100. *Spectroscopic Studies of Phenols: Effect of Substituents on Hydrogen Bonding.*

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The hindering effect of various alkyl groups on the formation of hydrogen bonds in phenols has been studied. It has been shown that alkyl groups, except t-butyl, in *ortho*-substituted phenols have only a slight effect on the formation of hydrogen bonds, while in di-*ortho*-substituted phenols the effects are more pronounced. The greater the hindering effect of an alkyl group, the more formation of associated states is suppressed.

THE formation of hydrogen bonds in phenols has been extensively studied by infrared methods. Fox and Martin [1] showed that the stretching vibration of a free hydroxyl group gave rise to sharp absorption near 3615 cm.$^{-1}$, while a hydroxyl group involved in hydrogen bonding gave a broad absorption band centred near 3330 cm.$^{-1}$, and that the difference

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[1] Fox and Martin, *Proc. Roy. Soc.*, 1937, **162**, *A*, 419.

between these frequencies may be used as a measure of the strength of the hydrogen bond formed.

The effect of hydrogen bonding on the first overtone band of the hydroxyl stretching vibration was studied by Wulf *et al.*,[2] particularly with reference to determining the *cis*- or the *trans*-orientation of the hydroxyl group relative to other groups in the aromatic nucleus.

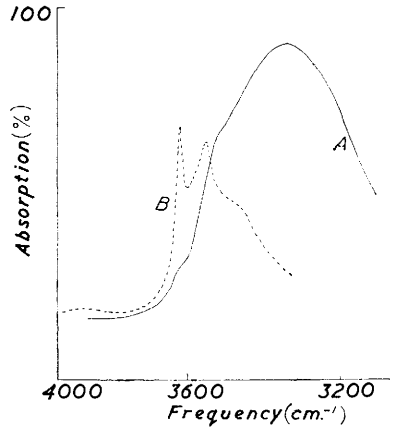
Coggeshall[3] measured the wavelength shifts of the fundamental hydroxyl stretching frequencies between the associated and the unassociated state in various methyl- and t-butyl-phenols; according to the amount of shift produced he classified phenols as unhindered, partially hindered, and hindered. Sears and Kitchen[4] extended these studies to other methyl-, t-butyl-, 1,1,3-trimethylpentyl- and isobornyl-phenols and derived an empirical hydrogen-bonding index which correlated the hindering powers of these groups: they showed that the wavelength shifts were greater for solids than for liquids or concentrated carbon tetrachloride solutions (for which they were essentially the same), and that comparison of the strength of hydrogen bonds should be based only on measurements in the liquid phase.

Slight differences in the free-hydroxyl stretching frequencies were reported by Sears and Kitchen but later Ingraham *et al.*[5] correlated these frequencies with the Hammett constant of the substituent in *meta*- and *para*-substituted phenols. This was recently extended to *ortho*-substituted phenols by Krueger and Thompson,[6] using the Taft values for the substituents.

Since previous workers used rock-salt prism spectrometers it was decided to re-examine some of their results with the higher resolution of a grating spectrometer and to extend these studies to other alkyl groups.

RESULTS

The spectra of the dilute carbon tetrachloride solutions showed only a sharp band near 3615 cm.$^{-1}$ due to the free hydroxyl group, indicating that at these dilutions no hydrogen bonding occurred. The spectra of the liquid films and concentrated carbon tetrachloride solutions were identical.



A, *Spectrum of phenols with no* ortho-*substituent (liquid phase).*

B, *Spectrum of* 2-t-*butyl*-4-*methylphenol* (*conc. solution in* CCl_4).

The free-hydroxyl stretching frequencies (ν_f) of phenols, with no *ortho*-substituents, are listed in Table 1, together with the bonded-hydroxyl frequencies for the liquid state and concentrated carbon tetrachloride solution, expressed in terms of the frequency shifts from the free-hydroxyl frequency as $\Delta\nu_m$ and $\Delta\nu_c$ respectively.

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[2] Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287.

