On the Hydrogen-Bond-Forming Powers of Atoms or Atomic Groups

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I. Introduction

It is well known that the energy of hydrogen bond, X—H···Y where X and Y denote two kinds of atoms, takes various values (from about 8 to 1 kcal./mol) depending upon the nature of the atomic groups which contain X and Y. However, as to how the energy relates with the nature of the atomic groups much is yet to be studied. Useful data concerning this question may be obtained from infrared absorption measurements of certain ternary solutions—the ternary solutions, each of which is composed of a large quantity of nonpolar solvent (such as CCl_4) and small quantities of two polar solutes (a proton-donator containing X—H and a proton-acceptor containing Y), and in which complex molecules with the hydrogen bond X—H···Y are present.* For, from these measurements the concentrations of hydrogen-bonded X—H and free X—H in the solutions at various temperatures are to be found, and on the basis of such data the bond energy of any X—H···Y can be determined. The difference in the values of energies thus obtained for different hydrogen bonds in the same medium must represent the difference in the nature of the atomic groups pertaining to the bonds, there being no difference in the environment in which the hydrogen bonds are formed.

This paper is concerned with preliminary investigations made with what have been stated above in mind. In the first place, some results of the infrared absorption measurements of certain ternary solutions are presented, with interpretations of them. Next, it is shown how the hydrogen bond energy can be determined from the results of these measurements, with a few examples of the values of the energy actually obtained. Lastly, the general relationship between the hydrogen-bond-forming powers of atoms and the nature of the atomic groups containing the atoms is discussed, on the basis of the data so far obtained.

II. Instrument and Samples

The instrument used is a reflection monochromator with a 60° prism of fluorite,⁽¹⁾ in conjunction with the thermocouple and galvanometer system.

The compositions of the ternary solutions examined are:⁽²⁾

phenol + ethyl ether + carbon tetrachloride
〃 +hexamethylene tetramine+ 〃
〃 + benzaldehyde + 〃
〃 + anisol + 〃
〃 + nitrobenzene + 〃
〃 +methyl benzoate+ 〃
methanol+ethyl ether + 〃
〃 + anisol + 〃
guaiacol+hexamethylene tetramine+ 〃
o-nitrophenol+ 〃 + 〃
methyl salicylate+ 〃 + 〃
salicylic aldehyde+ 〃 + 〃
p-oxybenzoic methylester+ 〃 + 〃

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* Of this idea the writer owes to Dr. T. Shimanouchi's suggestion.

(1) The fluorite prism used was kindly placed by O. Matsumura at the writer's disposal.

(2) Some of the materials used were kindly placed at the writer's disposal by Prof. S. Kambara, Mr. H. Tada, Mr. H. Baba, and Mr. T. Inukai.

For comparison, infrared absorption measurements were made also of the binary solutions with the following compositions:

phenol +carbon tetrachloride
methanol + 〃
guaiacol + 〃
o-nitrophenol + 〃
methyl salicylate + 〃
salicylic aldehyde + 〃
ethyl ether + 〃
hexamethylene tetramine + 〃
benzaldehyde + 〃
anisol + 〃
nitrobenzene + 〃
methyl benzoate + 〃

III. Infrared Absorption Data and their Interpretations

Formation of Intermolecularly Hydrogen-bonded Complexes in Certain Ternary Solution.—Figs. 1—10 show the results of infrared absorption measurements of phenol and methanol in various solutions. In these figures the abscissas denote wave-lengths in the 3μ region and the ordinates the absorption coefficients of phenol or methanol. These absorption coefficients were obtained by subtraction: the absorption coefficients of the solutions containing phenol or methanol [*e. g.* solution composed of phenol (0.01 mol/l.)+ ethyl ether (0.06 mol/l.)+carbon tetrachloride] minus the absorption coefficients of the solutions without phenol or methanol [*e. g.* solution composed of ethyl ether (0.06 mol/l.)+ carbon tetrachloride].

