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The Intramolecular Hydrogen Bond of the Diol Ethers as Model Compounds of the Diols*[1]

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The intramolecular and intermolecular hydrogen bonds of the diol ethers are examined as model compounds of the diols by means of a study of their infrared and NMR spectra. The hydrogen bond shift and the intramolecular hydrogen bond shift are obtained. The value of the intramolecular hydrogen bond shift is discussed in terms of the electric field effect due to lone-pair electrons of the proton acceptor.

In a previous paper,[1)] the free OH proton shifts of the diols have been estimated from a theoretical treatment, and their hydrogen bond shifts have been determined using both experimental and theoretical OH proton shifts. It has been pointed out that the hydrogen bond shift obtained arises predominantly from the intermolecular hydrogen bond, but the contribution of the intramolecular hydrogen bond can not be ignored.

The intramolecular hydrogen bond of the diols was investigated by Kuhn and others[2-9)] with infrared spectra. Kuhn reported[2)] that its strength is related to the number of methylene groups between two hydroxyl groups. That is to say, 1, 4-butanediol, which has four methylene groups, forms the strongest intramolecular hydrogen bond of the diols, making a stable seven-membered ring. Trimethylene glycol, which has three methylene groups, forms a stronger intramolecular hydrogen bond than ethylene glycol, with two methylene groups, and a weaker one than 1, 4-butanediol.

For the investigation of the intramolecular hydrogen bond with NMR, the measurements

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1) T. Yonezawa, H. Saitô, S. Matsuoka and K. Fukui, This Bulletin, **38**, 1431 (1965).

2) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

3) L. P. Kuhn, ibid., **76**, 4323 (1954).

4) L. P. Kuhn, ibid., **80**, 5950 (1958).

5) M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

6) P. von. R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961).

7) F. V. Brutcher, Jr., and W. Bauer, Jr., ibid., **84**, 2236 (1962).

8) H. Kwart and W. G. Vosburgh, ibid., **76**, 5400 (1954).

9) L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, Jr., and L. Eberson, ibid., **86**, 650 (1964).

TABLE I. COMPARISON OF INTRAMOLECULAR HYDROGEN BOND OF THE DIOLS WITH THE DIOL ETHERS

The diols[a)]	Free OH stretching cm^{-1}	Intramolecular hydrogen bonded OH stretching cm^{-1}	$\Delta\nu$ cm^{-1}	The diol ethers	Free OH stretching cm^{-1}	Intramolecular hydrogen bonded OH stretching cm^{-1}	$\Delta\nu$ cm^{-1}
$HOCH_2CH_2OH$	3644	3612	32	$HOCH_2CH_2OCH_3$	—[b)]	3605(3600)	35[c)]
				$HOCH_2CH_2OC_2H_5$	—[b)](3632)	3607(3600)	33[c)]
				$HOCH_2CH_2OC_4H_9$	—[b)](3632)	3607(3601)	33[c)]
$HOCH_2CH_2CH_2OH$	3636	3558	78	$HOCH_2CH_2CH_2OCH_3$	3640	3547	93
$HOCH_2CH_2CH_2CH_2OH$	3634	3478	156	$HOCH_2CH_2CH_2CH_2OCH_3$	3640	3456	184

a) Results by L. P. Kuhn.[2)]

b) In our experiment, this value is not obtained. Values in parenthesis are results by M. St. C. Flett.[5)]

c) The value assumed that free OH stretching is 3640 cm^{-1} as same as the value of trimethylene glycol monomethyl ether and 1, 4-butanediol monomethyl ether.

should be carried out with as low a concentration as possible in a non-polar solvent such as carbon tetrachloride. The solubility of the diols in carbon tetrachloride, however, is lower than 0.005 mol./l., and NMR spectra cannot be obtained at such a low concentration.

Therefore, the diol monoalkyl ethers (diol ethers) are used as model compounds to investigate the natures of intramolecular hydrogen bond of the diols. The intramolecular hydrogen bond of the diol ether has also been studied, by means of infrared spectra, by Kuhn and Wires[10)]; they reported the energy of the intramolecular hydrogen bond.

