethyl sulfoxide. And also these of H-6, H-7 indicate the low field shifts with dilution in most solvents except for dimethyl sulfoxide as is shown in Fig. 3 and 4. However, the resonance lines of H-5 cause high field shifts with dilution in most solvents. In this way, although the magnitude of the dilution shifts is affected by the species of solvents, the trend of low or high field shifts with dilution is, on the whole, probably real regardless of the species of solvents. This strongly suggests that there is a specific solute–solute interaction.

The origin of the low field shifts of the ring protons with dilution except for H-5 can be successfully accounted for by assuming the influence of the magnetic anisotropy (secondary field) arising from the ring current of neighbouring aromatic solute molecule, that is, the low field shifts with dilution can be explained by the decrease of mutual shielding effect acting between the aromatic solute rings.

The resonance lines of a proton near nitrogen atom in a molecule are known to shift to the lower field side. This is responsible for the magnetic anisotropy arising from a lone pair of electrons of the nitrogen atom.[4] But yet the influence of the lone pair of electrons has been unobvious in mechanism.[5-9] The high field shifts of H-5 with dilution can be accounted for by assuming the deshielding effect of the nitrogen atom in the surrounding solute molecule through space. If the solute molecules take such a steric arrangement that H-5 spatially locates near the nitrogen atom in another solute molecule and is situated in the deshielding field arising from the lone pair of electrons, the high field shifts of H-5 with dilution are successfully explicable.

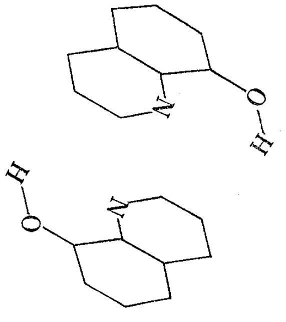

Fig. 5

Consequently, the discussions on the origins of the dilution shifts strongly suggest that there is the specific solute–solute interaction (self-collision complex)[10-16] taking a specific steric arrangement formed between solute rings, and where the relative orientation of these rings in the complex might be of a superposition, face to back, and one of 8-quinolinol being rotated by *ca.* 180° along a perpendicular axis in the molecular plane as is shown in Fig. 5.

Solvent Effect

The resonance lines of H-2 in carbon tetrachloride show the greatest change in chemical shift with dilution. However, the resonance lines in the other solvents which cause the solute-

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4) E.W. Randall and D.G. Gillies, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 6, Ed. J.W. Emsley, J. Feeney, and L.H. Sutcliffe, Pergamon Press, London, 1971.
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solvent interactions indicate less change in comparison with that in carbon tetrachloride (Fig. 1 and 2). That is to say, they show more gentle slopes than that in carbon tetrachloride. The same trend can be nearly found for the dilution shifts of the other protons, H-3, H-4, H-6 and H-7. In this way, the greatest change in chemical shift occurs in dilute solution of 8-quinolinol in carbon tetrachloride which is exactly the reverse of what would be expected for a solute-solvent interaction, although specific solute-solvent interactions are usually considered to be absent in carbon tetrachloride. Therefore, it appears that specifiac solute-solute interaction must be involves in this system.

TABLE I. Dilution Coefficients ($\Delta\delta/\Delta C$) of Each Ring Proton in Various Solvents

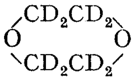
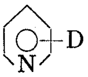
	Dilution coefficient ($\Delta\delta/\Delta c$) (Hz/M)[3]						
	H-2	H-3	H-4	H-5	H-6	H-7	OH
CS_2	−0.48	−1.03	−0.88	0.39	−0.37	−0.54	6.13
CCl_4	−0.22	−0.89	−0.83	0.16	−0.27	−0.50	4.32
$CDCl_3$	−0.19	−0.61	−0.61	0.06	−0.37	−0.65	2.76
CD_3CN	−0.22	−0.47	−0.71	0.44	−0.08	−0.35	4.36
$(CD_3)_2CO$	−0.0	−0.38	−0.36	0.32	−0.07	−0.22	1.84
	−0.07	−0.36	−0.35	0.43	−0.01	−0.10	1.13
	−0.17	−0.25	−0.34	—	—	—	−1.14
DMSO	0.30	0.05	0.08	0.67	0.28	0.21	0.81

TABLE II. Correlation Coefficients (R) between the Dilution Coefficients $(\Delta\delta/\Delta c)_{solv.}$ of Each Proton

	(R)		(R)
H2–H3	0.875	H4–H5	0.628
H4	0.918	H6	0.889
H5	0.523	H7	0.901
H6	0.888	OH	−0.813
H7	0.863	H5–H6	0.827
OH	−0.646	H7	0.850
H3–H4	0.944	OH	−0.319
H5	0.630	H6–H7	0.980
H6	0.918	OH	−0.734
H7	0.872	H7–OH	−0.739
OH	−0.828		

