

hours under nitrogen, and cooled, leading to recovered diene, 0.45 g. (21% yield), m.p. 152–154°, mixed m.p. 153–158°. A second fraction was diethyl hydrazodicarboxylate, 0.75 g. (19% yield), m.p. 129–131° from alcohol, mixed m.p. 129–132°. A third fraction appeared to be adduct, 0.96 g. (0.0025 mole), 25% yield, m.p. 139–140° from chloroform-petroleum ether. The absorption spectrum was taken in dioxane; λ_{\max} 259 μ , ϵ 15,840.

Anal. Calcd. for $C_{22}H_{24}O_4N_2$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.44; H, 6.08; N, 6.64.

Kinetics of Decomposition of I.—A sample of I, ca. 0.2 g., was weighed accurately and dissolved in isoöctane in a 5-ml. volumetric flask. Samples of the solution, 0.100 ml., were

carefully pipetted into ampoules approximately 30 ml. in volume and immediately frozen in liquid nitrogen. The ampoules were placed on a vacuum manifold, degassed by freezing and thawing at 10^{-6} mm., and sealed. They were placed in a constant temperature silicone oil-bath at the indicated temperatures for measured periods of time, removed from the bath and cooled in liquid nitrogen. The ampoules were opened, sufficient solvent was added to bring the volume of liquid to 5 ml., the solution was mixed and the absorption spectrum of the solution was obtained on a model 21 Cary spectrophotometer. The optical density at 3415 Å. was noted and a first-order rate constant was calculated for each point from the equation $\ln(O.D.)_0/(O.D.)_t = kt$.

[CONTRIBUTION FROM THE EASTERN RESEARCH LABORATORY OF THE DOW CHEMICAL CO., FRAMINGHAM, MASS.]

Intramolecular H-Bonds. I. A Spectroscopic Study of the Hydrogen Bond between Hydroxyl and Nitrogen

BY HAROLD H. FREEDMAN

RECEIVED JANUARY 23, 1961

A survey of simple compounds containing similar intramolecular OH \cdots O and OH \cdots N bonds indicates that, contrary to currently held views, the latter system forms the stronger H-bond. A detailed infrared spectroscopic study of internal five- and six-membered rings involving bonding of phenolic hydroxyl to azomethine nitrogen also supports the above conclusion. It is demonstrated that when the OH \cdots N=C bond is incorporated in a π -electron system, the strength of the bond parallels that of the carboxylic acid dimers and the enolized β -diketones. Some observations regarding the C=N stretching frequency of the phenolic Schiff bases are presented.

Introduction.—The overwhelming majority of investigations of hydrogen bonds which involve hydroxyl as the proton donor group are also concerned with oxygen as the proton acceptor atom, and comparatively few spectroscopic studies are available concerning H-bonding of hydroxyl to nitrogen as the acceptor atom. This can be seen readily from an examination of the two most comprehensive reference texts on infrared spectroscopy, Bellamy,^{1a} and Jones and Sandorfy,^{1b} both of which have extensive sections on OH \cdots O and NH \cdots N bonds with but casual mention of bonds involving OH \cdots N.^{2a}

A similar situation exists in the study of the strength of H-bonds by crystallographic methods. Donahue,³ in a review of hydrogen bonds in organic crystals, dismisses the OH \cdots N bond with the statement that only two examples were known (in 1950), and that this is due mainly to the preferential formation of OH \cdots O bonds. He further states that there is apparently no significant difference between NH \cdots O and OH \cdots N bonds. On the basis of Donahue's³ review, a linear relationship between bond distance and the OH stretching frequency for OH \cdots O bonds was derived by Rundle and Parasol⁴ and this was followed by a similar treatment by Lord and Merrifield.⁵ Further empirical relations were extended to NH \cdots O

and NH \cdots N bonds as well as OH \cdots O⁶ and, with the accumulation of crystallographic X-ray data, a more extensive treatment by Nakamoto, Margoshes and Rundle⁷ included a short section on OH \cdots N bonds. However, no comment was made as to the relative strength of the OH \cdots N bond, and it was further noted by these authors that four of the five compounds examined (in contrast to the 26 compounds containing OH \cdots O bonds) were oximes and that the molecular crystal structure was ambiguous.⁷

An indication that the strength of the OH \cdots N bond may have been greatly underestimated may be inferred from a recent discussion on the structure of formamidoxime⁸ in which the estimated frequency of the OH \cdots N bond is placed at 3260 cm.^{-1} , a value significantly lower than the mean frequency of 3350 cm.^{-1} as given by Sutherland⁹ for OH \cdots O bonds. Further, the spectroscopic evidence of Baker, Davies and Gaunt¹⁰ specifically supports the greater strength of intermolecular OH \cdots N over OH \cdots O bonds. These authors, in seeking evidence for alcohol-amine association in the base-catalyzed reaction of phenyl isocyanate with alcohols, studied the effect of the addition of triethylamine on the hydroxyl stretching band of methanol in both di-*n*-butyl ether and in benzene. Though their choice of solvents has adversely affected the quality of the resulting spectra, their conclusion that "the energy of the amine interaction with the hydroxyl group is of the same order

(1) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1958; (b) R. N. Jones and C. Sandorfy, in "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956.