As model compounds for the diols, 1, 4-butanediol monomethyl ether, trimethylene glycol monomethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and ethylene glycol monobuthyl ether are used. From the measurement of the NMR spectra, the hydrogen bond shift due to the formation of an intramolecular hydrogen bond is obtained. The hydrogen bond shift is about 4.8 p. p. m. for the diol ethers; this value is found to be smaller than those of the diols and alcohols.

The intramolecular hydrogen bond shift referred to the free OH shift is 1.21 p. p. m. for ethylene glycol monomethyl ether and larger than 1.65 p. p. m. and 1.67 p. p. m. for trimethylene glycol monomethyl ether and 1, 4-butanediol monomethyl ether, respectively. This value is interpreted in terms of the electrostatic nature of the hydrogen bond using the Marshall-Pople formula.[11)]

Experimental

Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether and carbon tetrachloride of guaranteed-grade reagent are used. Trimethylene glycol monomethyl ether and 1, 4-butanediol monomethyl ether are prepared from the corresponding diols by Smith's method.[12)] The diol ethers are used after vacuum distillation after having been dried over barium oxide.

The NMR spectra are usually measured with a JNM-3 40 mc spectrometer; however, a Varian DP-60 60 mc spectrometer is used for lower concentrations, and a sample tube 15 mm. in diameter is used for the lowest concentration. Benzene is used as an external standard.

The infrared spectra for the diol ethers are measured with a Perkin-Elmer 12-C spectrometer equipped with a LiF prism and using a 3 mm.—20 mm. cell.

Results and Discussion

Infrared Spectra.—The infrared spectra for the diol ethers were measured in carbon tetrachloride (0.005 mol./l.) in order to compare the strength of the intramolecular hydrogen bond of the diol ethers with that of the diols. Table I gives our results, together with those of Kuhn,[2)] on the diols.

Since no free OH stretching bands of ethylene glycol monomethyl- monoethyl- and monobutyl-ethers are observed in this concentration, the free OH proton may be said not to be present.

Then the shift of the OH stretching frequency, $\Delta\nu$, due to the intramolecular hydrogen bond in the infrared spectra of the diols is compared with that of the corresponding diol ethers, there is a distinct parallelism between the $\Delta\nu$ values of the diols and those of the diol ethers, though the $\Delta\nu$ values of the diol ethers are about twenty percent greater than those of the diols.

Therefore, it may be reasonable to adopt the diol ethers as a model compound of the diols so long as the fact that the $\Delta\nu$ values in the diol ethers are larger than those of the diols is kept in mind. In order to obtain information on the intramolecular hydrogen bond, the results of infrared spectra measured at various concentrations are shown in Fig. 1. Figure 1 shows that there is no free OH proton of ethylene glycol monomethyl ether in the range of the concentration between 0.005 to 0.5 mol./l., and that all OH protons make intramolecular hydrogen bonds

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[10)] L. P. Kuhn and R. A. Wires, ibid., **86**, 2161 (1964).

[11)] T. W. Marshall and J. A. Pople, *Mol. Phys.*, **1**, 199 (1958).

[12)] L. Smith and J. Sprung, *J. Am. Chem. Soc.*, **65**, 1276 (1943).

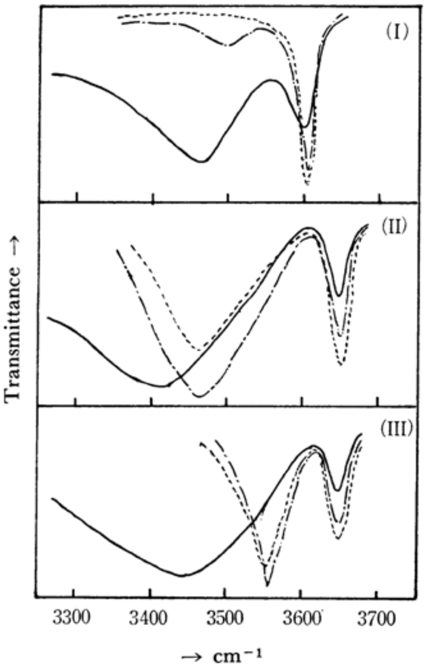

Fig. 1. Infrared spectra of diol ethers.
(I) Ethylene glycol monomethyl ether
(II) 1, 4-Butanediol monomethyl ether
(III) Trimethylene glycol monomethyl ether
---- 0.005 mol./l. ----- 0.05 mol./l.
—— 0.5 mol./l.

