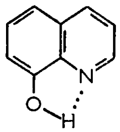
693. *Intramolecular Hydrogen Bonding in 8-Hydroxyquinolines.*

By G. M. Badger and A. G. Moritz.

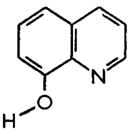
The changes in O–H stretching frequencies, integrated intensities, and half-intensity band-widths of a number of substituted 8-hydroxyquinolines and *o*-benzylideneaminophenols caused by substitution have been related to Hammett's σ-constants, and are discussed in relation to the strength of the hydrogen bond. Evidence is presented for the existence of *cis-trans* isomerism in 8-hydroxyquinoline.

Although intramolecular hydrogen bonds are strongest when the ring is six-membered, bonds of significant strength are formed even when this arrangement is not possible, as for example in tropolone. 8-Hydroxyquinoline (Ia) represents another system in which intramolecular hydrogen bonding would involve a five-membered ring. Hearn, Morton, and Simpson [1] concluded from the ultraviolet spectra of 8-hydroxy- and 8-methoxyquinoline that intramolecular hydrogen bonding is absent from the former. On the other hand, many physical characteristics of 8-hydroxyquinoline indicate the presence of such a bond. Moreover, there is evidence [2] that the tautomeric equilibrium of 8-hydroxy-5-phenylazoquinoline is affected by presence of a weak intramolecular hydrogen bond. The infrared spectra of 8-hydroxyquinoline and some related compounds have therefore been examined.

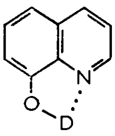
The stretching vibration of an unbonded hydroxy-group appears as a strong absorption band in the 3620 cm.$^{-1}$ region. A shift of this band to lower frequencies is now accepted as a criterion for the presence of hydrogen bonding. In dilute solution in carbon tetrachloride, 8-hydroxyquinoline gave a strong band at 3416 cm.$^{-1}$, *ca.* 200 cm.$^{-1}$ lower than that expected for an unbonded hydroxyl group. The inference of weak intramolecular hydrogen bonding is confirmed by the independence of this band of concentration in the range 0·002—0·10M. At higher concentrations intermolecular hydrogen bonding becomes possible and a diffuse band appeared at 3300—3100 cm.$^{-1}$. Even at a concentration of 1·3M, however, the intensity of the band at 3416 cm.$^{-1}$ was not significantly decreased compared with those of the C–H fundamental bands. Comparison with 1-naphthol, in which steric considerations are similar, showed that intermolecular hydrogen bonds are formed at much lower concentrations. This comparison is particularly sensitive as it has been suggested that weak intramolecular hydrogen bonds are formed in preference to stronger intermolecular bonds because of the entropy changes involved.[3]



(Ia)



(Ib)



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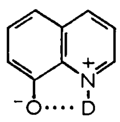

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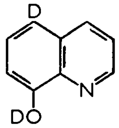

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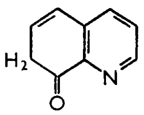

(V)

8-Hydroxyquinoline also showed a very weak absorption band at 3672 cm.$^{-1}$, assigned to the unbonded hydroxyl vibration (*trans*-structure; Ib). Twin peaks have often been observed in the spectra of *ortho*-substituted phenols in which weak intramolecular hydrogen bonding can occur and these have similarly been interpreted in terms of *cis*- and *trans*-structures.[4] Wulf and Liddel[5] have shown that 8-hydroxyquinoline has two bands of

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[1] Hearn, Morton, and Simpson, *J.*, 1951, 3318; see also Ewing and Steck, *J. Amer. Chem. Soc.*, 1946, **68**, 2181.

[2] Badger and Buttery, *J.*, 1956, 614.

[3] Jaffé, *J. Amer. Chem. Soc.*, 1957, **79**, 2373.

[4] Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, New York, 1940, p. 320.

