

Some other interesting results of the present work should be mentioned. First of all, the bonding of 6 molecules of H₂O and 1 molecule of HCl in the complex is such that all are released in a single dissociation step. In fact, it is not possible within the temperature and pressure ranges studied to form an anhydrous hydrochloride or a hydrate not involving HCl. Thus, the presence of both H₂O and HCl is necessary in order to stabilize the bond-

ing of either of them. Second, the complex hydrochloride is quite unstable with respect to dissociation. The error of previous workers in reporting a compound having the formula [Co(en)₂Cl₂].Cl·HCl·2H₂O probably was due to their failure to use vacuum rack techniques in handling the compound under a pressure of H₂O and HCl sufficient to maintain it as the hydrochloride.

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[CONTRIBUTION FROM THE DOW CHEMICAL COMPANY, WESTERN DIVISION]

Intramolecular Hydrogen Bonds to π -Electrons and Other Weakly Basic Groups

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Intramolecular hydrogen bonds between hydroxyl groups and π -electrons are shown to exist in compounds of the type 2-allylphenol. The $\Delta\nu_{\text{OH}}$ shifts are shown to depend on basicity of the π -bond and on the geometrical configuration around the bonding groups. These $\Delta\nu_{\text{OH}}$ shifts are compared with those of compounds where the hydrogen bonds involve electro-negative acceptor atoms.

The phenomenon of hydrogen bonding has been investigated extensively in many laboratories through the use of infrared spectroscopy. Consequently, much is known concerning the types of groups most likely to participate in such bonding, the energies and lengths of the bonds and the approximate form of the associated potential energy function.¹ The energies of intermolecular hydrogen bonds have been shown to be about 3 to 10 kcal./mole, although in some cases, the energies, as measured by $\Delta\nu_{\text{X-H}}$ shifts,^{2,3} have been estimated to be much less than this lower limit. However, the situation is somewhat confused for low-energy hydrogen bonds because the effects on $\Delta\nu_{\text{X-H}}$ shifts of non-specific interactions such as dipole-dipole association have, in general, been completely overlooked. Certainly, as the energy of hydrogen bonds decreases, the importance of these other effects in solutions of high dielectric strength increases and may become more significant than effects due to hydrogen bonding.

The situation is very much simpler for intramolecular hydrogen bonds because they can be studied in dilute solutions which have very low dielectric strength. In these cases, we find that bonds can be formed quite readily between rather unlikely groups and that the bond energies can indeed be very small. This is particularly true for groups substituted *ortho* to each other on an aromatic ring,⁴ thus giving rise to the so-called "*ortho* effect." In such compounds, the groups are more nearly constrained to the same plane and the probability of interaction is greatly increased (decrease in entropy of interaction).

This enables hydrogen bonds of low strength to be formed between hydroxyl groups and the halogens, π -electrons in both aromatic^{5,6} and olefinic

systems, sulfur or other electronegative groups having at least one available electron pair. Strengths of these bonds probably lie between 1-4 kcal./mole, although in some systems discussed below, the strength is less than 1 kcal./mole.

This paper will discuss the bonding of phenolic hydroxyl groups to π -electrons in such compounds as allyl and propenyl phenols and will show how the steric and inductive properties of substituent groups on both the aromatic ring and the olefinic double bond affect the frequency and the breadth of the bands. These bonds will be compared with those formed between phenolic hydroxyl groups and halogen, sulfur, nitro and pyrrol groups.

Experimental

The hydroxyl stretching frequencies were investigated in the fundamental region at 3,600 cm.⁻¹ by means of a Beckman DK-II spectrophotometer. The day-to-day reproducibility was better than ± 2 cm.⁻¹ for sharp bands. The resolution of the instrument at maximum performance was about 4 cm.⁻¹ but a spectral slit width of about 7 cm.⁻¹ was used to obtain most of the data. In order to determine the relative values of frequencies which differ by less than 4 cm.⁻¹, the respective samples were run differentially at equal total O-H absorbance. Relative differences of 0.5 to 1.0 cm.⁻¹ could be unequivocally determined.⁷

All materials, except as mentioned below, were either purchased from commercial sources or were synthesized according to directions found in the literature. The *cis*- and *trans*-isomers of 2-(γ -chlorallyl)-phenol were prepared in a manner similar to the described synthesis of the mixed product⁸ except that the original dichloropropene was first separated into its *cis* (b.p. 105-105.5°) and *trans* (b.p. 112.5-113°) forms by fractionation on a 30-tray Oldershaw column. The *cis*-2-(γ -chlorallyl)-phenol had a b.p. 87-88° at 1.0 mm., n_{D}^{25} 1.5610, and *trans*-2-(γ -chlorallyl)-phenol a b.p. 98-99° at 1.2 mm., n_{D}^{25} 1.5645.

