The Hydrogen Bond in the Diols. I

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The diols form intramolecular as well as intermolecular hydrogen bonds with two hydroxyl groups in a molecule. Though the intramolecular hydrogen bonds of the diols were investigated by Kuhn[1] using infrared spectra, intermolecular hydrogen bonds have never, so far as we know, been elucidated.

In the NMR spectra, the term "hydrogen bond shift" is defined[2] as the extreme shift of the proton signal between the non-associated state and the completely-associated state. In the associated state of the diols, both the intra- and the intermolecular hydrogen bonds are involved.

In the present paper, the hydrogen bond of the diols will be investigated by a nuclear magnetic resonance technique, and a procedure for estimating the hydrogen bond shifts of the diols will be proposed. For this purpose, the non-associated (free) OH proton shift, which is necessary to evaluate the hydrogen bond shift, will be calculated theoretically, since it seems very difficult to measure free OH proton shifts. Not only is there the technical difficulties arising from the slight solubility of the diols in an inert solvent as well as from their higher boiling points, but also the intramolecular hydrogen bond may occur even in the gaseous state or in an infinitely dilute solution. Therefore, the free OH proton shift will be obtained by a theoretical treatment, wherein the local diamagnetic shielding constants of OH protons in the diols and the shielding constant due to the paramagnetic anisotropy of the oxygen attached to the proton will be calculated by a molecular orbital method.

The measurement of the OH proton shift will be made at a temperature just above the freezing point in a pure liquid state, since a completely hydrogen-bonded state is realized at this temperature. Hence, the hydrogen bond shift of the diols can be derived from the difference between the chemical shift in the completely associated state and the theoretical shift stated above.

The hydrogen bond shifts thus obtained will then be compared with that of ethanol and found to be smaller. From these results, we can point out that the proportion of intramolecular hydrogen bonds can not be ingnored in the hydrogen bonds of the diols.

The Measurement of Proton Shifts

All materials used were of guaranteed grade. The vacuum distillation was made before use after drying over anhydrous sodium sulfate. The measurements of the NMR spectra were performed by a Varian DP-60 60 MC spectrometer equipped with a V-4340 variable temperature accessory at a temperature just above the freezing point. Samples were measured in a pure liquid state. The plots of the OH proton shift vs. the temperature are shown in Fig. 1. The bulk susceptibility correction was made in the observed chemical shifts, which are referred to methylene

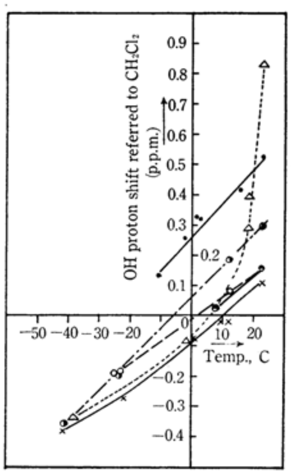

Fig. 1. Plots of OH proton shift vs. temperature. (uncorrected)

—×— 1,5-Pentanediol
—•— 2,3-Butanediol
···△··· Propylene glycol
--○-- Ethylene glycol
—◓— 1,4-Butanediol
·-◑-· Trimethylene glycol

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[1] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

[2] Cf. e. g., J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York (1959).

TABLE I. PROTON SHIFT OF THE DIOLS (referred to methylene chloride)

	Temp. of measurement °C	$-\chi_v$ $\times 10^{-6}$	Bulk susceptibility correction	Proton shift observed (corrected) p. p. m.				
				OH	CH	CH_2	CH_2	CH_3
$HOCH_2CH_2OH$	−25	0.695	−0.08	−0.28	—	+1.74	—	—
$HOCH_2CH(OH)CH_3$	−39	0.689	−0.09	−0.43	−1.58*	+1.92*	—	+4.28
$HOCH_2CH_2CH_2OH$	−42	0.701	−0.07	−0.43	—	+1.83	+3.77	—
$CH_3CH(OH)CH(OH)CH_3$	−11	0.705	−0.06	+0.07	—	—	—	+4.20
$HOCH_2CH_2CH_2CH_2OH$	8	0.705	−0.06	−0.03	—	+1.80	+3.87	—
$HOCH_2CH_2CH_2CH_2CH_2OH$	−42	0.705	−0.06	−0.44	—	+1.88	+3.96	—

* Values at a room temperature are quoted, because signals are not splited at −39°C.

chloride as an external standard. The volume susceptibility for correction is calculated from Pascal's rule. These shifs are listed, together with the temperature of measurement, in Table I.