[3] Coggeshall, *J. Amer. Chem. Soc.*, 1947, **69**, 1620.

[4] Sears and Kitchen, *J. Amer. Chem. Soc.*, 1949, **71**, 4110.

[5] Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.

[6] Krueger and Thompson, *Proc. Roy. Soc.*, 1959, **250**, *A*, 22.

A typical spectrum of these phenols, in the liquid state, is shown in the Figure (A); the bonded-hydroxyl absorption appears as a broad band centred near 3330 cm.$^{-1}$, while the free-hydroxyl absorption appears as a shoulder near 3615 cm.$^{-1}$. Another shoulder near 3490 cm.$^{-1}$ is also shown, the shift of this absorption from the free-hydroxyl frequency has been recorded as $\Delta\nu_d$.

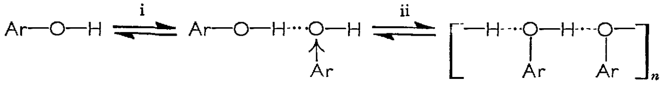
Similar data for phenols with one *ortho*-substituent are in Table 2. The spectra of these compounds in the liquid state are very similar to those in the Figure (A), except that the 3615 cm.$^{-1}$ absorption is more distinct and the frequency shifts are smaller. The spectrum of 2-t-butyl-4-methylphenol [Figure (B)] is different, however, in that the bonded-hydroxyl absorption appears as a broad shoulder on the side of a sharp absorption at 3546 cm.$^{-1}$, which is itself nearly as intense as the free-hydroxyl absorption.

Table 3 records the data for phenols with substituents in both *ortho*-positions. The spectra of these phenols are very similar to that in the Figure (B), there being only slight differences in the ratio of the ν_f and $\Delta\nu_d$ absorptions. In the case of 2,6-di-t-butyl-4-methylphenol there is only a sharp absorption (3646 cm.$^{-1}$), as in the dilute carbon tetrachloride solution spectra.

DISCUSSION

The results for $\Delta\nu_m$ and $\Delta\nu_c$ are essentially the same, and hence, as pointed out by Sears and Kitchen, it is possible to compare the hindering effects of various alkyl groups in the liquid phase.

For phenols with no *ortho*-substituent, the mean value of $\Delta\nu_c$ (266 cm.$^{-1}$) is in good agreement with that obtained by Bowman *et al.*[7] for *m*- and *p*-iso- and -t-butylphenol and is slightly lower than that of Sears and Kitchen. Friedel[8] reported a value of 250 cm.$^{-1}$ for phenols with no *ortho*-substituent in carbon disulphide solution. Table 1 shows that *meta*- and *para*-substituents do not affect the value of $\Delta\nu_c$ or $\Delta\nu_m$, and thus substituents in these positions do not produce any hindering effect on the hydroxyl group. Fox and Martin[9] reported an absorption for phenol at *ca.* 3490 cm.$^{-1}$ which they attributed to a hydrogen-bonded dimer; similar absorptions in this region were reported by Coggeshall[10] and Goddu[11] for various di(alkylhydroxyphenyl)methanes, owing to intramolecular hydrogen bonding. The bands in the region of 3490 cm.$^{-1}$ are thus due to hydrogen bonding of dimers; this is supported by the fact that as the values of $\Delta\nu_c$ decrease for *ortho*-substituted phenols so do the corresponding values of $\Delta\nu_d$. Hence in the liquid state, phenols with no *ortho*-substituents exist as an equilibrium mixture between the free phenol and the dimeric and polymeric associated forms, the equilibrium lying far to the right-hand side.



$$\mathrm{Ar{-}O{-}H} \overset{\text{i}}{\rightleftharpoons} \mathrm{Ar{-}O{-}H\cdots \underset{\substack{\uparrow\\ \mathrm{Ar}}}{O}{-}H} \overset{\text{ii}}{\rightleftharpoons} \left[\mathrm{{-}H\cdots \underset{\substack{|\\ \mathrm{Ar}}}{O}{-}H\cdots \underset{\substack{|\\ \mathrm{Ar}}}{O}{-}}\right]_n$$