Commercially obtained chemicals were distilled or recrystallized, where practical, before use.

The samples were run in CCl₄ at concentrations from approximately 0.7 to 0.0007 molar in cells with path lengths up to 10 cm. Moisture was removed by direct addition of P₂O₅ to the CCl₄ solution; in the time taken to obtain the spectra, no reaction could be detected with any of the samples.

Results

Jaffé⁹ recently pointed out that one prime differ-

(1) R. Schroeder and E. R. Lippincott, *J. Phys. Chem.*, **61**, 921 (1957).

(2) R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953).

(3) G. C. Pimentel and C. H. Sederholm, *ibid.*, **24**, 639 (1956).

(4) O. R. Wulf, U. Liddel and S. B. Hendricks, *THIS JOURNAL*, **58**, 2287 (1936).

(5) H. H. Jaffe, L. D. Freedman and G. O. Doak, *ibid.*, **76**, 1548 (1954).

(6) L. H. Jones and R. M. Badger, *ibid.*, **73**, 3132 (1951).

(7) A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

(8) C. D. Hurd and C. N. Webb, *THIS JOURNAL*, **58**, 2193 (1936).

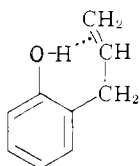
(9) H. H. Jaffé, *ibid.*, **79**, 2373 (1957).

ence between the stability or ease of formation of inter- and intramolecular hydrogen bonds was the difference in the size of the entropy change accompanying formation of the bonds. For intermolecular bonds, this change is in the neighborhood of 50 entropy units (e.u.) for the vapor state, a figure so high that such effects are unobserved for compounds associated through single hydrogen bonds. Most of this entropy is due to the loss of six degrees of freedom (three of translation and three of rotation) although at least one additional degree of freedom is recovered due to the new vibrational possibility. The entropy change in the liquid or solid state, however, is very much smaller because of the cage effects on the solute molecules; this results in partial retention of configuration for long periods of time (long compared to time per collision). Nevertheless, the entropy change is still much larger than the change accompanying the formation of an intramolecular bond. Therefore, we might expect to observe very weak hydrogen bonds more easily and more frequently when these bonds are of the intramolecular type.

The $\nu_{\text{O-H}}$ spectrum of 2-allylphenol, the first member of this series, is given in Fig. 1 for three different concentrations.

In the first curve (curve A) bands due to free O-H groups and to both intra- and intermolecularly bonded O-H groups can be observed. The very broad band, due to intermolecular association, decreases markedly in curve B (0.07 molar) and disappears entirely in curve C (0.007 molar).

The sharp band in each curve is due to the free hydroxyl group; its frequency (3605 cm.^{-1}) is nearly identical to that of phenol (within the resolving power of the instrument) but is probably about one cm.^{-1} higher due to the effect of the allyl group.¹⁰ The broad band at 3542 cm.^{-1} in curve C is due to intramolecular hydrogen bonding of the type



in which the O-H group is bonding to the π -electrons of the ethylenic double bond to give an average $\Delta\nu_{\text{O-H}}$ shift of about 63 cm.^{-1} . The half-width is several times greater than that of the non-associated band and probably has a larger absorptivity. In comparing curves A and C, it is apparent that the intensity of the band due to intramolecular association is approximately equal at both concentrations and that intermolecular association occurs at the expense of the intensity of the non-bonded hydroxyl.

There are three internal rotational degrees of freedom which contribute to a rather marked inverse temperature dependence of the intensity of the band due to intramolecular association. One of these is the rotation of the hydroxyl group about the phenyl-oxygen bond. However, this rotation

(10) Alkyl groups substituted on the aromatic ring are slightly electron donating and consequently increase the phenolic hydroxyl stretching frequency; A. W. Baker, ref. 7.