(2) (a) The recent appearance of a text devoted exclusively to a study of hydrogen bonding^{2b} does not significantly affect the validity of the above statement. (b) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(3) J. Donahue, *J. Phys. Chem.*, **56**, 502 (1952).

(4) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

(5) R. C. Lord and R. E. Merrifield, *ibid.*, **21**, 166 (1953).

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

(7) K. Nakamoto, M. Margoshes and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).

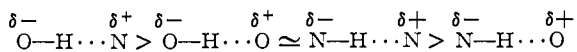
(8) W. J. Orville-Thomas and A. E. Parsons, *Trans. Faraday Soc.*, **54**, 460 (1958).

(9) G. B. M. Sutherland, *Disc. Faraday Soc.*, **9**, 274 (1950).

(10) J. W. Baker, M. M. Davies and J. Gaunt, *J. Chem. Soc.*, 25 (1949).

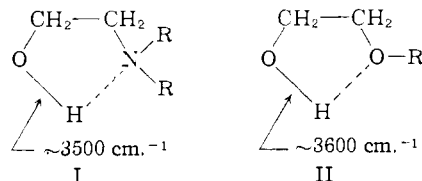
or possibly slightly greater than that of the self-association of the alcohol" would seem to be fully justified. This contrasts very sharply with the above-mentioned observations of Donahue³ and, indeed, with the general impression given by most major contributors to the much discussed subject of hydrogen bonding.

It is our main purpose to provide further spectroscopic evidence for the greater strength of the hydroxyl to nitrogen bond and to show that it is equally true for intramolecular as well as intermolecular systems. However, it may first be appropriate to justify the above premise in regards to the relative strength of H-bonds, by a simple qualitative argument: namely, that the strength of the bond will vary with the stability of the charges induced on the proton donor and acceptor atoms and that these charges will be stabilized according to the electronegativity of the atom. Inasmuch as the positive and negative charge will reside on the donor and acceptor atom, respectively, the greater electronegativity of oxygen *vs.* nitrogen will stabilize the bonds as



It is probable that the strongest and weakest bonds are as pictured, since the former places the partial negative charge on the most electronegative atom and the latter does just the opposite. Similar considerations cannot uniquely determine the relative strengths of the $\text{OH} \cdots \text{O}$ and $\text{NH} \cdots \text{N}$ bonds, but enough spectroscopic evidence¹¹ exists to show that the latter is less favored. Finally, it is a matter of common experience that the OH group is a relatively strong proton donor (*i.e.*, an acid) and the N atom a proton acceptor (*i.e.*, a base), and on this basis alone we might expect $\text{OH} \cdots \text{N}$ bonds to be energetically more favored than $\text{OH} \cdots \text{O}$ bonds.

Intramolecular Bonding of OH to N.—The presence of a five-membered ring involving $\text{OH} \cdots \text{N}$ bonding was first reported by Bergmann, Gil-Av and Pinchas¹² who noted a downward shift of the hydroxyl stretching frequency from its normal (monomeric) value of $\sim 3600 \text{ cm.}^{-1}$ to 3380–3450 cm.^{-1} for N-mono- and N,N-disubstituted 2-amino-ethanols in dilute carbon tetrachloride solution. However, their reported value of, for example, 3280 cm.^{-1} for the OH absorption of N-methyl-2-aminoethanol, seems much too low and we are in agreement with the more recent work of Flett¹³ who reports that amino-alcohols of the type shown in I exhibit a strong OH band at approximately 3500 cm.^{-1} in dilute carbon tetrachloride solution. In contrast, the corresponding



(11) Reference 1, p. 253.

(12) E. D. Bergmann, E. Gil-Av and S. Pinchas, *J. Am. Chem. Soc.*, **75**, 68 (1953).

(13) M. St. C. Flett, *Spectro. Chim. Acta*, **10**, 21 (1957).