The magnitude of the dilution shifts are considerably affected by the species of solvents. Accordingly, the solvent effects on the dilution shifts can be characterized by the slopes of the dilution curves.[3] Then, the dilution coefficients ($\Delta\delta/\Delta c$) of each ring proton in various solvents are defined from the slopes of the dilution curves assuming the nearly linear relationship between shift and concentration (Table I). By examining the relationships between the dilution coefficients $(\Delta\delta/\Delta c)_{solv.}$ of each ring proton, it is found good correlations between the dilution coefficients of every pair of H-2, H-3, H-4, H-6 and H-7, while it is not found good correlations between these of H-5 and the other protons (Table II). This suggests that the solvent effects on the ring protons except for H-5 are similar in mechanism. Similarly, the correlations between the dilution coefficients $(\Delta\delta/\Delta c)_{proton}$ of each solvent except for pyridine are examined. It is therefore found good correlations between $(\Delta\delta/\Delta c)_{proton}$'s of

TABLE III. Correlation Coefficients (R) between the Dilution Coefficients $(\Delta\delta/\Delta c)_{\mathrm{proton}}$ of Each Solvent

	(R)		(R)
CS_2–CCl_4	0.998	$CDCl_3$–CD_3CN	0.831
–$CDCl_3$	0.994	–$(CD_3)_2CO$	0.995
–CD_3CN	0.998	–$C_4H_8O_2$	0.992
–$(CD_3)_2CO$	0.989	–DMSO	0.832
–$C_4H_8O_2$	0.941	CD_3CN–$(CD_3)_2CO$	0.991
–DMSO	0.824	–$C_4H_8O_2$	0.946
CCl_4–$CDCl_3$	0.996	–DMSO	0.833
–CD_3CN	0.997	$(CD_3)_2CO$–$C_4H_8O_2$	0.974
–$(CD_3)_2CO$	0.997	–DMSO	0.890
–$C_4H_8O_2$	0.993	$C_4H_8O_2$–DMSO	0.964
–DMSO	0.944		

every pair of most solvents, but not dimethyl sulfoxide (DMSO), dioxane (Table III). It may therefore be concluded that DMSO, dioxane show the specific, selective attack to each ring proton, while the other solvents uniformly interact to each ring proton. In this way, the method of these correlation is most available one to investigate the solvent effects and especially is advantageous for examining the local solvent effects to distinct positions around a molecule. After all, the result of the solvent effect seems to be suggestive of the specific solute–solute interaction occured in this system, being independent of the nature of solvents.

Hydrogen Bond

Another important problem of the specific solute–solute interaction is of a hydrogen bond formed between the solute molecules. The dilution curves of OH in various solvent indicate the high field shifts as reported in the previous paper.[2)] And then, it was concluded that there is a intermolecular hydrogen bond rather than a intramolecular hydrogen bond. In present paper, further detail discussion, solvent effects on the dilution curves of OH are done.

The slopes of the dilution curves of OH are considerablly affected by the species of solvents. The resonance lines of OH in carbon disulfate (nonpolar solvent) show the greatest change in chemical shift with dilution, while the dilution shifts in the other solvents (polar solvent) which cause the specific solute-solvent interactions indicate less change in comparison with that in carbon disulfate. Therefore, it appears that a specific solute–solute interaction must be involves in this system regardless the species of solvents. Accordingly, favorable intermolecular hydrogen bonds formed between solutes are envisioned (Fig. 9).

Infrared Spectra

Infrared spectra of carbon tetrachloride solutions of 8-quinolinol are measured in the region of OH bands (3200—3800 cm^{-1}). There are a strong band at 3424 cm^{-1} and a weak band at 3664 cm^{-1}, whose bands can be assigned to OH stretching vibrations corresponding to the intermolecular hydrogen bond and free molecules, respectively. Temperature (*ca.* 15—*ca.* 70°) and concentration (3.3×10^{-1} M—3.3×10^{-3} M) dependences of these bands are examined. However, neither temperature nor concentration dependence of the strong band at 3424 cm^{-1} can be found, while that of the weak band at 3664 cm^{-1} can not be recognized because of the weakness of its band (Fig. 6 and 7). Therefore, this strongly suggests that the hydrogen bond due to the band at 3424 cm^{-1} may take more strong, stabilized form, presumably, dimer form of intermolecular hydrogen bond (See Fig. 9**b**). This result is not always in conflict with the aspect of hydrogen bond discussed above by NMR, rather this result seems to make the picture of hydrogen bond occured in this system clearer.

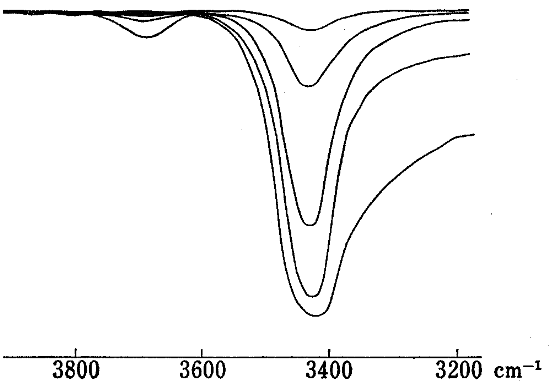


Fig. 6. Concentration Dependence (3.3×10^{-1}—3.3×10^{-3} M) of Infrared Spectra of 8-Quinolinol

Ordinate, per cent transmission on ordinary scale. Cell, 1 mm, 1 cm, 5 cm.