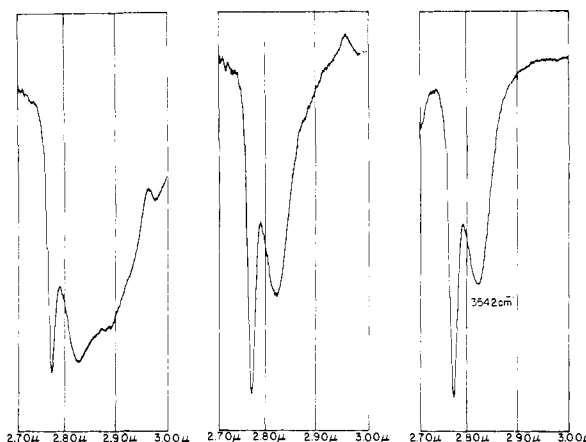
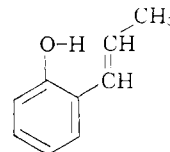


Fig. 1.—2-Allylphenol: left to right, curves A, B and C at concentrations 0.7, 0.07, 0.007 molar, respectively. The cell path lengths are: A, 0.1 mm.; B, 1.0 mm.; C, 1 cm. The ordinates are proportional to per cent. transmission; the horizontal line above the wave lengths is zero transmittance.

is hindered and the hydroxyl group is largely constrained to *cis-trans* configurations because of resonance interaction with the π -orbitals of the ring.¹¹ This restraint becomes slightly less effective as the temperature is raised.¹² The other two rotational modes are those about the alpha and beta carbon-carbon single bonds in the allyl group; either of these rotations can increase the distance between the oxygen and the ethylenic π -electrons and, therefore, decrease the strength of the hydrogen bond and increase the band width. These also contribute more to the temperature effect than does the rotation of the O-H group. In 2-propenylphenol



there is one less internal rotational degree of freedom which can change the distance between the hydroxyl group and the ethylenic π -electrons. Moreover, due to resonance interaction with the aromatic molecular orbitals, the ethylenic group tends to become co-planar with the ring. These effects strongly restrict the variation, due to thermal oscillation, of the distance between the bonding groups and, as a result, the association band is nearly as sharp as the free band (Fig. 2)¹³ with a $\Delta\nu_{\text{O-H}}$ of only 58 cm.^{-1} . The amount of bonded O-H in the propenyl compound is much less than in the allyl compound, and this is attributed to the fact that, since the π -orbitals of the ethylenic double bond are perpendicular to the ethylenic plane, the average interaction distance is greater and the hydrogen bond is weaker than in the allyl compound. Part of the reduction in strength of

(11) L. Pauling, THIS JOURNAL, **58**, 94 (1936).

(12) L. R. Zumwalt and R. M. Badger, *ibid.* **62**, 305 (1940).

(13) In this and all subsequent figures, the concentration is approximately 0.007 molar.

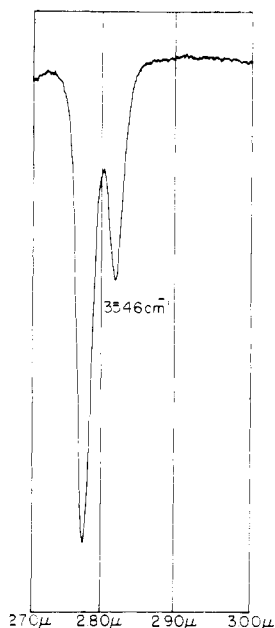
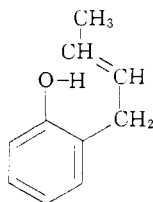


Fig. 2.—2-Propenylphenol at a concentration in CCl_4 of 0.007 molar in a 1.0 cm. cell. The associated band at 3546 cm^{-1} is nearly as sharp as the unassociated band at 3605 cm^{-1} but has an absorbance only one-fourth as large. The ordinate is proportional to per cent. transmission.

the hydrogen bond may also be caused by an unfavorable steric strain due to the smaller hydrogen bond ring system in the propenyl compound than in the allyl.¹⁴

As the basicity of the π -electrons in the ethylenic double bond increases, the strength of the hydrogen bond also increases. This can be shown by putting electron donating groups, such as methyl, directly on the double bond. This is known to increase the electron density in the double bond and should, therefore, increase the basicity. A representative example is the *trans* isomer of 2-(γ -methallyl)-phenol (*trans* 2-crotylphenol).