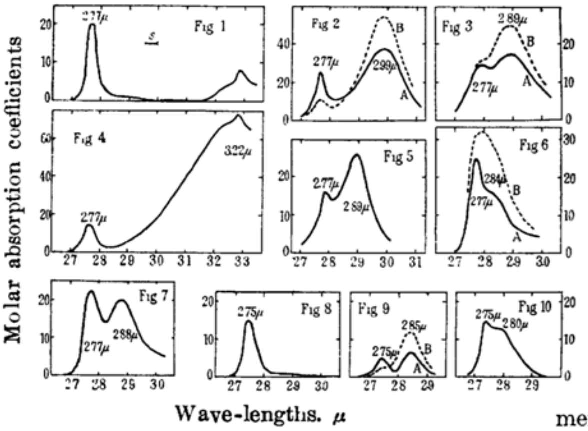

Fig. 1–10.—Infrared absorption curves of phenol and those of methanol in the solutions: Fig. 1, CCl_4+phenol 0.01 mol/l.; Fig. 2, (A) CCl_4+phenol 0.01 mol/l.+ethyl ether 0.06 mol/l., (B) CCl_4+phenol 0.01 mol/l.+ethyl ether 0.11 mol/l.; Fig. 3, (A) CCl_4+phenol 0.01 mol/l.+benzaldehyde 0.05 mol/l., (B) CCl_4+phenol 0.01 mol/l.+benzaldehyde 0.1 mol/l.; Fig. 4, CCl_4+phenol 0.01 mol/l.+ hexamethylene tetramine 0.01 mol/l.; Fig. 5, CCl_4+phenol 0.01 mol/l.+anisol 0.5 mol/l.; Fig. 6, (A) CCl_4+phenol 0.01 mol/l.+ nitrobenzene 0.08 mol/l., (B) CCl_4+phenol 0.01 mol/l.+nitrobenzene 0.18 mol/l.; Fig. 7, CCl_4+phenol 0.01 mol/l.+methyl benzoate 0.02 mol/l.; Fig. 8, CCl_4+methanol 0.02 mol/l.; Fig. 9, (A)CCl_4+methanol 0.01mol/l. +ethyl ether 0.1 mol/l., (B) CCl_4+methanol 0.01 mol/l.+ethyl ether 0.4 mol/l.; Fig. 10, CCl_4+methanol 0.02 mol/l.+anisol 0.5 mol/l. Temperature: 30°C. *s*: Effective slit-width.

The curve in Fig. 1 is for phenol in the solution of the composition: phenol (0.01mol/l.) +carbon tetrachloride. There is seen a single O—H band at 2.77μ. This indicates that the phenol molecules here are wholly in a free state without molecular association.

Figs. 2—7 show how the absorption is effected by adding proton-acceptors to the solution. For example, in Fig. 2, two curves A and B are for phenol in the ternary solutions, respectively with compositions: phenol (0.01 mol/l.)+ ethyl ether (0.06 mol/l.)+carbon tetrachloride and phenol (0.01 mol/l.)+ ethyl ether (0.11 mol/l.)+ carbon tetrachloride. Here, two O—H bands are present, one at 2.77 μ and the other at 2.99 μ. A comparison of the three curves, that in Fig. 1 and A and B in Fig. 2, reveals that by adding ethyl ether to the solution, phenol (0.01 mol/l.) +carbon tetrachloride, the absorption intensity of the O—H band at 2.77 μ becomes weaker and there appears another O—H band at 2.99 μ. Further experiments have shown that, on increasing the concentration of ethyl ether in the solution, there occurs a decrease in the absorption intensity of 2.77 μ band and an increase in the intensity of 2.99 μ band, but no shifting occurs in the positions of these O—H bands. These facts, taken together, may be interpreted as indicating that in the above-mentioned solutions a molecular complex: $C_6H_5OH\cdots O(C_2H_5)_2$, to which the 2.99 μ band is attributable, is formed by the intermolecular hydrogen bond $O-H\cdots O$, and that this complex molecule coexists with free phenol and ether molecules in equilibrium: $C_6H_5OH+O(C_2H_5)_2 \rightleftarrows C_6H_5OH\cdots O(C_2H_5)_2$. The curves in Figs. 3—7 are for phenol in the ternary solutions, whose compositions are given in the notes under the figures. Each of these solutions contains, besides phenol, proton-acceptor. In these solutions phenol exhibits O—H bands at 2.89 μ, 3.22 μ, 2.89 μ, 2.84 μ, and 2.88 μ, besides that at 2.77 μ, indicating that there are formed in the solutions complexes: $C_6H_5OH\cdots OCHC_6H_5$, $C_6H_5OH\cdots N_4(CH_2)_6$, $C_6H_5OH\cdots O(CH_3)C_6H_5$, $C_6H_5OH\cdots O_2NC_6H_5$, and $C_6H_5OH\cdots OC(OCH_3)C_6H_5$(3).