The Calculation of the Hydrogen Bond Shift

In order to obtain the hydrogen bond shift, free OH proton shifts were calculated theoretically by the following procedure. According to Pople,³⁾ the shielding constant of the free OH proton consits of the diamagnetic shielding constant, $\sigma_{\mathrm{dia}}(\mathrm{OH})$, which depends on electrons around the proton in question, and the shielding constant, $\sigma_{\mathrm{para}}(\mathrm{O})$, due to the paramagnetic anisotropy of the oxygen atom attached to the proton :⁴⁾

$$\sigma(\mathrm{OH}) = \sigma_{\mathrm{dia}}(\mathrm{OH}) + \sigma_{\mathrm{para}}(\mathrm{O}) \qquad (1)$$

The free OH proton shift, $\delta(\mathrm{OH})$, referred to gaseous methane, is then given as:

$$\delta(\mathrm{OH}) = \sigma_{\mathrm{dia}}(\mathrm{OH}) - \sigma_{\mathrm{dia}}(\mathrm{CH_4}) + \sigma_{\mathrm{para}}(\mathrm{O}) \quad (2)$$

since there is no contribution of the neighbor anisotropy in methane. The shielding constants, $\sigma_{\mathrm{dia}}(\mathrm{OH})$, $\sigma_{\mathrm{dia}}(\mathrm{CH_4})$ and $\sigma_{\mathrm{para}}(\mathrm{O})$, are calculated by a simple LCAO MO method for σ-electron systems.

The Diamagnetic Shielding Constant.—It has been shown that the local diamagnetic shielding constant of a proton is given by :³⁾

$$\sigma_{\mathrm{dia}} = \lambda q_{\mathrm{H}} \qquad (3)$$

where q_{H} is the total σ-electron density at the hydrogen atom and λ is a constant. In the present paper, λ is put as equal to 25 p. p. m.⁵⁾

The total σ-electron density, q_{H}, is calculated by a simple LCAO MO method for sigma systems, where the j-th molecular orbital is expressed as a linear combination of the atomic orbitals constructing bonds in a molecule :

$$\varphi_j = \sum_r c_r{}^j \chi_r \qquad (4)$$

TABLE II

$\alpha_{\mathrm{C}} = \alpha$	$\beta_{\mathrm{CC'}} = \beta$
$\alpha_{\mathrm{H}} = \alpha - 0.2\beta$	$\beta_{\mathrm{CO}} = 0.7\beta$
$\alpha_{\mathrm{O}}(\mathrm{sp}^2) = \alpha + 0.4\beta$	$\beta_{\mathrm{OH}} = 1.2\beta$
$\alpha_{\mathrm{O}}(\mathrm{sp}^3) = \alpha + 0.3\beta$	$\beta_{\mathrm{CH}} = 1.1\beta$
	$\beta_{\mathrm{CC}} = 0.4\beta$*
	$\beta_{\mathrm{OO}}(\mathrm{sp}^2) = 0.5\beta$
	$\beta_{\mathrm{OO'}}(\mathrm{sp}^3) = 0.4\beta$*

* Resonance integral between the different atomic orbitals of the same atom.

The parameters adopted for the coulomb and resonanance integrals are nearly the same as in our previous paper ;⁶⁾ they are listed in Table II. For the H_2O molecule, we have adopted two different values for the coulomb integral of the oxygen atom with sp^2 and sp^3 hybrid orbitals and for the resonance integral between the two different hybrid orbitals of the oxygen atom. For the diols and alcohols, however, we have adopted the integrals for the oxygen of sp^3 hybridization.

The total σ-electron densities in the diols and some related compounds are given in Fig. 2. No remarkable variation in the electron density in the C-O-H bond is observed for the diols and alcohols.