Its spectrum is given in Fig. 3, and in comparison with curve C of Fig. 1, it is seen that the relative amount of the compound in the bonded state is much greater in the methallyl compound and that the $\Delta\nu_{\text{O-H}}$ of 88 cm^{-1} is correspondingly larger. Therefore, the π -electrons are in reality more basic

(14) Two factors contributing to the strength of the hydrogen bond are the slightly increased acidity of the O-H group due to mesomeric electron withdrawal by the propenyl group, and steric interaction between the O-H group and substituents in the 6-position. The former effect is quite small but nevertheless, real, since the O-H frequency of 2-methoxy-4-propenylphenol is about $1\text{--}2\text{ cm}^{-1}$ lower than that of 2-methoxyphenol. This difference in $\nu_{\text{O-H}}$ is attributed to a lower electron density at the ring carbon adjacent to the O-H group due to electron withdrawal by the propenyl group.

The importance of the steric effect is shown by the $\nu_{\text{O-H}}$ frequencies of 2-methoxyphenol (A), 2,6-dimethoxyphenol (B) and 2-methoxy-6-propenylphenol (C) which are, resp., 3552 , 3548 and 3546 cm^{-1} . In each compound the O-H group is bonding to an *ortho*-oxygen, but the frequency is lowest in C and next lowest in B. Therefore, we must conclude that steric interaction forces the O-H group closer to the bonding 2-methoxy group in the order propenyl > methoxy > H. Ref. 7.

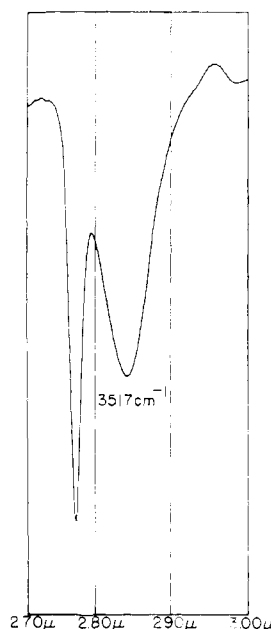


Fig. 3.—2-(γ -Methallyl)-phenol, 0.007 molar in a 1.0 cm. cell. The ordinate is proportional to per cent. transmission.

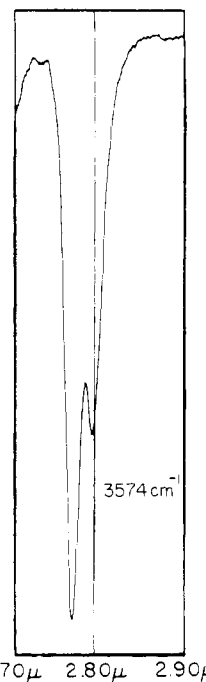
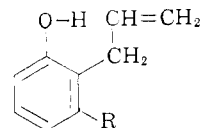


Fig. 4.—*cis*-2-(γ -Chloroallyl)-phenol, about 0.007 molar in a 1.0 cm. cell. The ordinate is proportional to per cent. transmission.

than those in the unsubstituted allyl group and form a stronger hydrogen bond with the hydroxyl group.

In contrast to the behavior of electron donating groups, electron attracting groups decrease the basicity of the ethylenic π -electrons and drastically reduce the amount of hydrogen bonding. For example, the O-H band of the *trans* isomer of 2-(γ -chloroallyl)-phenol is single, occurs at the normal phenolic position and shows only a small asymmetry on the low frequency side. The basicity has been reduced so much that only a slight amount of hydrogen bonding occurs. On the other hand, the *cis* isomer shows two sharp frequencies (Fig. 4) with a $\Delta\nu_{\text{O-H}}$ of only 31 cm^{-1} . The hydrogen bond in this compound most probably is not to the π -electrons but to the more basic chlorine atom. Molecular models demonstrate that this type of bonding is possible in the latter case but not in the former.