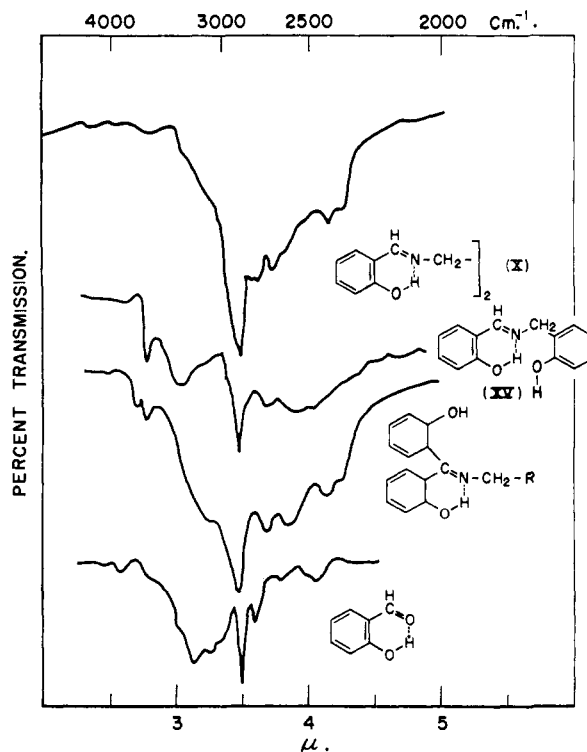
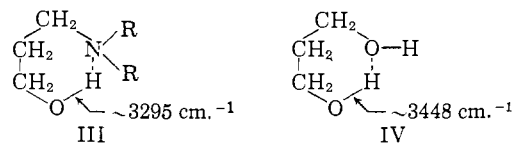


Fig. 1.—Dilute solution spectra of conjugate-chelates in chloroform (1.0-mm. cell).

five-membered ring involving an $\text{OH} \cdots \text{O}$ bond, the glycol-ether II, is reported by Flett¹³ to adsorb at $\sim 3600 \text{ cm.}^{-1}$ and, therefore, possesses an internal bond so weak as to be practically undistinguishable from a monomeric alcohol. Flett¹³ further finds that when the amino-alcohol ring size is increased to six-membered as in III the frequency is correspondingly decreased to $\sim 3295 \text{ cm.}^{-1}$, whereas Kuhn¹⁴ reports a frequency of 3448 cm.^{-1} for the



intramolecular $\text{OH} \cdots \text{O}$ bond of trimethylene glycol. The hydroxyl frequency shifts of these compounds relative to unbonded hydroxyl makes it obvious that stronger internal H-bonds are formed by the bonding of OH to N rather than by OH to O.

If, as has been mentioned previously, the relative acidity of the proton-donating and accepting atoms is of primary importance in determining the strength of the hydrogen bond, then substitution of an aromatic ring in place of alkyl or hydrogens should result in a stronger H-bond in the case of oxygen and a weaker one in the case of nitrogen. This is in accordance with the increased acidity of the phenolic hydroxyl over that of aliphatic alcohols and the decreased basicity of the nitrogen of anilines over those of aliphatic amines. In terms of simple resonance theory, interaction of the unshared p-electrons of the proton-donating OH

(14) L. B. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

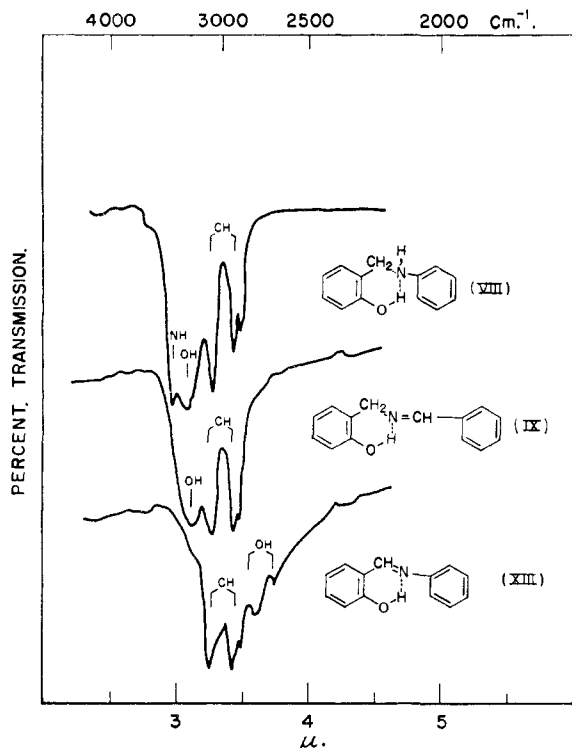
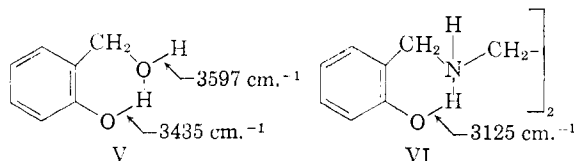


Fig. 2.—Dilute solution spectra of VIII, IX and XII in carbon tetrachloride (1.0-mm. cell).

group with the aromatic ring will increase its acidity (and donating ability) by virtue of the positive charge on the oxygen while a similar delocalization of the lone-pair electrons of the N-atom will decrease its proton-accepting ability.