Table 2 shows that an *o*-alkyl group reduces the values of $\Delta\nu_c$ and $\Delta\nu_d$, compared with those for phenols with no *ortho*-substituent, indicating that the hydrogen bonds formed in these phenols were weak. Friedel reported a value of *ca.* 130 cm.$^{-1}$ for phenols with one *ortho*-substituent in carbon disulphide solution. This reduction in the strength of these hydrogen bonds is due either to a screening effect of the *ortho*-substituent on the hydroxyl

TABLE 1. *Hydroxyl-frequency shifts (cm.$^{-1}$) of phenols with no* ortho-*substituents.*

Subst.	ν_f	$\Delta\nu_d$	$\Delta\nu_c$	$\Delta\nu_m$	Subst.	ν_f	$\Delta\nu_d$	$\Delta\nu_c$	$\Delta\nu_m$
None	3610	107	267	262	4-Bu^s	3615	105	278	
4-Me	3617	107	264	276	3-Bu^s	3615	122		
3-Me	3617	124		267	3,5-Me$_2$	3613	121	264	
4-Pr^i	3618	104	265		5-Pr^i-3-Me ...	3614	115	262	271
4-Et	3617	107	261	270	3,4-Me$_2$	3615	108	266	
4-Bu^n	3618	116		272		Mean	112	266	271

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[7] Bowman, Stevens, and Baldwin, *J. Amer. Chem. Soc.*, 1957, **79**, 87.
[8] Friedel, *J. Amer. Chem. Soc.*, 1951, **73**, 2881.
[9] Fox and Martin, *Nature*, 1937, **139**, 507.
[10] Coggeshall, *J. Amer. Chem. Soc.*, 1950, **72**, 2836.
[11] Goddu, *Analyt. Chem.*, 1958, **30**, 2009.

TABLE 2. *Hydroxyl-frequency shifts (cm.$^{-1}$) of phenols with one* ortho-*substituent.*
(Values from the literature in parentheses.)

Subst.	ν_f	$\Delta\nu_d$	$\Delta\nu_c$	$\Delta\nu_m$	Subst.	ν_f	$\Delta\nu_d$	$\Delta\nu_c$	$\Delta\nu_m$
2-Me	3615	85	168	172	2-Pr^i-5-Me	3614	78	174	
2,5-Me$_2$	3614	72	178		2-Pr^i-4-Et	3617	83		189
2,3,5-Me$_3$	3617	75	175		2-Bu^n	3620	85		191
2-Me-4-Pr^i	3619	80		181	2-Bu^s	3619	84		186
2-Me-4-Bu^s	3619	84		189	2-Bu^s-4-Me	3617	71	168	179
2-Pr^i	3618	72		172	2-Bu^s-4-Et	3618	72		185
2-Pr^i-4-Me	3615	72	170	173	2,4-Bu$^s_2$	3614	79		170
					2-Bu^i			(140) [7]	
					2-Bu^t-4-Me	3609	63	114	(105) [4]
					2-Bu^t-5-Me				(101) [3]
					2-Bu^t			(70) [7]	

TABLE 3. *Hydroxyl-frequency shifts (cm.$^{-1}$) of phenols with two* ortho-*substituents.*
(Values from the literature in parentheses.)