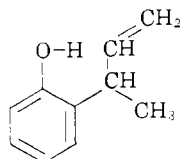
Steric Effects.—Substituents adjacent to the allyl group of 2-allylphenol interact sterically with



the allyl group and, at first glance, one might assume that this would be a buttressing effect favorable to the formation of the hydrogen bond. However, the spectrum of 2-allyl-3,5-dimethylphenol given in Fig. 5 shows that the amount of hydrogen bonding is much less than for the unsubstituted compound and that the $\Delta\nu_{\text{O-H}}$ has been

reduced from 63 to 48 cm^{-1} . Molecular models indicate that steric interaction between the methyl and methylene groups is least when the vinyl group is on one side of the aromatic plane and the two methylene hydrogen atoms on the opposite side. This significantly increases the average hydrogen bonding distance and results in a weaker hydrogen bond.

A steric effect favorable to hydrogen bonding is shown by 2-(α -methallyl)-phenol



The spectrum in Fig. 6 shows that the $\Delta\nu_{\text{O-H}}$ shift (86 cm^{-1}) is nearly the same as that for the γ -methallyl compound (88 cm^{-1}) but that the half width is approximately 30% smaller. The inductive effect of the methyl group on the double bond is probably very slight but it introduces a considerable barrier to rotation. The increase in hydrogen bonding and the decrease in band width is then due to restricting the π -electron system to a distance which is favorable for interaction with the hydroxyl group.

o-Phenylphenol is also a good example of the effect of steric restriction of rotation. The $\nu_{\text{O-H}}$ spectrum consists of two sharp bands, one at 3603 cm^{-1} near the normal free phenolic O-H and the other at 3558 cm^{-1} ($\Delta\nu_{\text{O-H}}$ of 45 cm^{-1}). The band at 3558 cm^{-1} due to bonded O-H is approximately 6 times as intense as that of the free O-H. The barrier to free rotation of the phenyl groups with respect to each other is probably large enough that the motion is mainly limited to a simple oscillation about the common bond. In such a motion, the O-H is essentially never out of hydrogen-bonding range of the aromatic π -electrons so that not only is the band sharp, but also the major amount of sample exists in the bonded form. As in the case of the *o*-halophenols, all of the non-bonded hydroxyl may be due to the *trans* O-H position rather than to an increase in the distance between the hydroxyl group and the aromatic π -electrons. These results are summarized in Table I.

TABLE I
FREQUENCY SHIFTS OF PHENOLS BONDING INTRA-
MOLECULARLY TO π -ELECTRONS

Substd. phenol	$\Delta\nu_{\text{O-H}}$, cm^{-1}	Proton accepting group
<i>trans</i> -2-(γ -Chloroallyl)	0	
<i>cis</i> -2-(γ -Chloroallyl)	31	Cl
2-Phenyl	45	π aromatic
2-Allyl-3,5-dimethyl	48	π C=C
2-Propenyl	58	π C=C conj.
2-Allyl	63	π C=C
2-(α -Methallyl)	86	π C=C
2-(γ -Methallyl)	88	π C=C

Comparison of π -Electrons with Other Proton Accepting Groups.—The $\Delta\nu_{\text{O-H}}$ shifts of hydrogen bonds formed to other types of *ortho* substituted electronegative groups are given in Table II. *o*-Allylphenol is included for comparison. The ele-

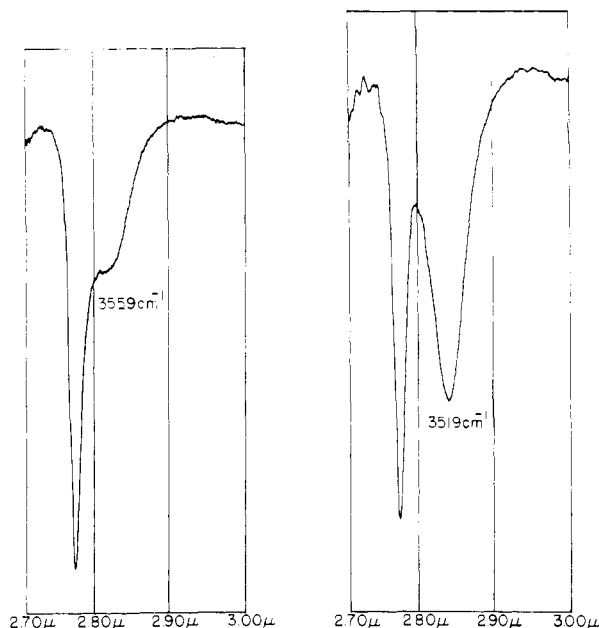


Fig. 5.—2-Allyl-3,5-dimethylphenol, 0.007 molar in a 1.0 cm. cell. The band minimum is not clearly resolved, but it is probably near the assigned value of 3559 cm^{-1} . The ordinate is proportional to per cent. transmission.