In the case of the six-membered ring involving an $\text{OH}\cdots\text{O}$ bond in which the donor atom is phenolic, as in *o*-hydroxybenzyl alcohol (V), only

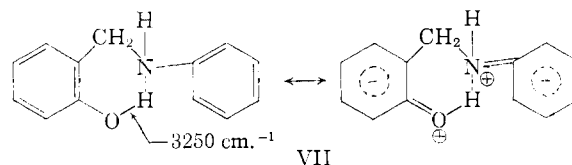


a small frequency lowering is realized as compared to its aliphatic counterpart, the glycol IV. The presence of intramolecular bonding in V has been previously reported by Martin¹⁵ who assigns the band at 3436 cm^{-1} to the $\text{OH}\cdots\text{O}$ bonded hydroxyl and a weaker band at 3600 cm^{-1} to unbonded OH. Our investigation of V is in complete agreement with these assignments and, though Martin¹⁵ makes no decision between the two possible bonded structures for V, it seems reasonable, on the basis of the relative proton donor tendencies of the phenolic *vs.* alcoholic OH, that the actual structure of V is as written. In contrast to V, a relatively large shift is observed when a phenolic hydroxyl is intramolecularly bonded to nitrogen. We find that the $\text{OH}\cdots\text{N}$ bond of α,α' -ethylenediimino-*o*-cresol (VI) appears at 3125 cm^{-1} in dilute chloroform solution, and if the generous assumption is made that 25 cm^{-1} of this

(15) A. E. Martin, *Nature*, **166**, 474 (1950).

low frequency shift is due to the effect of the solvent,¹⁶ then the presence of the phenolic hydroxyl donor group of VI has caused a downward displacement of about 150 cm^{-1} relative to the aliphatic hydroxyl group of III. Further, the presence of the strong $\text{OH}\cdots\text{N}$ bond of VI is in contrast to the weak $\text{OH}\cdots\text{O}$ bond of V and is reflected in the very substantial frequency difference of 285 cm^{-1} between these two compounds.

The expected frequency increase, in accordance with the decreased strength of the H-bond, is observed when phenyl is substituted on nitrogen. We find, in excellent agreement with Moritz,¹⁷ that the $\text{OH}\cdots\text{N}$ bond of N-2-hydroxybenzyl-aniline (VII) absorbs at 3250 cm^{-1} (Fig. 2), an



increase of about 100 cm^{-1} over the N-alkyl substituted VI. However, despite the decreased hydrogen-bond strength due to the decreased availability of the *p*-electrons of the nitrogen, the internal H-bond of VII is still considerably stronger than that of *o*-hydroxybenzyl alcohol (V) which has a similar geometry and a similar acidic hydroxyl, but has not the added handicap of the delocalization of the *p*-electrons of the acceptor atom. It is of interest, since VII has a somewhat stronger bond than III, that the increased acidity of the phenolic OH of VII has more than compensated for the decreased basicity of its nitrogen. It is also significant that Moritz¹⁷ finds no evidence for $\text{NH}\cdots\text{O}$ bonding in VII, despite the increased acidity of the NH bond of this compound.

Intramolecular Hydrogen Bonding of O—H to C=N.—It is well known, both as a matter of experience and on theoretical grounds, that the basicity of nitrogen decreases with an increase in its s-character.¹⁸ The availability of the unshared p-electrons of the nitrogen will decrease in the order $\text{R}_3\text{N} > \text{R}_2\text{C}=\text{NR} > \text{RC}\equiv\text{N}$, as the configuration of the nitrogen changes from sp_2 in the amine to sp_2 in the Schiff base and, finally, to sp in the nitrile. It is presumably this decreased basicity of the sp_2 nitrogen of the azomethine group which leads to the absence of internal bonding in the N-alkylidene-2-amino alkanols,¹² $\text{HOCH}_2\text{CH}_2\text{N}=\text{CR}_2$, whereas a reasonably strong five-membered chelate ring is present in the analogous compound containing a saturated nitrogen (*i.e.*, I). Similarly, the basicity of carbonyl oxygen will be less than that of hydroxyl oxygen and it is, therefore, surprising to find that the data of Flett¹³ indicate that non-conjugated five- and six-membered rings containing $\text{OH}\cdots\text{O}=\text{C}$ bonds do not absorb at significantly higher frequencies than compounds of

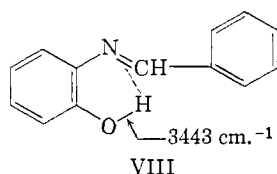
(16) In general, a downward frequency shift of approximately 15 cm^{-1} is observed in the hydroxyl stretching band when the solvent is changed from carbon tetrachloride to chloroform.