[5] Wulf and Liddel, *J. Amer. Chem. Soc.*, 1935, **57**, 1464; Hilbert, Wulf, Hendricks, and Liddel, *Nature*, 1935, **135**, 147.

weak intensity at *ca.* 6600 and 6830 cm.$^{-1}$, and this has already been interpreted as evidence for structures (Ia) and (Ib).[2]

These assignments are confirmed by deuteration of 8-hydroxyquinoline in neutral solution, the absorption bands at 3672 and 3416 cm.$^{-1}$ being replaced by a weak band at 2792 cm.$^{-1}$ and a strong twin peak at 2542 and 2526 cm.$^{-1}$. The band at 2792 cm.$^{-1}$ is probably the free OD vibration; the twin peak is tentatively assigned to Fermi resonance between the bonded OD vibration (II) and the first overtone of the 1264 cm.$^{-1}$ band. As is usual with such cases of accidental degeneracy, the intensities of the two bands are similar. In agreement with this assignment, when 8-hydroxyquinoline is deuterated in alkaline solution some C–H exchange occurs, for the resulting spectrum shows a small peak at *ca.* 2270 cm.$^{-1}$ due to an aromatic C–D stretching vibration. This spectrum [of 5(?)-deutero-8-deuteroxyquinoline (IV) shows no band near 1264 cm.$^{-1}$ and only a single bonded OD absorption at 2534 cm.$^{-1}$. The twin peak might be associated with the stretching frequencies of the O–D and $^+$N–D bonds (III), but the vibration limits of the two are insufficient to pass over the potential hill between the two.[6] The single peak of the hydroxy-compound would then presumably be due to the increased vibrational limits' (because of smaller mass) being above the potential hill. This interpretation seems to be precluded by Mason's [7] indication that the tautomerism to the zwitterionic structure is only slight in aqueous solvents and even less in solvents of low dielectric constant.

Séguin [8] has concluded from magnetochemical evidence that 8-hydroxyquinoline exists as the tautomer (V) to the extent of *ca.* 30% in benzene, pyridine, or quinoline, but that this is virtually absent from the solid. The spectra in benzene, in carbon tetrachloride, and in the solid do not show any carbonyl band at 1700—1680 cm.$^{-1}$, so that there is no significant proportion of structure (V). In the double-bond stretching region, however, the medium-strength band at 1628 cm.$^{-1}$ of carbon tetrachloride solutions, is very weak in the spectra of the solid; it is possible that this change is associated with the zwitterionic structure.[9] Incidentally this structure was not considered in the magnetochemical measurements.

Coulson [10] found that the various energy contributions to the strength of the hydrogen bond are difficult to evaluate. The effect of substituents on the strength of the intramolecular hydrogen bond is therefore of interest. R. M. Badger and Bauer [11] established that the magnitude of the shift of the hydroxyl stretching frequency can be used as a measure of the strength of the hydrogen bond, and Ingraham *et al.*[12] showed that a linear relation exists between the frequency shifts in substituted catechols and Hammett's σ-constants for the substituents.

The study of substituted 8-hydroxyquinolines offers additional advantages as there are six positions for substitution and the relative requirements of donor and acceptor groups in the system O–H • • • •N might be estimated. The infrared spectra of seventeen substituted 8-hydroxyquinolines have been examined and the frequency shifts for the hydroxyl vibration are given in Table 1. The plot of ν against the σ-constants for 5-substituted 8-hydroxyquinolines (Fig. 1) clearly shows that the deviations from linearity are considerably larger than the probable errors ($\pm$1 cm.$^{-1}$ in ν; $\pm$0·06 unit in σ [13]). A linear relation has been fitted by the method of least squares and the standard deviation between observed and calculated values of ν (the error in σ being assumed to be nil) was $\pm$12·1 cm.$^{-1}$. These deviations can be regarded as evidence that the nitrogen atom is not a constant *ortho*-substituent and that there is a variable interaction between the hydroxy-group and the hetero-atom. Using the relation $\nu = \nu_0 + \rho_\nu\sigma$, Ingraham *et al.*