Figs. 8, 9, and 10 give data of the solutions in which methanol is present, instead of phenol, as a proton-donator. The curves here (for methanol) are much like those in Figs. 1, 2, and 5 (for phenol), and similar interpretations may be given of these data. Thus, Fig. 9 shows that in the ternary solution with the composition: methanol (0.01 mol/l.) + ethyl ether (0.1 or 0.4 mol/l.) + carbon tetrachloride, there is formed a molecular complex: $CH_3OH\cdots O(C_2H_5)_2$, to which the 2.85 μ band is attributable; and Fig. 10 shows that in solution with the composition: methanol (0.02 mol/l.) + anisol (0.5 mol/l.) + carbon tetrachloride, there is formed a molecular complex: $CH_3OH\cdots OCH_3C_6H_5$, to which the 2.80 μ band is attributable.

Summarizing, it may be said that in a carbon tetrachloride solution containing small quantities of a proton-donator (D) and a proton-acceptor (A), there is formed a molecular complex DA, where D and A are intermolecularly hydrogen-bonded, and that the complex DA, coexists with free D and free A in equilibrium: $D+A\rightleftarrows DA$.

Hindrance of the Presence of *Intra*-molecular Hydrogen Bond to the Formation of *Inter*-molecular Hydrogen Bond.— What has been said in the preceding section is of phenol or methanol without *intra*-molecular hydrogen bond; however another relation is revealed of *o*-substituted phenols with *intra*-molecular hydrogen bond. The data obtained from the infrared absorption measurements, as to the effects of adding proton-acceptor to dilute carbon tetrachloride solutions of some substituted phenols are given in Table 1. All the phenols here examined, excepting *p*-oxybenzoic methylester, have O—H's in intramolecularly hydrogen-bonded state; and the positions and the intensities of the O—H bands of these phenols in their dilute carbon tetrachloride solutions remain unchanged by adding hexamethylene tetramine (a powerful proton-acceptor) to the solutions. *p*-Oxybenzoic methylester, with no *intra*-molecular hydrogen bond, exhibits a different behavior. There, on adding hexamethylene tetramine to its dilute carbon tetrachloride solution, a new O—H band appears at 3.22 μ, besides the free O—H band (at 2.77 μ), just like nonsubstituted phenol. The facts as above may be interpreted as indicating that the presence of the *intra*-molecular hydrogen bond, even such a weak one as in guaiacol, hinders the OH group therein involved from forming an *inter*-molecular hydrogen bond.

Table 1

Composition of solution	Concentration, mol/l.	Wave-length (in μ) of O—H band; with molar absorption coefficient in parentheses
Guaiacol	0.005	2.80 (80)
Carbon tetrachloride		
Guaiacol	0.005	2.80 (80)
Hexamethylene tetramine	0.03	
Carbon tetrachloride		
o-Nitrophenol	0.005	3.08 (80)
Carbon tetrachloride		
o-Nitrophenol	0.005	3.08 (80)
Hexamethylene tetramine	0.03	
Carbon tetrachloride		
Methyl salicylate	0.005	3.11 (120)
Carbon tetrachloride		
Methyl salicylate	0.005	3.11 (120)
Hexamethylene tetramine	0.03	
Carbon tetrachloride		
Salicylic aldehyde	0.005	3.1
Carbon tetrachloride		
Salicylic aldehyde	0.005	3.1
Hexamethylene tetramine	0.03	
Carbon tetrachloride		
p-Oxybenzoic methylester	0.005	
Hexamethylene tetramine	0.03	2.77 (20) 3.22 (120)
Carbon tetrachloride		

Effective slit width: 0.025 μ
Temperature: 10°C.