The Shielding Constant due to the Paramagnetic Anisotropy of the Oxygen Atom.—The shielding constant arising from the magnetic anisotropy of the adjacent atom is written :

$$\sigma_{\mathrm{para}}(\mathrm{O}) = \frac{1}{3R^3H}\{\mu_x(1-3\cos^2\theta_x) + \mu_y(1-3\cos^2\theta_y) + \mu_z(1-3\cos^2\theta_z)\} \quad (5)$$

where μ_x, μ_y and μ_z denote the components of the magnetic dipole moment induced at the oxygen atom by the paramagnetic current

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3) J. A. Pople, *Proc. Roy. Soc.*, **A239**, 549, 557 (1954).

4) Evidently, the terms due to the neighbor anisotropy of other atoms do exist. These terms may be small since they are located rather far from the proton in question.

5) This value corresponds to the effective nuclear charge, $z=1.40$, in the Slater-type 1s orbital.

6) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 33, 1201 (1960) ; 34, 442 (1961) ; 35, 38 (1962).

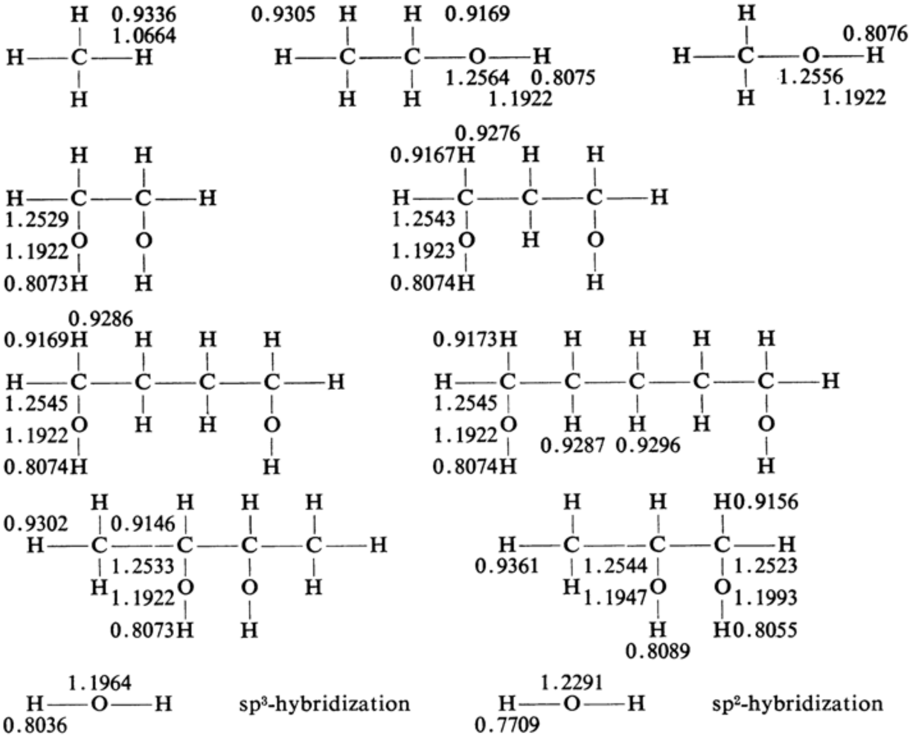
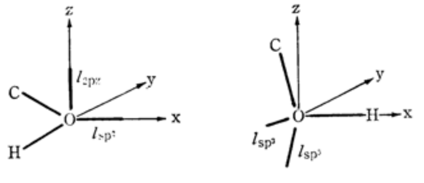


Fig. 2. Total σ-electon density in the diols and related compounds.

around the oxygen atom; H is the external magnetic field; $\cos\theta_x$, $\cos\theta_y$ and $\cos\theta_z$ are the direction cosines of the vector, $\boldsymbol{R}$, connecting the oxygen atom to the hydrogen atom in question, and R is the distance between them.



sp² hybridization　　sp³ hybridization

Fig. 3. Coordinate system used.