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[6] Tsuboi, *Bull. Chem. Soc. Japan*, 1952, **25**, 385.
[7] Mason, *J.*, 1957, 5010.
[8] Séguin, *Bull. Soc. chim. France*, 1946, 566.
[9] Mason, *J.*, 1957, 4874.
[10] Coulson, *Research*, 1957, **10**, 149.
[11] Badger and Bauer, *J. Chem. Phys.*, 1937, **5**, 839.
[12] Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.
[13] Hammett, " Physical Organic Chemistry," McGraw Hill, New York, 1940, p. 192.

found a value of $-12{\cdot}6$ for ρ_ν for the hydroxyl stretching frequencies in substituted phenols. Electron-attracting groups decrease the hydroxyl frequency in *p*-substituted phenols; but if other interactions are possible (*e.g.*, hydrogen bonding) then the looser coupling in the hydroxyl bond enables a stronger hydrogen bond to be formed and consequently a larger shift in the hydroxyl stretching frequency. The value of ρ_ν is thereby increased: our value for ρ_ν, obtained by the method of least squares, is $-54{\cdot}7$, more than four times that for the simple phenols.

Very few results have been published on the absorption intensities of the hydroxyl group in the infrared region, although the effects of substituents in aliphatic alcohols[14] and in phenols[15] have been determined. The relation between log *A* and σ for phenols appears to be essentially linear. Moreover the half-intensity band-width shows a definite increase as the electron-attracting power of the substituent increases. The integrated intensities for the 8-hydroxyquinolines have been determined to examine the effect of substituents on an intramolecular bond, and the results are included in Table 1.

No apparent relation exists between the integrated intensity and the σ-constant, although the intensity appears to increase with the electron-attracting power of the substituent. This result is not unexpected as the substituent will also alter the electron density around the nitrogen atom, and in the discussion to follow it will be shown that the intensity is directly related to this quantity. The intensity of the hydroxyl band given by 8-hydroxy-5-phenylazoquinoline appears anomalous, and there is a similar discrepancy for the phenols[15] and anilines.[16] The high intensity does not involve the quinone phenylhydrazone tautomer (in which the OH and NH bands could be degenerate) as no carbonyl band is observed, indicating that the tautomeric equilibrium is shifted mainly towards the azo-form. The half-intensity band-widths show only minor variation with the σ-constant, but appear to increase with the electron-attracting power of the substituent.

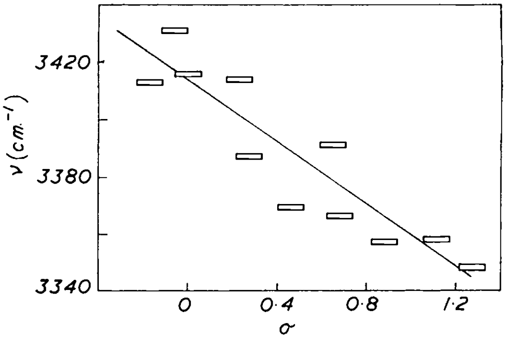
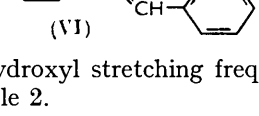


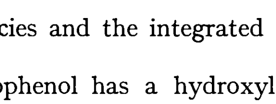
FIG. 1. *Relationship between hydroxyl stretching frequency* (ν) *for* 5-*substituted* 8-*hydroxyquinolines and the* σ- *or* σ^*-*constant for the substituent.*

Rectangles are used to indicate probable errors (± 1 *cm.*$^{-1}$ *in* ν, $\pm 0{\cdot}06$ *in* σ).

The steric relation in *o*-benzylideneaminophenol (VI) must be almost identical with that in 8-hydroxyquinoline. In order to simplify the problem of the effect of substituents on the strength of the hydrogen bond a few benzylideneaminophenols have been examined.



(VI)



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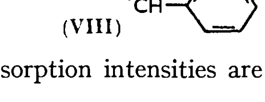

(VIII)

The hydroxyl stretching frequencies and the integrated absorption intensities are given in Table 2.

Although *p*-benzylideneaminophenol has a hydroxyl stretching frequency at 3618

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[14] Brown and Rogers, *J. Amer. Chem. Soc.*, 1957, **79**, 577.