Fig. 6.—2-(α -Methallyl)-phenol, 0.007 molar in a 1.0 cm. cell. The ordinate is proportional to per cent. transmission and the abscissa line above the wave length markers is zero transmittance.

ment or group to which the bond is made is given in the third column. All data for Table II were obtained in this Laboratory as described above.

The data of Table II show that for intramolecular hydrogen bonds formed between the hydroxyl group and elements attached directly to the ring, the strength of the bonds increases generally in the order $\text{F} < \text{O} < \text{Cl} < \text{Br} < \text{I} < \text{S} < \text{=O} < \text{N}$. It is known that both the electronegativity of the element and its free electron pair overlap distance contribute to the strength of the hydrogen bond, although, in this sequence, electronegativity is of minor importance. Moreover, accepted values of atomic diameters are not a measure of the overlap distance. For example, the published¹⁵ atomic diameter and electronegativity of trivalent nitrogen are only slightly different from those of chlorine. Yet nitrogen forms the strongest bonds of any of the elements listed in Table II, a fact which must be due to the characteristic shape of the orbital of its free electron pair.

The directiveness or overlap of the nitrogen non-bonding electrons is demonstrated by the hydroxyl spectra of 2-amino-3,5-dimethylphenol and 2-dimethylamino-3,5-dimethylphenol given in Fig. 7. The spectrum of the 2-amino compound is nearly identical to that of the *para* isomer and consists of a sharp band due to non-bonded O-H and two bands characteristic of the symmetric and antisymmetric NH_2 stretching vibrations. Therefore, no bonding takes place between the -O-H and NH_2 groups.

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 60, 164.

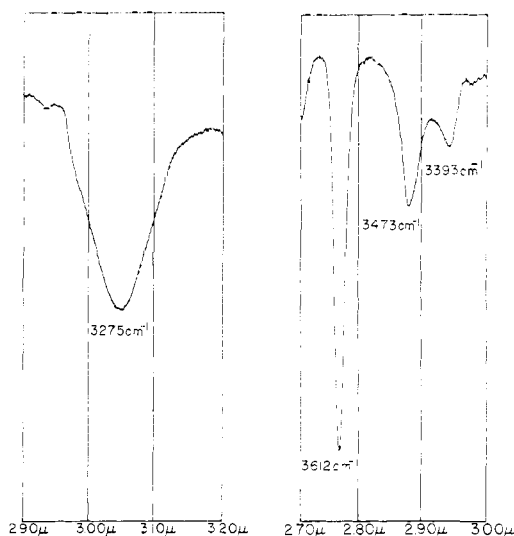


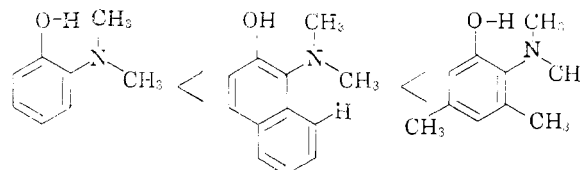
Fig. 7.—2-Dimethylamino-3,5-dimethylphenol (left) and 2-amino-3,5-dimethylphenol (right). The bands at 3473 and 3393 cm^{-1} of 2-amino-3,5-dimethylphenol are due to antisymmetric and symmetric stretching frequencies of unassociated N-H groups. The band at 3612 cm^{-1} is due to a stretching vibration of the unassociated O-H. Both curves were obtained in CCl_4 solution at concentrations of about 0.007 molar.

On the other hand, the spectrum of 2-dimethylamino-3,5-dimethylphenol shows the presence of a very strong hydrogen bond.

This striking difference in intramolecular hydrogen bonding is attributed to a number of causes. The amino group, because of resonance interaction with the aromatic π -electrons, tends to align itself parallel to the ring. It does not, however, become coplanar as evidenced by the fact that *p*-phenylenediamine has an appreciable dipole moment, and, therefore, the nitrogen bonds maintain some of their tetrahedral character. The effect of resonance is to orient the amino group with both hydrogen atoms lying on one side of the plane and the orbital of the non-bonding pair of electrons on the other side. The formation of a hydrogen bond is prevented because the distance between the hydroxyl group and the electron pair is too large and possibly because of steric interaction between the NH and O-H protons. Likewise, N-H...O bonds are not formed because of the unfavorable bonding distance.