In the calculation of the magnetic dipole moment, as we do not have sufficient knowledge to determine whether the hybridization of the oxygen atom in the X-O-Y bond is of the sp³ or the sp² type, the calculation has been performed for both cases. The coordinate system chosen in this treatment is shown in Fig. 3. The notations, l_{2pz}, l_{sp^2} and l_{sp^3} in Fig. 3 imply the lone pair electrons occupying 2pz, sp² and sp³ hybrid orbitals respectively.

When we substitute the values of the direction cosines for two different cases, Eq. 5 becomes:

$$\left.\begin{aligned} \sigma_{\mathrm{para}}(\mathrm{O}) &= \frac{1}{12R^3H}(\mu_x+4\mu_z-5\mu_y) \\ &\qquad \text{for sp}^2\text{ hybridization} \\ \sigma_{\mathrm{para}}(\mathrm{O}) &= \frac{1}{3R^3H}(\mu_y+\mu_z-2\mu_x) \\ &\qquad \text{for sp}^3\text{ hybridization} \end{aligned}\right\} \quad (6)$$

The formulas for μ_x, μ_y and μ_z of the oxygen atom in C-O-H and H-O-H bonds, which are derived in order to check the validity of the present treatment, are written as:

(1) COH

Case 1. oxygen of sp² hybridization

$$\left.\begin{aligned} \mu_x &= \frac{1}{2}\left(\frac{e\hbar}{mc}\right)^2 H\left\{\frac{(a^*)^2}{\varepsilon^*_{\mathrm{OH}}-\varepsilon_{l2\mathrm{pz}}} + \frac{(c^*)^2}{\varepsilon^*_{\mathrm{CO}}-\varepsilon_{l2\mathrm{pz}}}\right\} \\ \mu_y &= \frac{1}{6}\left(\frac{e\hbar}{mc}\right)^2 H\left\{\frac{(a^*)^2}{\varepsilon^*_{\mathrm{OH}}-\varepsilon_{l2\mathrm{pz}}} + \frac{(c^*)^2}{\varepsilon^*_{\mathrm{CO}}-\varepsilon_{l2\mathrm{pz}}}\right\} \\ \mu_z &= \frac{1}{3}\left(\frac{e\hbar}{mc}\right)^2 H\left\{\frac{(a^*)^2}{\varepsilon^*_{\mathrm{OH}}-\varepsilon_{l\mathrm{sp}^2}} + \frac{(c^*)^2}{\varepsilon^*_{\mathrm{CO}}-\varepsilon_{l\mathrm{sp}^2}} + \frac{(ac^*)^2}{\varepsilon^*_{\mathrm{CO}}-\varepsilon_{\mathrm{OH}}} + \frac{(ca^*)^2}{\varepsilon^*_{\mathrm{OH}}-\varepsilon_{\mathrm{CO}}}\right\} \end{aligned}\right\} \quad (7)$$

Case 2. Oxygen of sp^3 hybridization

$$\left.\begin{aligned}
\mu_x &= \frac{2}{3}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{(c^*)^2}{\varepsilon^*_{CO}-\varepsilon_{lsp^3}}\biggr\} \\
\mu_y &= \frac{1}{4}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{3(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{lsp^2}} \\
&\qquad +\frac{1}{3}\frac{(c^*)^2}{\varepsilon^*_{CO}-\varepsilon_{lsp^3}}\biggr\} \\
\mu_z &= \frac{1}{4}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{2(ac^*)^2}{\varepsilon^*_{CO}-\varepsilon_{OH}} \\
&\qquad +\frac{2(ac^*)^2}{\varepsilon^*_{OH}-\varepsilon_{CO}}+\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{lsp^3}} \\
&\qquad +\frac{(c^*)^2}{\varepsilon^*_{CO}-\varepsilon_{lsp^3}}\biggr\}
\end{aligned}\right\} \quad (8)$$

(2) HOH

Case 1. Oxygen of sp^2 hybridization

$$\left.\begin{aligned}
\mu_x &= \left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{l2pz}}\biggr\} \\
\mu_y &= \frac{1}{3}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{l2pz}}\biggr\} \\
\mu_z &= \frac{2}{3}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{lsp^2}} \\
&\qquad +\frac{(aa^*)^2}{\varepsilon^*_{OH}-\varepsilon_{OH}}\biggr\}
\end{aligned}\right\} \quad (9)$$