[15] Stone and Thompson, *Spectrochim. Acta*, 1957, **10**, 17.

[16] Krueger and Thompson, *Proc. Roy. Soc.*, in the press.

cm.$^{-1}$, a value comparable with that for phenol itself (3610 cm.$^{-1}$), *o*-benzylideneaminophenol absorbs at 3442 cm.$^{-1}$. This band is independent of concentration up to 0·1M and weak hydrogen bonding comparable to that existing in 8-hydroxyquinoline is inferred. It may be noted that the low m. p. of *o*-benzylideneaminophenol compared with that for the *p*-isomer supports the view that intramolecular hydrogen bonding occurs in the former. *N*-Salicylideneaniline (VII), however, shows a diffuse band superimposed on the C–H stretching bands at *ca.* 2850 cm.$^{-1}$, and strong intramolecular hydrogen bonding involving a six-membered ring is inferred. With *o*-salicylideneaminophenol (VIII) the two hydroxyl absorption bands occur at 3550 and 3000 cm.$^{-1}$. Both hydroxy-groups are therefore bonded to the nitrogen atom. However comparison with the corresponding

TABLE 1. *Absorption of substituted* 8-*hydroxyquinolines in the hydroxyl stretching region.*

8-Hydroxyquinoline	M. p.	Ref.	ν_{OH}	$\Delta\nu$	$\Delta\nu_{\frac{1}{2}}$ [a]	*A* *
8-Hydroxyquinoline [b]	75°	—	3416	0	56	1·30
5-Fluoro-	110—110·5 [e]	*f*	3431	−15	56	1·38
5-Chloro-	125	*g*	3414	2	52	1·40
5-Iodo-	126—127	*h*	3387	29	— [c]	—
5-Formyl-	177—178 [e]	*i*	3358	58	64	2·09
5-Acetyl-	112	*j*	3357	59	64	2·18
5-Benzoyl-	117—118	*j*	3369	47	64	2·03
5-Methyl-	122—123	*g*	3413	3	57	1·55
5-Nitro-	173	*k*	3348	68	64	1·88
5-Phenylazo-	185—185·5	*l*	3391	25	64	2·48
5-Ethoxycarbonly-	125	*g*	3366	50	62	1·70
5 : 7-Dichloro-	179·5—180	*g*	3396	20	60	1·91
5 : 7-Dibromo-	197—198	*m*	3388	28	62	2·13
7-Chloro-	146	*g*	3396	20	59	1·53
5-Chloro-7-iodo-	177—178	*g*	3387	29	58	2·15
2-Methyl-	74	—	3408	8	61	1·57
5 : 7-Di-iodo-	210	*n*	3380	36	— [d]	—
5-Fluoro-7-iodo-	147—148 [e]	*o*	3404	12	— [c]	—

* In units of 10^4 moles^{-1} l. cm.$^{-2}$. [b] The hydroxyl stretching frequency reported here for 8-hydroxyquinoline (3416 cm.$^{-1}$) differs from that given by Flett (*Spectrochim. Acta*, 1957, **10**, 21) (3431 cm.$^{-1}$), but agrees reasonably with that reported by Mason (3412 cm.$^{-1}$). Our experience with the Grubb-Parsons S4 double-beam spectrometer is that it must be used without the wavelength cam, and calibrated by a method such as that of Downie, Magoon, Purcell, and Crawford (*J. Opt. Soc. Amer.*, 1954, 43, 941) in order to justify an accuracy of ±1 cm.$^{-1}$. [c] Insufficient available for accurate determination. [d] Too insoluble for accurate determination. [e] Corrected. [f] Sample provided by Professor C. A. VanderWerf, *J. Org. Chem.*, 1952, **17**, 229. [g] Sample provided by Professor A. Albert. [h] Matsumura, *J. Amer. Chem. Soc.*, 1927, **49**, 810. [i] Clemo and Howe, *J.*, 1955, 3552. [j] Matsumura, *J. Amer. Chem. Soc.*, 1930, **52**, 4433. [k] Kostanecki, *Ber.*, 1891, **24**, 150. [l] Matsumura, *J. Amer. Chem. Soc.*, 1930, **52**, 4164. [m] Prepared by direct bromination. [n] Prepared by direct iodination. Helin and VanderWerf, *J. Org. Chem.*, 1952, **17**, 229.