IV. On the Determination of the Inter-molecular Hydrogen Bond Energy

The infrared absorption data of the solutions as those given above are useful for the determination of the energies of *inter*-molecular hydrogen bonds between proton-donating and proton-accepting molecules. From these data the values of energies are obtainable in the way as follows.

For the ternary solutions ($D+A+CCl_4$) with such low concentrations of D and A as those examined here, it is admissible to consider that there are present only the complex molecules DA and the free molecules, D and A, but none of other complex molecules such as D_2, D_2A, etc. Then the total concentrations

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(3) As a result of the electron migration from the methoxyl O to the carbonyl group in the methyl benzoate molecule, the carbonyl O in this molecule is expected to have a stronger negative charge, and must therefore be a stronger proton-acceptor than the methoxyl O.

of D and of A in the solutions may be taken as equal respectively to the sum of the concentrations of DA and D, and to the sum of the concentrations of DA and A, *i. e.*,

$$\text{Total concentration of D} = (\text{DA}) + (\text{D})$$

and $$\text{Total concentration of A} = (\text{DA}) + (\text{A}),$$

where (DA), (D), and (A) denote the concentrations (mol/l.) of DA, D, and A, respectively.

Now, from the intensity of the absorption band due to DA or free D and the known total concentrations of D and A, is obtainable the value of the equilibrium constant:

$$K = \frac{(\text{DA})}{(\text{D}) \times (\text{A})} \qquad (1)$$

for $\text{D} + \text{A} \rightleftarrows \text{DA}$. In order to facilitate the finding of the values of K, Fig. 11 is constructed, where are given the relation between (DA)+(A) and

$$\alpha = \frac{(\text{DA})}{(\text{D}) + (\text{DA})} \qquad (2)$$

(which represents the degree of forming the complex DA for D), for various values of K and for the fixed concentration, 0.01 mol/l., of (D)+(DA).

The change of free energy (ΔF) accompanying the formation of DA is obtainable from K by the equation: $\Delta F = -RT \ln K$, and then the change of total energy (ΔE) and the change of entropy (ΔS) accompanying the formation of DA (in carbon tetrachloride medium) are obtainable from ΔF for different temperatures by the equation: $\Delta F = \Delta E - T\Delta S$.

Two examles of the actual determinations of the energies of *inter*-molecular hydrogen bonds between D and A in the carbon tetrachloride solutions are given below:

ΔE of the Hydrogen Bond between Phenol and Ethyl Ether.—A determination was made of the O—H···O bond energy from the intensity measurements of the 2.99 μ band which is due to the molecular complex: $C_6H_5OH \cdots O(C_2H_5)_2$ (*cf.* Fig. 2). By preliminary examinations, it has been ascertained that the relation between the observed transmittance and the absorption path-lengths of the solutions (phenol+ethyl ether+CCl_4) for the 2.99 μ ray accords with the Lambert's law, at any concentrations and temperatures (30—60°C.). Moreover, it has been ascertained that on the 2.99 μ band there is no superposition of other bands. These facts show that the observed molar absorption coefficient (κ) at 2.99 μ of phenol in these solutions may be taken as being proportional to α, thus

$$\kappa = \kappa_0 \alpha \qquad (3)$$

Here, the proportionality constant κ_0 corresponds to the maximum value of κ, *i. e.*, the molar absorption coefficient of the molecular complex: $C_6H_5OH \cdots O(C_2H_5)_2$, at 2.99 μ. The values of κ was observed of the solutions of various concentrations of ethyl ether and of constant concentration of phenol, 0.01 mol/l., and are given by ○ (at 30°C.), △ (at 45°C.), and □ (at 60°C.), in Fig. 12. The dotted lines in Fig. 12. represent the values of κ calculated from the equations (1), (2), and (3) by giving

