Substituent Effects on the Chemical Shift of the Hydroxy-proton of 2,6-Dimethylphenols and 1-Naphthols in Dimethyl Sulphoxide

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The chemical shifts of the hydroxy-proton of 2,6-dimethylphenol and ten 4-substituted 2,6-dimethylphenols and of 1-naphthol and nine 4-substituted 1-naphthols have been measured for dimethyl sulphoxide solutions. Analysis of published data on the chemical shifts of phenols in dimethyl sulphoxide reveals that $+M$ as well as $-M$ 4-substituents exhibit enhanced resonance effects. Substituent effects in 2,6-dimethylphenols and in 1-naphthols parallel these effects in phenols. The Hammett ρ values for the three series are −1·49, −1·43, and −1·55 respectively. In naphthols $-M$ 4-substituents do not exhibit enhanced resonance effects over and above those observed in the correspondingly substituted phenols.

The chemical shifts of the hydroxy-protons of substituted phenols in dimethyl sulphoxide have been correlated with Hammett substituent constants.[1-3] Conjugatively electron-withdrawing substituents require enhanced σ^- values, demonstrating an important resonance interaction between hydroxy-group and substituent. Substituent electronic effects on the chemical shift thus parallel the effects on the dissociation of phenols. Substituent effects on dissociation of 1-naphthols[4] and of 2,6-dimethylphenols[5] show some significant differences from the dissociation of phenols. For the dissociation of 2,6-dimethylphenols the ρ value is greater than for dissociation of phenols, a result attributed to steric inhibition of solvation in the 2,6-dimethylphenoxide ions. In dissociation of 1-naphthols σ values for $-M$ 4-substituents are substantially more enhanced than in phenol dissociation. We have measured the chemical shifts of 4-substituted 2,6-dimethylphenols and of some substituted 1-naphthols to determine if there are differences between substituent effects in these series and the phenol series.

EXPERIMENTAL

1-*Naphthols and* 2,6-*Dimethylphenols*.—These were generally prepared by literature methods and had physical properties in satisfactory agreement with literature values. 4-Fluoro-2,6-dimethylphenol[5] was obtained in a much improved yield (40%) when the diazonium fluoroborate salt, prepared from 4-amino-2,6-dimethylanisole, was thermolysed and the product 4-fluoro-2,6-dimethylanisole cleaved to the phenol with hydrobromic acid. 4-*Fluoro*-2,6-*dimethylanisole* had b.p. 182—183°, n_D^{20} 1·4827 (Found: C, 70·4; H, 7·0; F, 11·9. $C_{10}H_{11}FO$ requires C, 70·1; H, 7·2; F, 12·3%).

Dimethyl sulphoxide was distilled from calcium hydride under reduced pressure and stored over type 4A molecular sieves. Chemical shift measurements were made at 40° with a Varian A-60 spectrometer and following the procedure of Ouellette.[1] Shifts were measured using the 221 Hz ^{13}C–H satellite of dimethyl sulphoxide as the internal standard. On each occasion that a sample or set of samples were measured the chemical shift of the parent compound (2,6-dimethylphenol or 1-naphthol) was also determined. In this way the effect of any day-to-day variations of the spectrometer performance on the relative chemical shift was minimised. Generally, shift values were reproducible to 0·02 p.p.m. However, in the cases of 4-hydroxy-3,5-dimethylbenzaldehyde, 4-acetyl-1-naphthol, and 4-cyano-1-naphthol the hydroxy-resonance peak was broad and for these compounds there is a larger uncertainty in the shift value, ±0·05 p.p.m. In the cases of 4-hydroxy-1-naphthaldehyde and 4-nitro-1-naphthol 100 accumulated scans using a time-averaging computer allowed the broad peak to be located and the shift value is estimated to be accurate to ±0·1 p.p.m. 4-Nitro-2,6-dimethylphenol exhibited a very broad peak with a half-height width of 1·4 p.p.m. Shift [illegible] (τ) are shown in Table 1.