(17) A. G. Moritz, *Spectrochim. Acta*, **13**, 242 (1959).

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, N. Y., 1960.

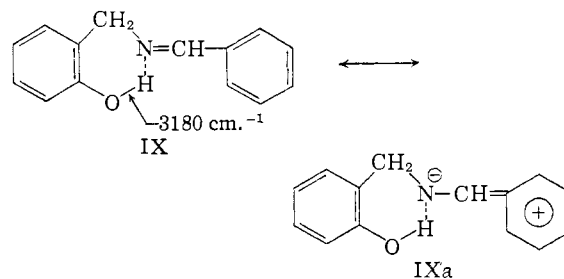
the type II and IV in which the acceptor oxygen is sp^3 rather than sp^2 . It is hoped that future investigations will include data on the comparative strengths of non-conjugated six-membered chelate rings involving aliphatic $OH \cdots O=C$ and aliphatic $OH \cdots N=C$, but for the present the discussion will be limited to internal five- and six-membered rings involving phenolic hydroxyl as the proton donor and the nitrogen of the azomethine group as the proton acceptor.

The presence of a weak but definite five-membered chelate ring in benzylidene-*o*-aminophenol (VIII) has been demonstrated recently by two independent investigations.^{17,19} Its OH absorption is found at 3443 cm^{-1} in dilute carbon tetrachloride solution, a value which is 175 cm^{-1} lower than its non-hydrogen bonded *p*-amino isomer.¹⁷ In



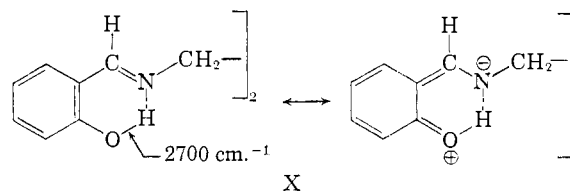
dilute chloroform solution, we find the hydroxyl stretching frequency of the *ortho* and *para* compounds at 3430 and 3584 cm^{-1} , respectively, the latter value being quite comparable to the value for phenol itself in the same solvent. Though the absence of intramolecular hydrogen bonding in benzylidene-*p*-aminophenol needs no explanation, the presence of a chelate ring in VIII seems rather remarkable in view of the fact that *o*-aminophenol shows absolutely no evidence for intramolecular hydrogen bonding^{20,21} and the nitrogen of the latter compound is considerably more basic than the azomethine nitrogen of VIII. Baker and Shulgin¹⁹ explain the presence of H-bonding in VIII by stressing the comparatively large electron density and polarity of the lone-pair orbital of its sp^2 nitrogen. We believe that it is equally likely that H-bonding is occurring by means of the formation of a quasi six-membered ring involving the π -electrons of the $C=N$, as shown, rather than the unshared p -electrons of the nitrogen.²² A similar explanation has been advanced previously by Baker and Shulgin²¹ for an analogous situation (see compound XIV).

When the OH of the six-membered, non-conjugated ring is bonded to an sp^2 rather than an sp^3 nitrogen, as in benzylidene-*o*-hydroxybenzylamine (IX), the hydroxyl of the moderately strong $OH \cdots N$ bond is found at 3180 cm^{-1} in dilute carbon tetrachloride (Fig. 2). This is actually at a lower frequency than the hydroxyl of VII despite

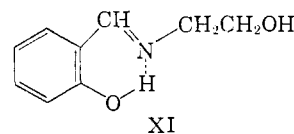


the fact that the latter contains an sp^3 , and therefore presumably more basic, nitrogen. The increased bond strength of IX over VII must be attributed to the presence of the benzylidene phenyl ring which increases the electron density at the N by a resonance mechanism (see IXa), thus increasing its basicity and the strength of the internal H-bond. In contrast, the anilinium phenyl ring of VII decreases the basicity of its nitrogen. Though the compound analogous to IX in which the $C=N$ is not conjugated with a phenyl ring is not available at this writing, it may be predicted that it will exhibit its OH band at a frequency greater than 3250 cm^{-1} , in keeping with the decreased basicity of its sp^2 nitrogen.

We now turn to intramolecular bonded systems in which the $OH \cdots N=C$ bond is incorporated in a π -electron system. These include Schiff bases derived from salicylaldehyde or other *o*-phenolic carbonyl compounds and are distinguished from the previously discussed cases in that the hydroxyl group is conjugated through an aromatic ring with the azomethine linkage, as in N,N' -disalicylideneethylenediamine (X).



A detailed description of the conjugate-chelate²³ system found in *o*-phenolic Schiff bases is not available in the literature, even though as early as 1936 the presence of a strong H-bond in salicylideneaniline was inferred by its lack of absorption in the hydroxyl first-overtone region.²⁴ Both Daasch and Hanninen²⁵ and Bergmann and co-workers¹² have examined the spectrum of N -(*o*-hydroxybenzylidene)-aminoethanol (XI). The former workers



note that XI exists as the Schiff base rather than the oxazolidine, but make no comment on the presence of the conjugate-chelate ring. The latter

(19) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **81**, 1523 (1959).