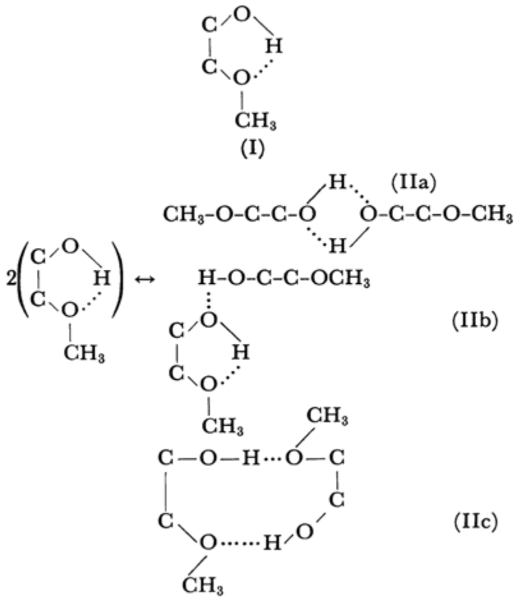

Fig. 2. Intra- and intermolecular hydrogen bond of ethylene glycol monomethyl ether in the lower concentration.

forming five-membered rings (Fig. 2 (I)). Now, in the concentration near 0.05 mol./l., the absorption band due to the intermolecular hydrogen bond is present in addition to the intramolecular bond itself, so it seems that there is an equilibrium between the monomer and the dimer, as is shown in Fig. 2 (II). The structure shown in Fig. 2 may be adequate, though we can consider other structures. This consideration is confirmed by the fact that no free OH absorption is observed in the infrared spectra of the diol ethers. Of the three structures, II-b is expected to be preferable.

Figure 3 is obtained by making the plot of the molecular extinction coefficient, $\varepsilon=(1/cd)\log(I_0/I)$, vs. the mole fraction of ethylene glycol monomethyl ether, where c is the concentration (mol./l.) and d, the thickness of the cell. If we use the ε_0 value, which is the value obtained by extrapolating the curve to an infinite dilution, the $\varepsilon/\varepsilon_0$ value is the fraction of the OH group which makes the intramolecular hydrogen bond. As is shown in Fig. 3, the OH shift of ethylene glycol monomethyl ether in an infinitely-diluted solution seems to indicate the intramolecular hydrogen bond shift. However, in trimethylene glycol monoethyl ether and 1, 4-butanediol monomethyl ether, there are free OH protons at the concentration of 0.005 mol./l., and so the value obtained by the extrapolation of the curve to an infinite dilution cannot always be expected to correspond with that resulting from a completely intramolecular hydrogen-bonded state. Namely, there seems to be an equilibrium in the infinite dilution as is shown in Fig. 4. It seems curious at first sight that trimethylene glycol monomethyl ether and 1, 4-butanediol monomethyl ether, which make stable

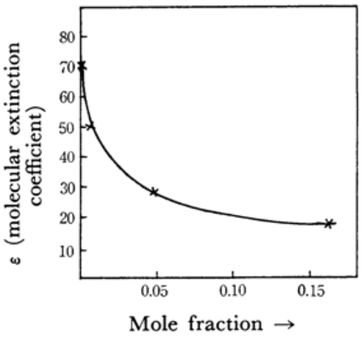

Fig. 3. A plot of ε vs. mole fraction of ethylene glycol monomethyl ether.