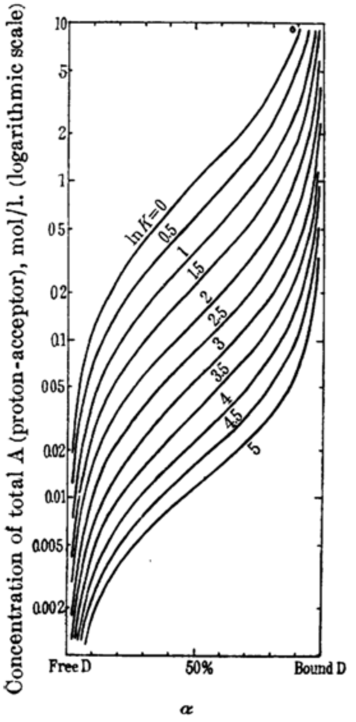

Fig. 11.

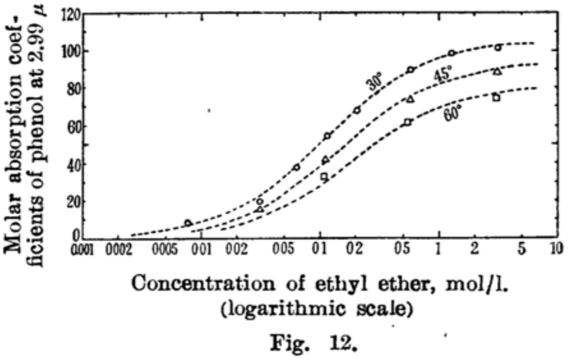

Fig. 12.

following values to κ_0 and K in them: $\kappa_0=105$, $K=10.0$ at 30°C.; $\kappa_0=94$, $K=7.4$ at 45°C.; $\kappa_0=82$, $K=5.75$ at 60°C.(4) (also *cf.* Fig. 11). As is seen in the figure, the observed and calculated values of κ are in close agreement with each other, and hence, from the values of K given here the values of ΔF, ΔS, and ΔE for the O−H···O bond formation can be calculated. These are tabulated below.

Table 2

Temperature, °C.	K	ΔF, kcal./mol	ΔS, E. U.	ΔE, kcal./mol
30	10.0	−1.38		
45	7.4	−1.26	−7.6	−3.7
60	5.75	−1.16		

ΔF (at 30°C.) of the Hydrogen Bond between Phenol and Hexamethylene Tetramine.—A determination was made of the ΔF (at 30°C.) of the O−H···N bond from the intensity measurement of the 2.77 μ band which is due to free phenol molecules (*cf.* Fig. 4). As a preliminary examination the transmittance of the 2.77 μ ray was measured in binary solutions composed of phenol+carbon tetrachloride, varying the concentration of phenol from 0 to 0.006 mol/l. but keeping the absorption path-length (6.11 cm.) and the temperature (30°C.) of the solution constant;(5) and then, similar measurements were made with the ternary solutions which contain hexamethylene tetramine of 0.03 mol/l. The results obtained are shown in Fig. 13. From this figure the concentrations of the phenol molecules in a free state and of those bound by the hexamethylene tetramine molecules were read. In Fig. 14, the ratio of the total concentration of hexamethylene tetramine to the concentration of bound phenol in each solution is plotted versus the reciprocal of the concentration of the free phenol. Here, all the plotted points fall approximately on a single straight line. From the inclination of this straight line, K and ΔF for the O−H···N bond formation at 30°C. were obtained after I. M. Klotz's method,(6) with the results: $K=40$, $\Delta F=-2.4$ kcal./mol.

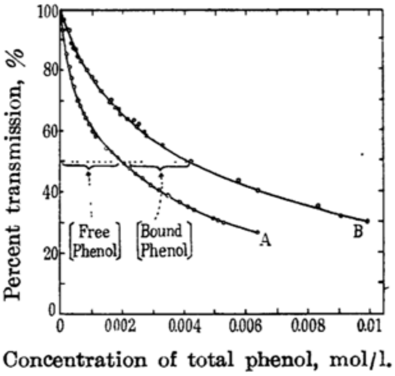

Fig. 13.—Percent transmittance of phenol in (A) binary solutions, CCl_4+phenol, and (B) ternary solutions, CCl_4 + phenol + hexamethylene tetramine (0.03 mol/l.). Wavelength: 2.77 μ. Cell thickness: 6.11 cm. Temperature: 30°C.