TABLE 2. *Absorption of benzylideneaminophenols in the hydroxyl stretching region.*

Compound	M. p.	Ref.	ν_{OH}	$\Delta\nu_{\frac{1}{2}}$ [a]	*A*
p-Benzylideneaminophenol	183°	*a*	3618	—	—
o-Benzylideneaminophenol	89—90	*b*	3442	85	1·72
o-2-Nitrobenzylideneaminophenol	104	*a, c*	3459	70	1·56
o-3-Nitrobenzylideneaminophenol	131	*a, c*	3461	70	1·47
o-4-Nitrobenzylideneaminophenol	160—160·5	*a, c*	3458	66	1·49
o-4-Dimethylaminobenzylideneaminophenol...	119	*c*	3420	108	2·06
o-4-Methoxybenzylideneaminophenol	91—91·5	*d*	3433	95	1·88
o-4-Chlorobenzylideneaminophenol	117—118	*e*	3448	79	1·77
o-4-Methylbenzylideneaminophenol	108—109	*f*	3434	88	1·76
N-Salicylideneaniline	51	*g*	*ca.* 2850	—	—
o-Salicylideneaminophenol	185	*d*	*ca.* 3550, *ca.* 3000		—

[a] Pope, *J.*, 1908, **93**, 532. [b] Pictet and Ankersmit, *Annalen*, 1891, **266**, 138. [c] Möhlau and Adam, *Chem. Zentr.*, 1907, I, 108. [d] Haegele, *Ber.*, 1892, **25**, 2753. [e] o-4-*Chlorobenzylideneaminophenol* was prepared from *o*-aminophenol and *p*-chlorobenzaldehyde in hot ethanol. It formed yellow needles, m. p. 117—118° (from ethanol) (Found: C, 67·3; H, 4·3. $C_{13}H_{10}ONCl$ requires C, 67·4; H, 4·4%). [f] Singleton and Pollard, *J. Amer. Chem. Soc.*, 1940, **62**, 2288. [g] Emmerich, *Annalen*, 1887, **241**, 341.

monohydroxy-compounds (OH absorptions at 3442 and 2850 cm.$^{-1}$, respectively) indicates that both bonds are weakened when the lone pair is shared in this way.

The effect of other substituents is best seen by the relation between the hydroxyl stretching frequency and Hammett's σ-values. The linear relation $\nu = \nu_0 + \rho_\nu\sigma$ has been fitted by the method of least squares with a standard deviation of $\pm 2{\cdot}2$ cm.$^{-1}$. The value of ρ_ν (28·3) has the opposite sign to that found for phenols and catechols, *i.e.*, the effect of electron-attracting groups is to increase the hydroxyl frequency. This is consistent with the view that the substituents alter the electron density around the nitrogen atom but have little or no direct electronic effect on the hydroxyl group except through the hydrogen bond.

A linear relation ($A = A_0 + \rho_A\sigma$; $\rho_A = -0{\cdot}40$; standard deviation, 3·1% in A) also exists between the integrated intensities and the σ-constant, which contrasts with the phenols or 8-hydroxyquinolines in which no simple relation exists. This may be related mainly to the change in partial ionic character of the hydroxyl bond caused by hydrogen bonding which we have already suggested is determined by the electron density around the nitrogen atom. A similar relation ($\Delta\nu_{\frac{1}{2}}^a = \Delta\nu_{0\frac{1}{2}}^a + \rho\sigma$; $\rho = -27{\cdot}9$; standard deviation, $\pm 2{\cdot}6$ cm.$^{-1}$) also exists for the half-intensity band-widths which are sensitive to changes in hydrogen bonding. On the other hand, the 8-hydroxyquinolines showed only minor variations and this may result from the opposing effect of electron-withdrawing substituents to decrease the electron density around the nitrogen but to increase the polarization of the hydroxyl bond.