TABLE 1

Chemical shift values and derived $\bar{\sigma}$ values for substituted 2,6-dimethylphenols and 1-naphthols

		Xylenols		Naphthols	
Substituent	σ [a]	τ	$\bar{\sigma}$	τ	$\bar{\sigma}$
4-OH	−0·48			0·78	−0·49
4-OMe	−0·30	2·38	−0·27	0·51	−0·32
4-F	0·05	1·97	0·02		
4-Cl	0·27	1·66	0·23		
4-Br	0·29	1·63	0·25	−0·41	0·27
4-Me	−0·15	2·19	−0·14	0·21	−0·13
4-COMe	0·75	0·99	0·70	−1·07	0·70
4-CN	0·86	0·69	0·90	−1·40	0·91
3-NO_2	0·70			−1·07	0·70
4-NO_2	1·14	0·7 [b]		−1·64	1·06
H	0·00	1·95	0·03	−0·02	0·02
4-CHO	0·86	0·69	0·90	−1·48	0·96
4-Bu^t	−0·16	2·17	−0·12		
4-NO		−1·10 [c]			

[a] $\bar{\sigma}$ Value used to correlate the chemical shift data for xylenols and naphthols. [b] Value not used in correlations because of low precision. [c] Value for the hydroxy-group of the quinone monoxime tautomer.

DISCUSSION

In order to reveal the operation of specific resonance effects in the chemical shifts of substituted phenols we examined the correlation of chemical shift with σ^0 for each of the three reported studies[1-3] and following the recommended procedure.[6] Thus, six of the compounds studied by Ouellette contain *meta*-substituents belonging to the select group cited by Taft and Lewis[6] and in

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[3] M. T. Tribble and J. G. Traynham, *J. Amer. Chem. Soc.*, 1969, **91**, 379.

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the initial correlation the τ and σ^0 data for these substitutents alone were used. The slope (ρ) of the correlation line was $-1{\cdot}476$ and the intercept (τ^0) was $0{\cdot}779$. Effective $\bar{\sigma}$ values for all substituents were evaluated from the correlation line [$\bar{\sigma} = (0{\cdot}779 - \tau)/1{\cdot}476$] and of the sixteen chemical shift values for which σ^0 values for the substituents are known[7,8] eleven gave $\bar{\sigma}$ values which agreed with σ^0 to within $\pm 0{\cdot}07$. Accordingly a new line was fitted to the data for these eleven substituents. This line gave $\rho = -1{\cdot}438$, correlation coefficient $r = 0{\cdot}991$, standard deviation $s = 0{\cdot}044$, standard deviation of the slope $s_\rho = 0{\cdot}063$, and $\tau^0 = 0{\cdot}772$. The remaining five substituents exhibited significant deviations ($|\bar{\sigma} - \sigma^0| > 0{\cdot}07$) from this line and $\bar{\sigma}$ values for these are shown in Table 2. Similar treatment of the data of Traynham and Knesel[2] gave, after the second correlation, a fit for nine of fourteen substituents with $\rho = -1{\cdot}506$, $r = 0{\cdot}996$, $s = 0{\cdot}039$, $s_\rho = 0{\cdot}052$, and $\tau^0 = 0{\cdot}731$. For the five deviant substituents, $\bar{\sigma}$ values are shown in Table 2. The data of Tribble and Traynham gave, after the second correlation, a fit for ten of twenty substituents with $\rho = -1{\cdot}529$, $r = 0{\cdot}995$, $s = 0{\cdot}053$, $s_\rho = 0{\cdot}054$, and $\tau^0 = 0{\cdot}760$. Values of $\bar{\sigma}$ for the other ten substituents are shown in Table 2. As the previous investigators have recognised it is evident that $\bar{\sigma}$ values for $-M$ 4-substituents are enhanced in the σ^- sense (the substituents are more electron-withdrawing than the σ^0 values would imply). However, it is also evident that substituents with strong $+M$ effects are much more electron-releasing than expected. Traynham and Knesel[2] have noted this effect in the case of the hydroxy-group and have attributed it to the enhancement of the electron-releasing ability of this group when it is hydrogen-bonded to a dimethyl sulphoxide molecule. The enhancement of the $+M$ effects for the amino- and acetylamino-substituent may be similarly explained but the explanation cannot apply to the fluoro- or methoxy-substituents which also have enhanced $+M$ effects. The fluoro-substituent appears to exhibit an enhanced $+M$ effect in many reactions in which such an effect would not be anticipated. Neither of the explanations[9,10] suggested for this behaviour seem applicable in the present system.