Subst.	ν_f	$\Delta\nu_d$	$\Delta\nu_c$	$\Delta\nu_m$	Subst.	ν_f	$\Delta\nu_d$	$\Delta\nu_c$	$\Delta\nu_m$
2,6-Me$_2$			(108) [4]	(120) [4]	2,6-Bu$^s_2$	3620	30		85
2,4,6-Me$_3$			(104) [4]	(98) [4]	2,6-Bu$^s_2$-4-Me	3623	31		93
2,6-Me$_2$-4-Bu^s	3628	58	101		2,4,6-Bu$^s_3$	3620	29		85
2-Me-6-Pr^i	3624	66		117	2,6-Bu$^t_2$	3651		3	
2-Me-6-Bu^s	3624	60		119	2,6-Bu$^t_2$-4-Me	3649		3	(9) [4]
2-Me-4,6-Bu$^s_2$	3619	58		121	2,4,6-Bu$^t_3$			(4) [4]	
2,4-Me$_2$-6-Bu^t				(54) [4]	2,6-Bu^t-4-Cl			(5) [4]	(5) [4]
4,6-Bu$^t_2$-2-Me				(45) [4]	2,6-Bu^t-4-Bu^s			(7) [4]	
2,6-Pr$^i_2$-4-Me	3628	53		111					

group, or to the steric hindrance of the substituent towards coplanarity of the hydroxyl group with the aromatic ring with the resultant decrease in the acidic nature of the hydroxyl group. The effect is of the same order of magnitude for various alkyl groups, except for a t-butyl group whose effect is most pronounced. Coggeshall and Saier[12] showed that partially hindered phenols existed as an equilibrium mixture of the free-hydroxyl form and the hydrogen-bonded dimer. It was found here that most *ortho*-substituted phenols exist in a similar equilibrium to that for phenols with no *ortho*-substituent, except that for those with an *o*-t-butyl group the main equilibrium is stage (i), as proposed by Coggeshall.

Table **3** shows that when there are two *o*-alkyl groups, other than t-butyl, the values of $\Delta\nu_c$ and $\Delta\nu_d$ are still smaller, indicating that the hydrogen bonds are weaker than in the case of one *o*-t-butyl group. There is still a small proportion of the polymeric form in equilibrium with the free and the dimeric form. The different effects of these alkyl groups, *i.e.*, methyl, i-propyl, and s-butyl, also become apparent in these cases. One *o*-t-butyl group produces the same effect as a methyl and a methyl, i-propyl, or s-butyl group in both *ortho*-positions. s-Butyl groups in both *ortho*-positions produce a marked effect, reducing $\Delta\nu_d$ and $\Delta\nu_m$ to 30 and 85 cm.$^{-1}$ respectively.

For di-*o*-t-butylphenols only one sharp absorption is observed under the conditions used in this work and $\Delta\nu_c$ are close to those recorded by Sears and Kitchen, showing that very little, if any, hydrogen bonding occurs.

It is concluded, therefore, that in mono-*ortho*-substituted phenols the various alkyl groups other than t-butyl have little effect on the hydrogen bonding, while in the case of di-*ortho*-substituted phenols there is a steady increase in the hindering effect of the alkyl group with increasing branching. Further, as the strength of the hydrogen bonds formed by phenols in the liquid state decreases polymerisation is suppressed so that hindered phenols exist essentially in the monomeric form.

EXPERIMENTAL

The phenols examined were commercial samples, purified by fractional distillation or recrystallisation, or had been synthesised previously.

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[12] Coggeshall and Saier, *J. Amer. Chem. Soc.*, 1951, **73**, 5414.

The spectra were determined on a Grubb–Parsons G.S.2A double-beam grating spectrometer over the range 4000—2860 cm.$^{-1}$. The free-hydroxyl stretching frequencies were measured in " AnalaR " carbon tetrachloride (*ca.* 4—6 × 10^{-3}M), with a 2 mm. cell. Concentrated solutions were prepared according to the procedure of Sears and Kitchen,[4] which involves wetting the phenol with just sufficient carbon tetrachloride to effect solution, and the spectra were determined in a 0·02 mm. cell. Phenols, liquid at room temperature, were measured in a similar cell without solvent. Several phenols were examined in the molten state at temperatures slightly above their m. p.

Wavelength measurements were calibrated in terms of the data of Fox and Martin [1] and Barnard *et al.*,[13] who reported the free-hydroxyl stretching frequency of phenol in carbon tetrachloride solution as 3610 cm.$^{-1}$.

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[13] Barnard, Hargrave, and Higgins, *J.*, 1956, 2845.