(20) H. E. Ungnade, *ibid.*, **76**, 5133 (1954).

(21) A. W. Baker and A. T. Shulgin, *ibid.*, **80**, 5358 (1958).

(22) The premise that $OH \cdots \pi$ rather than $OH \cdots N$ bonding is taking place in VIII in no way affects the conclusions of Baker and Shulgin¹⁹ that substituents in the benzylidene ring affect the strength of the H-bond, and consequently the OH frequency, by virtue of their electron-withdrawing or -donating properties. The transmission of these electrical effects to the highly polar π -electrons of the $C=N$, with a subsequent change in its electron density and ability to act as a proton acceptor, seems at least as reasonable as the alternative explanation involving the non-bonding electrons of the nitrogen.

(23) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *ibid.*, **71**, 1068 (1949).

(24) S. B. Hendricks, O. R. Wulf, G. E. Hilbert and U. Liddel, *ibid.*, **58**, 1991 (1936).

(25) L. W. Daasch and U. E. Hanninen, *ibid.*, **72**, 3673 (1950),

group assign the band at 3610 cm.^{-1} to the unbonded aliphatic OH and, though they correctly assume the presence of the conjugated $\text{OH}\cdots\text{N}=\text{C}$ six-membered ring, they incorrectly assign a band at 3420 cm.^{-1} to this system.²⁶ Finally, Badger and Moritz¹³ state that (XIII) N-salicylideneaniline shows a diffuse hydroxyl band superimposed on the C-H stretching bands at $\sim 2850\text{ cm.}^{-1}$ and infer the presence of a strong intramolecular hydrogen bond.

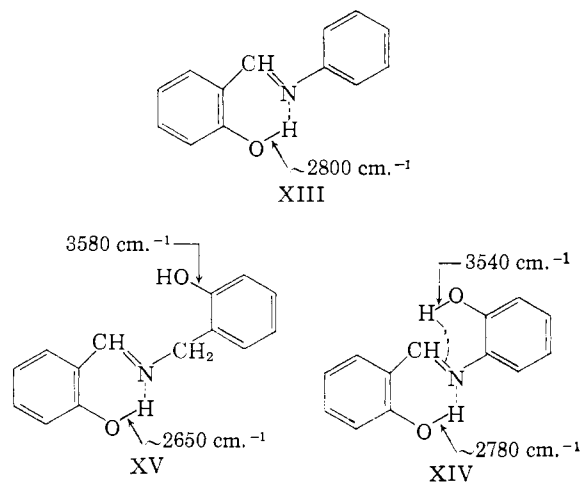
Though the nature of the greatly perturbed hydroxyl band of the conjugate-chelate ring involving the $\text{OH}\cdots\text{N}=\text{C}$ hydrogen bond does not enable us to assign to it an exact frequency, our examination of 17 compounds containing this system²⁷ leaves little doubt that the absorption band envelope extends from approximately 3300 down to 2300 cm.^{-1} . Assuming that the band is roughly symmetrical, this would place the center at about 2800 cm.^{-1} and, indeed, there is invariably a strong peak in this vicinity in all the compounds examined, in either chloroform or carbon tetrachloride solutions, though there may or may not be an adjacent band of somewhat lesser intensity at approximately 2700 cm.^{-1} as well as additional fine structure at lower frequencies. This is demonstrated in Fig. 1, in which the spectra of three typical compounds are reproduced. In general, the dilute solution spectra of *o*-hydroxy Schiff bases show a very strong resemblance to both the well-known carboxylic acid dimers and the equally well-known enolized β -diketones, both of which may be considered to be classical examples of extremely strong resonance-stabilized H-bonds.^{28,29} This resemblance is particularly striking in the case of the Schiff bases derived from 2,2'-dihydroxybenzophenone, an example of which is reproduced in Fig. 1 and which will be discussed in detail in a future publication. In the solid state, one would be hard pressed to distinguish these Schiff bases from the dimeric carboxylic acids in the 3μ region inasmuch as the broad structureless band which is barely discernible as a shoulder on the high frequency side of the C-H stretching frequencies in Fig. 1 becomes almost as pronounced as in the carboxylic acid dimers.