FIG. 2. *Relation between the hydroxyl stretching frequency ν, and the σ-constant for the substituent. Rectangles indicate probable errors.*

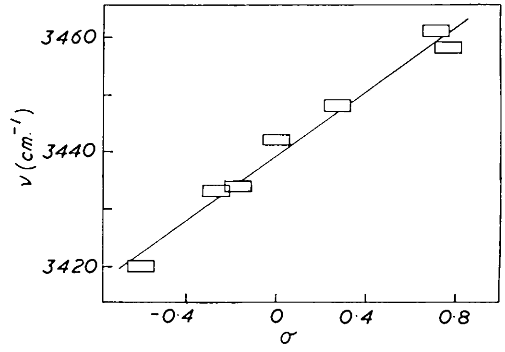
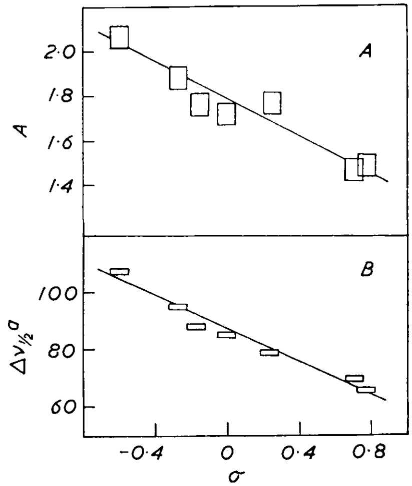


FIG. 3. *Relation between the integrated intensity A* (FIG. 3*A*) *and the half-intensity band width $\Delta\nu_{\frac{1}{2}}^a$* (FIG. 3*B*) *with the σ-constant of the substituent. Rectangles indicate probable errors* (± 2 *cm.$^{-1}$ in $\Delta\nu_{\frac{1}{2}}^a$, 3% in A*).



EXPERIMENTAL

Deuteration.—8-Hydroxyquinoline was dried in a vacuum over phosphoric oxide and then treated with a large excess of deuterium oxide (99·78%; d_4^{20} 1·10515; molar ratio > 100 : 1) at 80—90°. Under these conditions equilibrium was reached within a few seconds. The product was then dried in a vacuum and dissolved in freshly dried carbon tetrachloride. All operations were carried out in a dry-box to ensure the complete absence of water, as there was a rapid exchange with water vapour in solution. No C–D band could be detected in the product obtained in this way.

In another experiment a mixture of deuterium oxide and 8-hydroxyquinoline was made slightly alkaline with solid potassium hydroxide and then heated at 80—90° for 36 hr. Sublimation at 80—90°/20 mm. gave the deuterated product, m. p. 74°, which showed C–D stretching vibration at *ca.* 2270 cm.$^{-1}$.

Infrared Spectra.—The spectra were determined with a Grubb-Parsons S4 double-beam spectrometer, a calcium fluoride prism being used. In the 3450—3340 cm.$^{-1}$ region ammonia gas was used for direct calibration before each determination. Reproducibility was better than ±1 cm.$^{-1}$ in this region where the effective slit width was *ca.* 8 cm.$^{-1}$. Dilute solutions ($<0{\cdot}005$M) in carbon tetrachloride were examined in 2-cm. cells, intermolecular hydrogen bonding being unimportant at this concentration. The integrated absorption intensities were measured by a method similar to that of Brown and Rogers [14] except that the limits of integration were extended to ±140 cm.$^{-1}$ (±180 cm.$^{-1}$ for the benzylideneaminophenols). The absolute accuracy is difficult to evaluate but a re-determination of *n*-propyl alcohol gave $A = 0{\cdot}52$, in good agreement with the literature value.[14] The relative intensities are considered to be within 3—5%.

We thank Professors Adrien Albert and C. A. VanderWerf for generous gifts of 8-hydroxyquinoline derivatives, and the Rockefeller Foundation for a grant for the purchase of the infrared spectrometer. One of us (A. G. M.) has been working with a C.S.I.R.O. Scholarship.

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