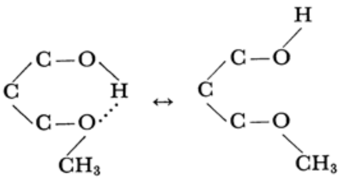

Fig. 4. Equilibrium between free and intramolecular hydrogen bonded state in infinitely diluted solution.

six- and seven-membered rings, respectively, in the intramolecular hydrogen bond, are in the equilibrium shown in Fig. 4, while ethylene glycol monomethyl ether, which makes a weaker hydrogen bond than they, is not in such an equilibrium. Because of the hindered rotation around the C–C and C–O bond axes, the probability of breaking the OH⋯O intramolecular hydrogen bond might increase as the number of C–C and C–O bonds between two hydroxyl groups becomes greater. Therefore, it may be understood that a free OH proton exists in 1, 4-butanediol monomethyl ether and trimethylene glycol monomethyl ether.

NMR Spectra.—NMR spectra at various concentrations of a carbon tetrachloride solution were measured, using benzene as an external standard. The plots of the OH proton shift vs. the mole fraction of the diol ethers are given in Fig. 5 and Fig. 6 for concentrations lower than 0.03 mol./l. The same plot for ethanol, as reported by Becker et al.,[13] is reproduced in Fig. 5 using the same scale. It may be seen in Fig. 5 that the change in the OH proton shift against the concentration in the diol ethers is smaller than that in ethanol. This is probably because there are a number of intramolecular hydrogen bonds in place of free OH protons in the ethanol at these concentrations.

The Hydrogen Bond Shift and the Intramolecular Hydrogen Bond Shift.—*Free OH Proton Shift.* — The free OH proton shift was calculated by the procedure reported in the previous paper,[1] using a simple LCAO MO method for the sigma electron system reported. The parameters used are the same as those in the previous paper. The sigma electron density for the OH proton of the diol ethers is given in Table II. The observed OH proton shifts referred to the benzene proton are shown in Table III. The bulk susceptibility correction is made in a usual way. The volume susceptibility needed for the correction is measured by Gouy's balance.

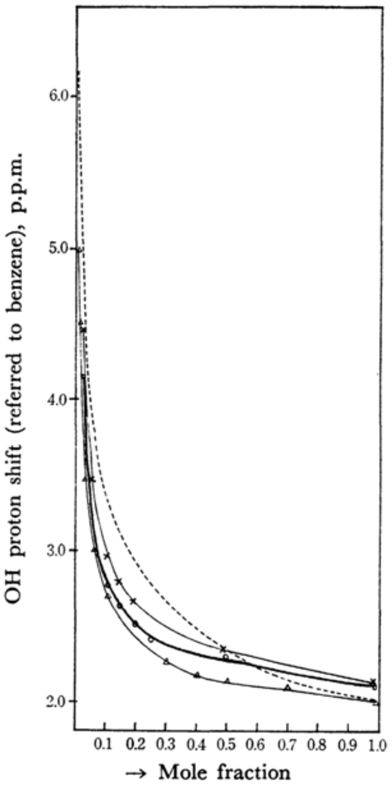

Fig. 5. A plot of OH proton shift vs. mole fraction of diol ethers (uncorrected).
------ Ethanol
—×— Ethylene glycol monomethyl ether
—○— Trimethylene glycol monomethyl ether
—△— 1,4-Butanediol monomethyl ether

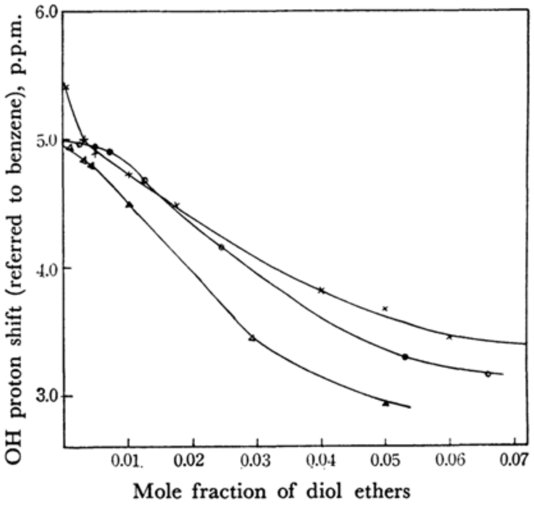

Fig. 6. A plot of OH proton shift (referred to benzene) vs. mole fraction of diol ethers (uncorrected).
—×— Ethylene glycol monomethyl ether
—○— Trimethylene glycol monomethyl ether
—△— 1,4-Butanediol monomethyl ether