Case 2. Oxygen of sp^3 hybridization

$$\left.\begin{aligned}
\mu_x &= \frac{2}{3}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{lsp^3}}\biggr\} \\
\mu_y &= \frac{5}{6}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{lsp^3}}\biggr\} \\
\mu_z &= \frac{1}{2}\left(\frac{e\hbar}{mc}\right)^2 H\biggl\{\frac{2(aa^*)^2}{\varepsilon^*_{OH}-\varepsilon_{OH}} \\
&\qquad +\frac{(a^*)^2}{\varepsilon^*_{OH}-\varepsilon_{lsp^3}}\biggr\}
\end{aligned}\right\} \quad (10)$$

These equations are derived according to the procedure of Pople.[3] In Eqs. 7, 8, 9 and 10, ε_{XY} and ε^*_{XY} denote the energies of the bonding and antibonding X-Y orbitals, and ε_{l2pz} ,ε_{lsp^2} and ε_{lsp^3} are those of one electron of the lone pair in 2pz, sp^2 and sp^3 hybridized orbitals. The wave functions of the bonding and antibonding C-O and O-H obtitals are expressed, for the sake of simplicity, by the linear combination of two atomic orbitals with the coefficients which appear in Eqs. 7, 8, 9 and 10:

$$\left.\begin{aligned}
\varphi_{OH} &= a\chi_O+b\chi_H \\
\varphi^*_{OH} &= a^*\chi_O+b^*\chi_H \\
\varphi_{CO} &= c\chi_O+d\chi_C \\
\varphi^*_{CO} &= c^*\chi_O+d^*\chi_C
\end{aligned}\right\} \quad (11)$$

TABLE III. MOLECULAR ORBITAL COEFFICIENTS

MO	O-H		C-O	
Coefficients of MO's for	a^2	$(a^*)^2$	c^2	$(c^*)^2$
sp^2 system	0.600	0.400	0.500	0.500
sp^3 system	0.539	0.461	0.500	0.500

TABLE IV. MOLECULAR ORBITAL ENERGIES ε_{X-Y}'S

Energy of ε_{X-Y} in sp^2 system	Energy of ε_{X-Y} in sp^3 system
$\varepsilon_{O-H}=0$	$\varepsilon_{O-H}=0$
$\varepsilon_{C-O}=-2.0$ eV.	$\varepsilon_{C-O}=-2.0$ eV.
$\varepsilon_{lsp^2}=+1.0$ eV.	$\varepsilon_{lsp^3}=+2.5$ eV.
$\varepsilon_{l2pz}=+2.0$ eV.	$\varepsilon^*_{O-H}=+10.0$ eV.
$\varepsilon^*_{C-O}=+12.0$ eV.	$\varepsilon^*_{C-O}=+12.0$ eV.
$\varepsilon^*_{O-H}=+10.0$ eV.	

To carry out the numerical calculation, these energies and coefficients were determined by a similar procedure, one which appeared in one of our previous papers,[7] using empirical data such as the ionization potentials, bond moments and absorption spectra of related compounds, R was taken as 0.958 Å, corresponding to a standard bond distance of the O-H bond. These values are summarized in Tables III and IV. All the energy levels in Table IV are given relative to the value of ε_{OH} for the two cases stated above. Here we made a crude assumption that the variation in the molecular orbital coefficients and energies representing the characteristics of the O-H and C-O bonds for the diols and related compounds may be ignored.

The shielding constants, $\sigma_{para}(O)$, thus calculated with the aid of Eq. 6 become:

	H_2O	COH
sp^2 system	+3.42 p.p.m.	+2.89 p.p.m.
sp^3 system	+2.02 p.p.m.	+2.18 p.p.m.

On the shielding constant, $\sigma_{para}(O)$, for the proton in H_2O, Pople[3] obtained +2.75 p. p. m. by using the results of the LCAO MO SCF calculation performed by Ellison and Shull.[8] Using the same results, Matsuoka and Hattori[9] obtained an alternative value of +3.47 p. p. m. It may be concluded that the present result for H_2O is reasonable.