The dimethylamino group forms a very strong hydrogen bond to the O-H because the two methyl groups introduce sufficient steric interaction with the adjacent ring substituents to force the dimethylamino plane to be essentially at right angles to the aromatic plane. Consequently, the orbital of the free electron pair is directed toward the hydroxyl group thus permitting the formation of a strong hydrogen bond. Similar effects are observed in the spectra of 2-aminophenol, 1-amino-2-naphthol and the corresponding N,N-dimethyl compounds. The strength of the hydrogen bond increases in the direction shown by the formulas because of an increasing steric interaction which forces the dimethylamino group closer to the O-H.

The increase in interaction is in the order $\text{CH}_3 > \text{peri-H} > \text{H}$. Changes of the spectra due to a comparison of the chemically different phenol and



naphthol are ruled out because the frequencies given by 2-aminophenol and 1-amino-2-naphthol are identical.

TABLE II
FREQUENCY SHIFTS OF PHENOLS BONDING INTRAMOLECULARLY TO ELECTRONEGATIVE ATOMS

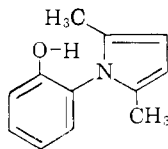
	$\Delta\nu_{\text{O-H}}$, cm^{-1}	Proton acceptor
2-Fluorophenol	18	F
2-Methoxyphenol	52	O
2-Methoxy-4-propenylphenol	53	O
2,6-Dimethoxyphenol	56	O
2-Methoxy-6-propenylphenol	58	O
2-Chlorophenol	61	Cl
2-Allylphenol	63	π -electrons
2,4-Dichlorophenol	63	Cl
2,4,5-Trichlorophenol	67	Cl
2-Bromophenol	78	Br
2-(2,5-Dimethylpyrryl)-phenol	80	N
2-Chloro-4-nitrophenol	83	Cl
2,4-Dibromophenol	83	Br
2- α -Chloromethyl-4-nitrophenol	85	Cl
2-Iodophenol	105	I
2,2'-Thiodiphenol	149	S
2,2'-Thiobis-(3,4,6-trichlorophenol)	93 and 170	Cl and S, resp.
2,2'-Thiobis-(4,6-dichlorophenol)	84 and 172	Cl and S, resp.
2-Hydroxy-3,5,6-trichloro-1,4-benzoquinone	188	C=O
2-Hydroxy-1,4-naphthoquinone	197	C=O
2,5-Dihydroxy-3,6-dichloro-1,4-benzoquinone	238	C=O
2-Dimethylaminophenol	244	N
1-Dimethylamino-2-naphthol	311	N
2-Dimethylamino-3,5-dimethylphenol	329	N
2-Nitrophenol	346	NO_2
2,4-Dinitrophenol	388	NO_2
3,5-Dimethyl-2-nitrophenol	437	NO_2

The Nitro Group.—The strength of the hydrogen bond to an *o*-nitro group has long been recognized as being due to bonding to one of the oxygen atoms. The chelate ring contains 6 atoms and the O...O distance can be smaller than is possible in 5-membered rings of the above types. Very interesting steric effects are shown which can either aid or interfere with the hydrogen bond when small groups or atoms are substituted in the 3-position. For 3,5-dimethyl-2-nitrophenol the hydrogen bond is strengthened by the presence of the 3-methyl group. This is shown by the extreme $\Delta\nu_{\text{O-H}}$ shift

of 437 cm^{-1} compared to 346 cm^{-1} for 2-nitrophenol. The band is also very broad. Rather twisting the nitro group out of the aromatic plane, the methyl group has caused a small bending of the nitro group toward the O-H with a resultant increase in strength of bonding.

A 3-chloro substituent, on the other hand, causes a large reduction in the strength of the hydrogen bond. This probably is due to a steric interaction which is large enough to rotate the nitro group out of the plane of the aromatic ring. In this position, the distance between the O-H group and the nitro oxygens is too large for strong bonds. Furthermore, the basicity of the nitrogen is quite small because of the large amount of nitro resonance which makes the non-bonding pair of electrons on the nitrogen unavailable for bond formation. These effects are demonstrated by 3,4,6-trichloro-2-nitrophenol¹⁶ which has a $\Delta\nu_{\text{O-H}}$ shift of only 82 cm^{-1} . This shift is about what one would expect for a bond formed to the 6-chlorine atom, and the width of the band is correspondingly very small.