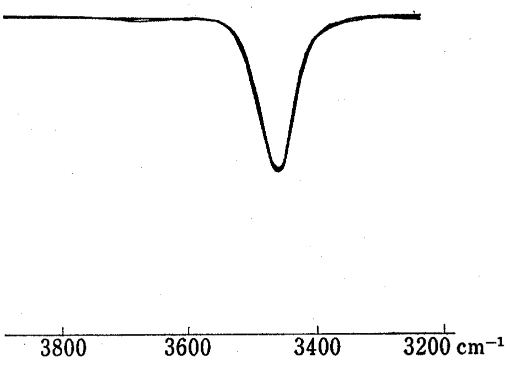


Fig. 7. Temperature Dependence (*ca.* 15—70°) of Infrared Spectra of 8-Quinolinol (4.1×10^{-3} M in CCl_4)

Ordinate, per cent transmission on ordinary scale. Cell, 1 cm.

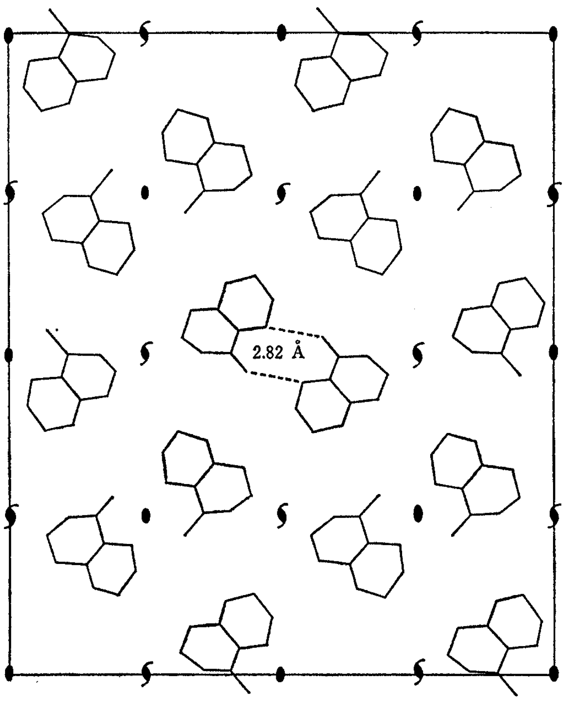


Fig. 8. Crystal Structure of 8-Quinolinol

Projection of the unit cell contents upon (001).

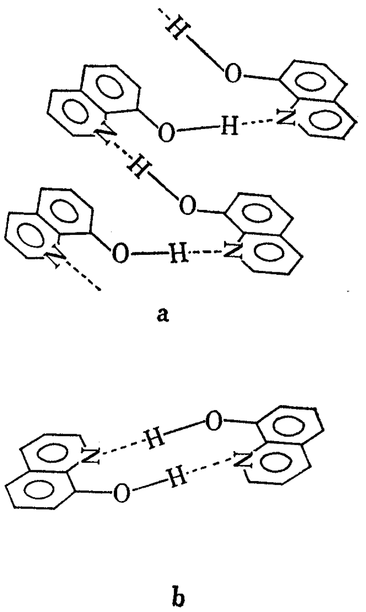


Fig. 9

Crystal Structure of 8-Quinolinol

A crystal structure of a molecule seems to be not always independent of the structure in liquid state, and occasionally be closely related to it. So an analysis of a crystal structure of 8-quinolinol is expected to give an useful information of not only the structure of its molecule itself but also the relative steric arrangement between 8-quinolinol molecules in solution. It is noteworthy that a crystal structure of 8-quinolinol has not yet made clear, while a number of X-ray crystallographic analysis of its metal complex. Datta had tryed to, but failed to obtain the crystal structure of this compound.[17] Our calculation with the structure factors F(h, k, l) of his data can successfully provide the crystal structure

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17) Dissertation Abstr., **20**, 1189 (1959).

as is shown in Fig. 8. Space group is Fdd_2. Unit cell contains 16 molecules. All of the angles (α, β, γ) are 90°, a=29.52 Å, b=25.22 Å, c=3.85 Å. The interatomic distance O–N is 2.82 Å which is enough to form the intermolecular hydrogen bond. The dimerized intermolecular hydrogen bonds are found in the unit cell. This appears to support the dimer form of the intermolecular hydrogen bond in solution proposed above by infrared spectroscopy. Then, the interplane distance is 3.85 Å. And also these crystallographic result is suggestive of at least superposition formed between 8-quinolinol rings presumed above. Further precision analysis by the counter measurement is now in progress.

In conclusion, the proposed models of the self-collision complex and the dimerized intermolecular hydrogen bond, supporting by the infrared spectra and the crystallographic analysis, are not necessarily final conclusion because of remaining still obscure. However, one of possibility of the models is at least present. Further investigations on relaxation time T_1 of each resonance line and dipole moments of this compound which are closely related to intermolecular interaction are in progress. However, we can not so far obtain noteworthy imformation.

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