With the shielding constants calculated by Eqs. 3 and 6, the free OH shift of the proton in H_2O becomes −0.65 p. p. m. for the sp^2 hybrid system and −1.03 p. p. m. for the sp^3 system, whereas the chemical shift of gaseous H_2O is −0.60 p. p. m.[10] Hence, the agreement between theoretical and experiment is

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[7] T. Yonezawa, K. Fukui, H. Kato, H. Kitano, S. Hattori and S. Matsuoka, This Bulletin, **34**, 707 (1961).

[8] E. O. Ellison and H. Shull, *J. Chem. Phys.*, 33, 2348 (1955).

[9] S. Matsuoka and S. Hattori, unpublished.

[10] J. A. Pople, W. G. Schneider and H. J. Bernstein, " High-resolution Nuclear Magnetic Resonance, " McGraw-Hill, New York (1959), pp. 90, 410.

TABLE V. HYDROGEN BOND SHIFTS OF THE DIOLS (in units of p. p. m.)

	Free OH proton[a] shift (calculated)	Maximum[a] OH proton shift	Hydrogen bond[a] shift (calculated)	Frequency shift of OH stretching due to intramolecular hydrogen bond in the infrared spectra (cm^{-1})
$HOCH_2CH_2OH$	-0.56	-6.28	5.72	32[b]
$HOCH_2CH(OH)CH_3$	-0.56	-6.43	5.87	45[c]
$HOCH_2CH_2CH_2OH$	-0.56	-6.43	5.87	78[b]
$CH_3CH(OH)CH(OH)CH_3$	-0.56	-5.93	5.37	39[b]
$HOCH_2CH_2CH_2CH_2OH$	-0.56	-6.03	5.47	156[b]
$HOCH_2CH_2CH_2CH_2CH_2OH$	-0.56	-6.44	5.58	30[c]

a) The observed proton shift referred to methylene chloride is converted to the shift referred to gaseous methane.
b) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).
c) Measured by present authors using Perkin-Elmer 125 spectrometer.

better when sp^2 hybridization is assumed for the oxygen atom. For ethanol, the OH shift calculated relative to gaseous methane becomes -0.97 p. p. m. if the hybridization of the oxygen atom is assumed to be sp^3 and if the experimental value is -0.48 p. p. m.[10] In the following calculation, the value of $+2.60$ p. p. m. is adopted for the shielding constant, $\sigma_{\mathrm{para}}(O)$, in the diols, since better agreement is obtained if we adopt $+2.60$ p. p. m. for the shielding constant, $\sigma_{\mathrm{para}}(O)$, which ranges from $+2.89$ p. p. m. to $+2.18$ p. p. m. with the change in the hybridization of the oxygen atom, as has been shown above.

Results and Discussion

The hydrogen bond shift, Δ, is defined as the difference between the free OH proton shift, δ_2, and the maximum OH proton shift as measured in a pure liquid state referred to gaseous methane, δ_1, as follows:

$$\Delta=\delta_2-\delta_1 \tag{12}$$

The free OH proton shift is obtained theoretically as has been described above, while the OH maximum shift is measured at a temperature just above the freezing point. The hydrogen bond shifts thus calculated are listed in Table V. The second column of the table shows free OH shifts; the third column, OH proton shifts referred to gaseous methane, and the final column, frequency shifts of the OH stretching vibrations due to intramolecular hydrogen bonds in the infrared spectra.

The hydrogen bond shifts listed in Table V show that the values for the diols are 5.37 -5.87 p. p. m. and are smaller than that of ethanol, 6.15 p. p. m.[11] This seems reasonable, since in the diols there exists a considerable number of intramolecular hydrogen bonds and probably some free OH groups, which cause a small hydrogen bond shift, while there is no free OH proton in the linear structure of the alcohols at a low temperature. The infrared spectra show the intramolecular hydrogen bond to be weaker than the intermolecular bond. This correlation in NMR spectra will be discussed in a following paper.

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[11] Ibid., p. 412.