TABLE 2

$\bar{\sigma}$ Values from chemical shifts of phenols

Substituent	σ^0	$\bar{\sigma}$[a]	$\bar{\sigma}$[b]	$\bar{\sigma}$[c]
3-NH_2	−0·14			−0·31
4-NH_2	−0·38	−0·66		
4-NHAc	0·04			−0·13
3-OH	0·04		−0·17	
4-OH	−0·17		−0·51	−0·45
4-OMe	−0·15	−0·28	−0·34	−0·29
4-F	0·17	0·04	0·06	0·06
4-CF_3	0·54			0·65
4-COMe	0·47	0·82		0·68
4-CO_2Et	0·46			0·65
4-CN	0·66			0·86
4-NO_2	0·83	1·21	1·14	1·09
4-CHO			0·84	0·87
4-Bu^t		−0·19		−0·14

[a] Calc. from ref. 1. [b] Calc. from ref. 2. [c] Calc. from ref. 3.

An alternative method of determining the relative importance of resonance and inductive effects of substituents is to examine the correlation of the shift data by equation (1).[8] Tribble and Traynham's data for

$$\tau = \tau^0 + \rho_I\sigma_I + \rho_R\sigma_R^0 \qquad (1)$$

sixteen 4-substituents was fitted to this equation and gave $\rho_I = -1{\cdot}53$ and $\rho_R = -2{\cdot}36$. The greater relative sensitivity to resonance effects of the chemical shift is evident.

1-*Naphthols and Xylenols*.—The recommended procedure cannot be applied to obtain ρ values for these series. In the correlation of chemical shift with substituent, constant σ^0 values were used for those substituents shown to be well behaved in the phenol series and mean $\bar{\sigma}$ values derived from the phenol data (Table 2) for other substituents. These σ^0 or mean $\bar{\sigma}$ values are shown in the second column of Table 1. For xylenols the correlation gave $\rho = -1{\cdot}430$, $r = 0{\cdot}996$, $s = 0{\cdot}061$, $s_\rho = 0{\cdot}46$, and $\tau^0 = 1{\cdot}985$. ρ For xylenols is thus not larger than ρ for phenols.

Tribble and Traynham[3] have observed that 2,6-dimethylphenol is very much more shielded than would be predicted from the additive effect of two *ortho*-methyl groups. They suggest that the hydrogen-bonded hydroxy-group is too large to be coplanar with the methyl groups and that there is steric inhibition of resonance of the hydroxy-group with the ring. As a consequence the electron density at oxygen is higher than it would otherwise be and the attached hydrogen atom is more shielded. Steric inhibition of resonance should produce a marked effect on the $\bar{\sigma}$ values for $-M$ substituents and the $\bar{\sigma}$ values would be expected to be less enhanced in xylenols than in phenols. However the deviations ($\bar{\sigma} - \sigma$) of these substituents from the correlation line are neither large nor consistently negative. Furthermore, when a correlation line was fitted to the data for other substituents and the $\bar{\sigma}$ values for the $-M$ substituents were evaluated the deviations for these substituents were positive rather than negative. Thus substituent effects of the $-M$ substituents are not reduced in the xylenol series as compared with the phenol series.

4-Nitroso-2,6-dimethylphenol has been shown to exist in solutions effectively completely in the quinone monoxime form.[11] The hydroxy-resonance appears at what would be anomalously low field for a phenol. Norris and Sternhell have shown that in the case of 4-nitrosophenol, where both tautomers can be observed, the quinone monoxime form exhibits its hydroxy-

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resonance at consistently lower field than that of the nitrosophenol form.

For naphthols, $\rho = -1{\cdot}554$, $r = 0{\cdot}996$, $s = 0{\cdot}084$, $s_\rho = 0{\cdot}049$, and $\tau^0 = 0{\cdot}011$. For $-M$ substituents the deviations ($\bar{\sigma} - \sigma$) are not large and positive as they would be if resonance effects for these substituents were more enhanced than in the phenol series. Thus the $\bar{\sigma}$ values observed in naphthol dissociation[4] presumably reflect an effect present in the $-M$ substituted naphthoate anions and which is not present in the naphthols themselves.

Substituted 1-naphthols resonate at *ca.* 0·75 p.p.m. downfield from the correspondingly substituted phenols. The downfield shift may be attributed to the additional ring current effect of the fused ring and in part also to the $-M$ effect[4] of the ring.

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