A similar reduction in basicity of nitrogen occurs in other systems where the non-bonding pair of electrons is in resonance with π -electrons. Resonance reduces the orbital overlap of the non-bonding electrons and decreases their availability in hydrogen bonding. An example of this is 2-(2,5-dimethylpyrryl)-phenol (Table II).

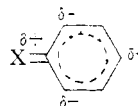


The O-H band is very sharp and has a $\Delta\nu_{\text{O-H}}$ of 78 cm^{-1} as compared with 244 cm^{-1} for 2-dimethylaminophenol. Free rotation of the pyrryl group is strongly hindered by the two methyl groups, and therefore, the width of the band is very small.

At first glance, there appear to be two possible proton acceptors in this system. One is the non-bonding electron pair on the nitrogen and the other is the conjugated π -electron system as in *o*-phenylphenol. However, the non-bonding pair of electrons is promoted to a molecular orbital involving the pyrrole ring, thus giving six π -electrons in the conjugated system as demanded by the concept of aromaticity. Therefore, one cannot distinguish between the two bonding possibilities. Since the $\Delta\nu_{\text{O-H}}$ of the pyrryl compound is nearly twice as large as that of *o*-phenylphenol, it is probable that electron density is piled up around the nitrogen because of its greater electronegativity. We can conclude that the hydrogen bond is formed to the π -electron system at or near the nitrogen atom.

Six-membered Halogen Chelate Rings.—In compounds where the halogen is once removed from the ring, as in 2- α -chlorocresol, the $\Delta\nu_{\text{O-H}}$ shift of the hydrogen bond is about equal to or slightly greater

than in compounds where the halogen is attached directly to the ring. Since there is one additional rotational degree of freedom with its accompanying increase in entropy, the proportion of the compound in the bonded state changes from about 98% to about 30% or less. The near equality in bonding strength in both types of compounds is probably mainly due to a balancing of the three factors, a lower acidity of the O-H group, a greater basicity of the halogen and a smaller possible O...X internuclear distance. The increase in basicity is due to elimination of resonance interaction of the type



which results in a decreased electron density around the halogen compared to an aliphatic halogen. This is a well-known effect and decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$. However, since the net electronic effect of the halogens on the ring is one of electron withdrawal, a ring halogen also increases the acidity of the O-H group, and consequently the strength of the hydrogen bonds. This augmenting effect is reduced or eliminated when the halogen is once removed from the ring.

These effects are clearly shown in the spectrum of 2- α -chloromethyl-4-nitrophenol. The $\Delta\nu_{\text{O-H}}$ is 85 cm^{-1} compared to 83 cm^{-1} for 2-chloro-4-nitrophenol, and the band half width is about twice as large.

The importance of basicity of the halogen and acidity of the hydroxyl group in hydrogen bond formation also is demonstrated in compounds such as 2-chloro- α -phenethyl alcohol. The halogen and the hydroxyl group bear the same relationship to each other as in the *o*-halophenols, but the acidity of the O-H has been reduced to a value nearly equivalent to that of aliphatic alcohols. In both 2-chloro- α -phenethyl alcohol and the bromo analog, the -O-H band is single but is asymmetric on the high frequency side. Identical features are shown by α -phenethyl alcohol, indicating that two bands are contributing to the structure—one due to non-bonded O-H with a frequency of about 3620 cm^{-1} and one due to bond formation to the aromatic π -electrons at about 3610 cm^{-1} .

The intensity of the latter band is several times stronger than the former, evidence that only a small proportion of the hydroxyl is out of range of the π -electrons.

These conclusions are strengthened by the spectrum of β -phenethyl alcohol; the two bands due to free and bonded O-H are clearly resolved and have the frequencies of 3628 and 3600 cm^{-1} , resp. The free O-H band is the stronger despite the greater $\Delta\nu_{\text{O-H}}$ shift of the associated O-H as compared to the α -phenethyl alcohols, again indicating that the additional degree of rotational freedom plays a key role in the degree of association.

(16) Ken Bradley, The Dow Chemical Company, Midland, Michigan, private communication.