Included for comparison in Fig. 1 is the dilute solution spectrum of salicylaldehyde. This has been considered as typical of the conjugated-chelate rings stabilized by a strong $\text{OH}\cdots\text{O}=\text{C}$ bond,²³ and has been studied previously in carbon tetrachloride solution by both Flett¹³ and by Martin¹⁵ who place its hydroxyl absorption frequency at 3300 and 3200 cm.^{-1} , respectively. In chloroform we find the main hydroxyl frequency of salicylaldehyde to be at approximately 3100 cm.^{-1} with only traces of fine structure at the lower fre-

quencies where is found the major OH absorption of the salicylaldehyde-derived Schiff bases. We must once more conclude that, in the conjugate-chelate systems as well, the $\text{OH}\cdots\text{N}=\text{C}$ bond is stronger than the $\text{OH}\cdots\text{O}=\text{C}$.

The extreme breadth and complexity of the hydroxyl band typical of the salicylideneanilines makes it difficult, if not impossible, to observe the effect of electron-donating or -accepting ring substituents on the OH stretching frequency. Though salicylidene-*o*-methoxyaniline absorbs at the relatively low frequency of $\sim 2600\text{ cm.}^{-1}$ and salicylidene-*p*-nitroaniline at the relatively high frequency of $\sim 2780\text{ cm.}^{-1}$, in keeping with the ability of the *o*-methoxy group to donate and the *p*-nitro group to accept electrons, the estimated limit of error for these compounds of $\pm 100\text{ cm.}^{-1}$ makes any conclusions necessarily dubious.

The availability of the π -electrons of the C=N group of salicylidene-*o*-aminophenol (XIV) for H-bonding has been postulated by others¹⁹ and we have confirmed the existence of this weak internal H-bond in dilute chloroform solution. Examination of its spectrum shows the presence of the conjugated-chelate ring system with its center at $\sim 2780\text{ cm.}^{-1}$ and the π -bonded OH as a sharp band at 3540 cm.^{-1} . When the π -bonded OH can no longer participate in a quasi six-membered ring as in VIII and XIV, then the hydroxyl frequency reverts to that of unbonded OH. This is demonstrated by salicylidene-*o*-hydroxybenzylamine (XV) (Fig. 1) in which the center



of the broad hydroxyl band of the conjugated-chelate ring is found at $\sim 2650\text{ cm.}^{-1}$, approximately 150 cm.^{-1} lower than in XIII and XIV, and reflecting the increase in bond strength when the phenyl group is insulated by means of the intervening methylene from the bonding electrons of the nitrogen. The unbonded OH of XV is found at 3580 cm.^{-1} , which is 40 cm.^{-1} higher than the π -bonded OH in XIV and is identical with the absorption frequency of benzylidene-*p*-aminophenol and *p*-hydroxybenzylideneaniline, both of which absorb at 3580 cm.^{-1} in dilute chloroform solution and neither of which can form internal hydrogen bonds. The above findings are in agreement with a recent report³⁰ concerning intramolecular $\text{OH}\cdots$

(26) The origin of this 3420 cm.^{-1} band is not known, but our studies show that it is much too high to be due to the chelate ring and it is also too high to be the first overtone of the azomethine band which, as will be shown below, is unusually strong in these compounds and is very likely to be confused with a weak hydroxyl band.

(27) Schiff bases derived from 2,2'-dihydroxybenzophenone will be discussed in a separate publication.

(28) D. N. Shigorin, in "Proceedings of the Conference on Molecular Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 226.

(29) S. Bratoz, D. Hadzi and G. Rossmly, *Trans. Faraday Soc.*, **52**, 464 (1956).

π -bonding in the ω -hydroxy-1-alkenes ($\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{OH}$) in which this type of interaction is absent for compounds in which n is greater than 2. The non-availability of the lone-pair p -electrons of the nitrogen in XV, due to preferential formation of the conjugate-chelate ring, is in contrast to IX in which competition for the lone-pair does not exist and, as was shown above, a fairly strong non-conjugate chelate ring is present.

Both XIV and XV (Fig. 1) have an ill-defined but definite absorption band in the 3200 cm.^{-1} region which could not be correlated satisfactorily with the presence of a hydrogen-bonded hydroxyl. That this band is indeed not due to hydroxyl absorption is confirmed by its presence in the dilute solution spectrum of p -hydroxybenzylideneaniline in which hydrogen bonding is not possible. It is believed that this band is in reality the first overtone of the strong 1600 cm.^{-1} azomethine stretching band, in direct analogy with the 3400 cm.^{-1} band often found in the spectra of keto-alcohols³¹ and recently reported by Heinert and Martell³² for the pyridine aldehydes. The assignment of this $3.1\ \mu$ band to a first overtone of the $\text{C}=\text{N}$ is supported by the data tabulated³³

	$2\nu_{\text{C}=\text{N}},\text{ cm.}^{-1}$	
	Calcd.	Found
p -Hydroxybenzylideneaniline	3258	3279
Salicylidene- o -hydroxybenzylamine (XV)	3268	3289
Salicylidene- o -aminophenol (XIV)	3242	3200