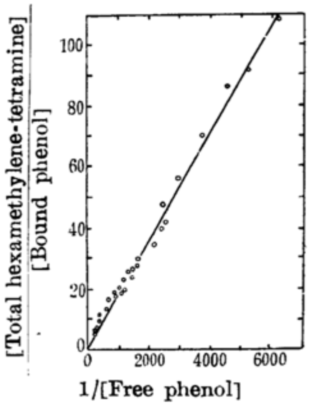

Fig. 14.

V. Hydrogen-Bond-Forming Powers of Atoms or Atomic Groups

The values of ΔF at 30°C. for the hydrogen bond between phenol and ethyl ether and for that between phenol and hexamethylene tetramine are, as have been given in the preceding section, −1.38 kcal./mol, and −2.4 kcal./mol, respectively;—*i. e.*, the latter bond is stronger than the former. While it is difficult to determine the exact values of ΔF and ΔE for

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(4) On raising the temperature from 30 to 60°C., the position of the maximum absorption in the band due to the molecular complex shifts slightly (about 0.02 μ) to a shorter wave-length, and κ_0 decreases from 105 to 82. This fact shows that the structure of the molecular complex concerned is not strictly the same at different temperatures. In the present investigation, which aims at approximate estimation of ΔE, this difference in structure has been ignored.

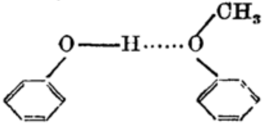
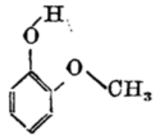
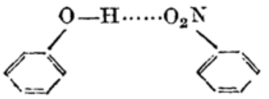
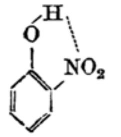
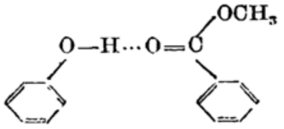
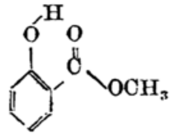
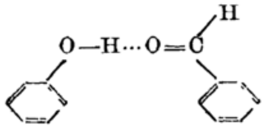
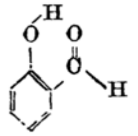
(5) This preliminary examination was necessary because the observed absorption at 2.77 μ of phenol in carbon tetrachloride solution, even when its concentration is as low as 0—0.01 mol/l., does not obey Beer's law. This disobedience is but apparent, due to too low resolving power of the monochromator used (effective slit width: 0.05 μ) for the sharpness of the selective absorption of phenol at 2.77 μ.

(6) I. M. Klotz, F. M. Walker, and R. B. Pivan, *J. Am. Chem. Soc.*, **68**, 1486 (1946). Because of the low solubility of hexamethylene tetramine in CCl_4, it is impossible to use Klotz's method in determining the maximum number of phenol molecules that can be bound by one hexamethylene tetramine molecule. (Probably the maximum number is 4.)

the intermolecular hydrogen bonds in the other complexes examined, the order of the strengths of these hydrogen bonds in these complexes may be determined by observing the frequencies and the intensities of the O—H bands concerning the hydrogen bonds in question. Generally speaking, the frequency and the intensity of the hydrogen-bonded O—H band are taken as measures of the strength of the bond, if other conditions are equal. For, the lower frequency of the bonded O—H band indicates the greater loosening of the O—H accompanying the hydrogen bond formation, and the larger intensity indicates the higher concentration of the hydrogen-bonded O-H and accordingly indicates the larger value of K for the formation of the hydrogen-bonded complex. Inspections of Figs. 2, 5, 9, and 10, with what have been just stated in mind, reveal that the O—H···O bonds in the complexes: phenol-ethyl ether and phenol-anisol are stronger respectively than the O--H···O bonds in the complexes: methanol-ethyl ether and methanol-anisol, and that the OH of phenol is stronger than the OH of methanol in the tendency of donating its proton on its forming hydrogen bonds with other molecules. Similarly, from inspections of Fig. 2—7 and 9—10 it may be concluded that the proton-accepting powers of atoms in the molecules examined are in the following order, from stronger to weaker: N of hexamethylene tetramine, O of ethyl ether, O of benzaldehyde, O (carbonyl) of methyl benzoate, O of anisol, O of nitrobenzene.