TABLE II. σ-ELECTRON DENSITY OF THE DIOL ETHERS

	OH	αCH_2
$HOCH_2CH_2OCH_3$	0.8073	0.9158
$HOCH_2CH_2OC_2H_5$	0.8069	0.9126
$HOCH_2CH_2OC_4H_9$	0.8069	0.9126
$HOCH_2CH_2CH_2OCH_3$	0.8074	0.9167
$HOCH_2CH_2CH_2CH_2OCH_3$	0.8074	0.9169

The hydrogen bond shift is calculated as follows; the observed OH proton shift in a neat liquid state at room temperature* is corrected

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[13] E. D. Becker, U. Liddel and J. N. Shoolery, *J. Mol. Spectry.*, **2**, 1 (1958).

* As the term "hydrogen bond shift" corresponds to the maximum hydrogen bond, measurements must be carried out just above freezing point. However, we here extend the definition of this term to the measurement at room temperature in comparison to the hydrogen bond between the diols and the diol ethers.

TABLE III. HYDROGEN BOND SHIFT OF THE DIOLS REFERRED TO BENZENE

	OH proton shift (obs.) p.p.m.	Volume susceptibility[a] $-\chi_v \times 10^6$	Bulk susceptibility correction	OH proton shift (corrected) p.p.m.	Free OH proton shift[b] p.p.m.	Hydrogen bond shift p. p. m.
$HOCH_2CH_2OCH_3$	2.12	0.660	+0.07	2.19	6.77	4.58
$HOCH_2CH_2OC_2H_5$	2.18	0.644	+0.04	2.22	6.76	4.54
$HOCH_2CH_2OC_4H_9$	2.18	0.660	+0.06	2.34	6.76	4.52
$HOCH_2CH_2CH_2OCH_3$	2.07	0.630	+0.01	2.08	6.77	4.69
$HOCH_2CH_2CH_2CH_2OCH_3$	2.00	0.657	+0.06	2.06	6.77	4.71

a) Measured by present authors.
b) Free OH proton shift referred to benzene.

TABLE IV. INTRAMOLECULAR HYDROGEN BOND SHIFT (unit: p.p.m.)

	OH proton shift (extrapolated to infinite dilution)	OH proton shift (corrected)	Free OH proton shift (calcd.)	Intramolecular hydrogen bond shift
$HOCH_2CH_2OCH_3$	5.44	5.56	6.77	1.21
$HOCH_2CH_2CH_2OCH_3$	5.00	5.12	6.77	>1.65
$HOCH_2CH_2CH_2CH_2OCH_3$	4.98	5.10	6.77	>1.67

by the bulk susceptibility correction and subtraction from the calculated free OH proton shift. The results are given in Table III. Table III shows that the hydrogen bond shift of the diol ethers is smaller than that of ethanol, 4.8 p. p. m., and that of the diols, about 5.4 p. p. m.** The reason why the hydrogen bond shift of the diol ethers is smaller than that of the diols may be that the diols have two hydroxyl groups and both of them may be both proton acceptors and donners, while in the diol ethers the methoxy group replaced by the hydroxyl group may only be a proton acceptor. Therefore, the association of the diols is easier than that of the diol ethers.

It may be found by comparing Table III with Table I that the hydrogen bond shift of the diol ethers becomes larger as the intramolecular hydrogen bond is stronger.

The Intramolecular Hydrogen Bond Shift of the Diol Ethers.—In the case of ethylene glycol monomethyl ether, the intramolecular hydrogen bond shift is obtained by extrapolating the curve of the OH proton shift to an infinitely-diluted solution, as was described in the previous section. In the cases of 1, 4-butanediol monomethyl ether and trimethylene glycol monomethyl ether, however, the extrapolated values are not precisely correspondent to the intramolecular hydrogen bond shift, as has been mentioned in connection with the results of the infrared spectra. If free OH protons are present, the extrapolated value of the intramolecular hydrogen bond shift is smaller than the genuine intramolecular hydrogen bond shift, because the proton shift in an infinitely-diluted solution, δ, referred to the free OH proton shift is expressed as;

$$\delta = (1-\omega_f)\delta_{\text{intra}} \qquad (1)$$

where δ_{intra} is an intramolecular hydrogen bond shift and ω_f the fraction of the free OH proton. Thus, $\delta < \delta_{\text{intra}}$ is concluded to hold in the case of $\omega_f > 0$. The intramolecular hydrogen bond shifts thus obtained are listed in Table IV.