Effect of H-Bonding on the $\text{C}=\text{N}$ Frequency.—

Though it is well known that hydrogen bonding to a $\text{C}=\text{O}$ group invariably results in downward displacement of the $\text{C}=\text{O}$ stretching frequency, no information is available in regard to the effect of H-bonding on the azomethine stretching mode. We have extended our investigation of $\text{OH}\cdots\text{N}=\text{C}$ bonding to include a brief investigation of the $\text{C}=\text{N}$ band, the results being incorporated in Table I. In dilute chloroform solution the $\text{C}=\text{N}$ stretching mode is found, in agreement with previous workers,³⁴ in the vicinity of 1625 cm.^{-1} and in every case but one (p -hydroxybenzylideneaniline) it is the strongest band in the 6μ region and is thus easily distinguished from the phenyl stretching modes which occur at lower frequencies.

Comparison of the o -hydroxy aromatic Schiff bases with its most closely related carbonyl analog, the hydroxybenzaldehydes, reveals an unexpectedly large difference in both the resonance interaction of ring substituents and the effect of hydrogen bonding on the $\text{C}=\text{N}$ absorption frequency. Thus, introduction of the strongly electron-donating hydroxyl group in the p -position of benzaldehyde causes a downward displacement of 15 cm.^{-1} in the carbonyl band³⁵ while a similar substitution of a p -hydroxy group in either the benzylidene or

(30) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 567 (1959).

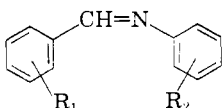
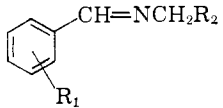
(31) Reference 1b, p. 452.

(32) D. Heinert and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 3933 (1959).

(33) Reference 1b, p. 487.

(34) L. E. Clougherty, J. A. Sousa and G. M. Wyman, *J. Org. Chem.*, **22**, 462 (1957).

TABLE I
 $\text{C}=\text{N}$ STRETCHING FREQUENCIES^a

R_1	R_2	No.	$\nu_{\text{C}=\text{N}},\text{ cm.}^{-1}$ ^b	$\Delta\nu$
				
H	H		1630(s)	..
p -OH	H		1629(vw)	-1
o -OH	H	XIII	1622(s)	-7
H	p -OH		1630(s)	0
H	o -OH	VIII	1626(s)	-4
o OH	o -OH	XIV	1621(s)	-9
				
H	o - OHC_6H_4	IX	1657(s)	+27
o -OH	o - OHC_6H_4	XV	1634(s)	+4
H	$-\text{CH}_2\text{N}=\text{CH}_6\text{H}_5$	XVI	1646(s)	+16
o -OH	$-\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4-$		1634(s)	+4
o -OH	X			

^a Dilute solutions in chloroform measured in 1.0-mm. cell.
^b s = strong, vw = very weak.

aniline ring of benzylideneaniline leaves the $\text{C}=\text{N}$ unchanged within our experimental error. Formation of the conjugate-chelate ring in salicylaldehyde causes an additional decrease of 19 cm.^{-1} in the $\text{C}=\text{O}$ absorption and, if we assume that the resonance interaction of the OH is very similar in both the o - and the p -positions, this frequency decrease is due almost entirely to hydrogen bonding to the $\text{C}=\text{O}$. However, the $\text{C}=\text{N}$ band of salicylideneaniline shows a frequency decrease of only 7 cm.^{-1} despite the fact that the H-bond strength of the conjugate-chelate ring of this compound has been shown to be greater than that of salicylaldehyde. Weaker intramolecular H-bonds give a correspondingly smaller frequency decrease; the non-conjugated five-membered $\text{OH}\cdots\text{N}=\text{C}$ ring of N -benzylidene- o -aminophenol causes a downward shift of only 4 cm.^{-1} and the combination of the conjugate-chelate ring and weak π -bond in XIV gives a total downward frequency displacement of 9 cm.^{-1} .

When the resonance system of the benzylideneanilines is eliminated by replacement of the phenyl ring on the nitrogen by alkyl, then the expected frequency increase is observed. Thus, the azomethine stretching frequency of N,N' -dibenzylideneethylenediamine (XVI) and benzylidene- o -hydroxybenzylamine (IX) are observed at frequencies which are, respectively, 16 and 27 cm.^{-1} higher than that of benzylideneaniline. Most of this frequency increase is restored when an o -hydroxyl group is introduced on the benzylidene ring. Thus, in the conjugate-chelate compounds XV and X, the $\text{C}=\text{N}$ frequency is found in both cases at 1634 cm.^{-1} , a frequency increase, relative to benzylideneaniline, of only 4 cm.^{-1} .

(35) Data taken from H. W. Thompson, R. W. Needham and D. Jameson, *Spectrochim. Acta*, **9**, 208 (1957).