From the order of the proton-donating and proton-accepting powers of the atoms and atomic groups as exemplified in the above, the following general rule may be advanced: The proton-donating power of X—H depends upon the tendency with which X attracts the electron of H to leave the proton bare; and the proton-accepting power of Y depends upon the tendency with which Y attracts electrons from the adjacent atoms or adjacent atomic groups to charge itself electrically negative. This rule agrees with and adds to what L. Pauling said concerning the strength of the hydrogen bond: "The strength of the hydrogen bond should increase with the increase in the electronegativity of the two bonded atoms (X and Y)."(7) The validity of the rule here advanced may be demonstrated also from the behavior of the O atom attached to the benzene ring. Thus, the electron migration in phenol molecule from O to benzene ring(8) results in an increase of the tendency of the H in OH to be left bare, and accordingly in increase of the proton-donating power of the OH group; this electron migration, on the other hand, results in a decrease of the negativity of the O atom attached to the benzene ring, and accordingly in the decrease of its proton-accepting power. (This last effect is apparent

Table 3

Inter-molecular hydrogen bonds	ν_{OH}, cm.$^{-1}$	$\Delta\nu_{OH}$, cm.$^{-1}$	*Intra*-molecular hydrogen bonds	ν_{OH}, cm.$^{-1}$	$\Delta\nu_{OH}$, cm.$^{-1}$
	3460	150		3560	50
	3520	90		3250	360
	3470	140		3220	390
	3460	150		~3200	~400

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(7) L. Pauling: The Nature of the Chemical Bond, 287 (1940). The words in the parentheses are the present writer's.

(8) K. F. Herzfeld: *Chem. Rev.*, **41**, 233 (1947); S. Nagakura and H. Baba: *J. Chem. Soc. Japan*, **71**, 527 (1950).

from the fact that the O atom in anisol has less proton-accepting power than that in ethyl ether.—*Cf.* the order in proton-accepting powers given above.)

Appendix.—In the course of the present investigation, an interesting fact has come to the writer's notice, *viz.*—The frequency of O−H, bonded with a certain atomic group, takes different values according as the bond is *intra*-molecular or *inter*-molecular. Table 3 gives the values of ν_{OH} (the frequency of O−H stretching vibration) and $\Delta\nu_{OH}$ (its difference from the frequency, 3610 cm^{-1}, of free O−H stretching vibration) given for some molecules and molecular complexes with *intra*-molecular and *inter*-molecular hydrogen bonds.

As is shown in the table, ν_{OH} in guaiacol is higher than that in the complex: $C_6H_5OH\cdots OCH_3C_6H_5$. This fact may be explained from the difference in the structural positions of oxygen atoms in these compounds; for, in guaiacol the oxygen atom of the methoxyl group which is the proton-acceptor, is situated at a position much displaced from the extention of the line representing the O−H bond vector. ν_{OH}'s for the other three O−H···O bonds listed in the table take lower values when the bonds are formed *intra*-molecularly than when they are formed *inter*-molecularly. This may be explained by assuming that there occurs a conjugation across the hydrogen bonds(9) when the bonds are formed *intra*-molecularly in *o*-nitrophenol, methyl salicylate, and salicylic aldehyde.

The writer wishes to express his sincere thanks to Professor San-ichiro Mizushima and Dr. Takehiko Shimanouchi for their kind guidance throughout this work. His thanks are also due to O. Matsumura for his lending the fluorite prism used, and to Professor S. Kambara, Mr. H. Tada, Mr. H. Baba, and Mr. T. Inukai for their placing some of the materials used at the writer's disposal. The cost of this research has been partly defrayed from Grant in Aid for Scientific Research from the Ministry of Education.

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(9) R. S. Rasmussen, D. D. Tunnichiff, and R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949); R. S. Rasmussen and R. Brattain, *ibid.*, 1073; I. M. Hunsberger, *J. Am. Chem. Soc.*, **72**, 5626 (1950).