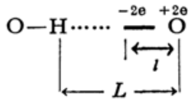
The hydrogen bond shift of the diols seems to be a little larger than that of the diol ethers, considering that the $\Delta\nu$ values of the diol ethers are somewhat larger than those of the diols, as is shown in Table I.

A Theoretical Consideration of the Intramolecular Hydrogen Bond Shift.—It was reported by Kuhn that there is the following relation between the bond length, L, of OH···O and the shift of the wave number, $\Delta\nu$, for the intramolecular hydrogen bond of the diols[2]:

$$\Delta\nu = 250/L - 74 \qquad (2)$$

Assuming that the above relation is valid for the diol monomethyl ethers, the OH···O bond lengths of the intramolecular hydrogen bond of the diol ethers and the diols may be evaluated from the above equation.

By using the value obtained above and the electrostatic model for the hydrogen bond described by Pople,[14] the intramolecular hydrogen bond shift can be evaluated. The electrostatic model is shown below, where L is the length of H···O and l, the length of the lone-pair dipole of the oxygen atom.



The variation in shift due to the electric field, E, was found by Marshall-Pople[11] to be as follows:

** Values at room temperature; see Ref. 1.

[14] J. A. Pople, "Hydrogen Bonding," Ed. by Hadzi, Pergamon Press, New York (1959), p. 71.

TABLE V. CALCULATED INTRAMOLECULAR HYDROGEN BOND SHIFT BASED ON THE MARSHALL'S FORMULA

	$\Delta\nu$ cm^{-1}	L Å	Intramolecular hydrogen bond shift p. p. m. Calcd.		
			l=0.11Å	l=0.29Å	Obs.
$HOCH_2CH_2OH$	32	1.99	0.06	1.39	
$HOCH_2CH_2OCH_3$	35	1.99	0.06	1.39	1.56
$HOCH_2CH_2CH_2OH$	78	1.64	0.18	2.00	
$HOCH_2CH_2CH_2OCH_3$	93	1.49	0.35	3.74	>1.65
$HOCH_2CH_2CH_2CH_2OH$	156	1.40[a]	0.52	5.70	>1.67
$HOCH_2CH_2CH_2CH_2OCH_3$	184				

a) As Eq. 2 is applied in the range of $1.6<L<3.3$, this value is estimated referring the crystal data.[16]

$$\delta_{\mathrm{E}} = -\frac{881}{216}\frac{a^3}{mc^2}E^2 \qquad (3)$$

In this equation, the intramolecular hydrogen bond shift is calculated by using the E value due to the dipolar field of lone-pair electrons of the proton acceptor, where L is estimated by means of Eq. 2 and where l is assumed to be 0.11 Å[14] and 0.29 Å[15] in the two cases. The calculated bond lengths and intramolecular hydrogen bond shifts are listed in Table V, along with the hydrogen bond shifts of the diol ethers obtained in the experiments. The results of the calculation depend greatly on the length of the lone-pair dipole, l. The calculated values in the case of l=0.29 Å can explain the experimental value, while the values corresponding to l=0.11 Å are too small to explain it. Although the intramolecular hydrogen bond shift cannot be discussed precisely because of the uncertainty of our knowledge of the lone-pair dipole and the OH⋯O bond length, this hydrogen bond shift may be understood in terms of the electric field effect of the proton acceptor.*

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[15] W. G. Schneider, *J. Chem. Phys.*, **23**, 26 (1955).

[16] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco (1960), p. 260.

* Other contributions such as that of the charge transfer structure to the hydrogen bond has been studied by ^{14}N NMR for the OH⋯N system (H. Saitô, K. Nukada, H. Kato, T. Yonezawa and K. Fukui, *Tetrahedron Letters*, **1965**, 111).