Infrared Spectroscopic Study of the Interaction between 2,6-Diarylphenols and Alkyl Cyanides

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The O–H stretching absorptions of 2,6-diarylphenols are composed of two symmetrical bands (intramolecular OH · · · π and intermolecular OH · · · N interactions) in the presence of alkyl cyanides in carbon tetrachloride solution.

The equilibrium constants *K* for the competitive interactions were determined. The equilibrium study suggested that the *K* values depend on the dihedral angle between the phenol ring and the 2,6-aryl groups. Comparison of log *K* with ν_0(OH) (the frequency of the OH · · · N band at infinite dilution in CCl_4) revealed a linear relation. Furthermore it was found that the frequency shifts caused by the concentration of cyanide can be explained by the Kirkwood–Bauer–Magat relationship.

Equilibrium studies have been made on the association of phenols with cyanides,[1-3] but not using phenols in which only intramolecular OH · · · π bonding is possible, such as 2,6-diphenylphenol.[4] We have now investigated the hydroxy-stretching frequencies of a group of such phenols (I)—(VI) in the presence of alkyl cyanides in carbon tetrachloride.

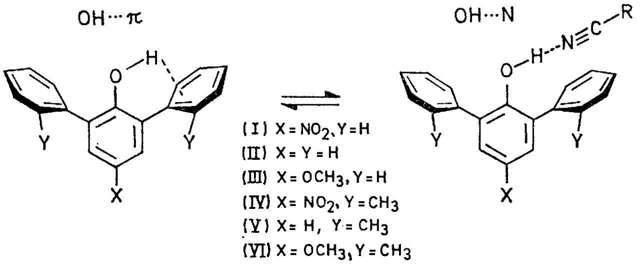

Table 1

OH · · · π Band frequencies and dihedral angles for 0.003—0.007M-2,6-diarylphenols (I)—(VI) in CCl_4

Compound	ν(OH · · · π)/cm^{-1}	*A*/mol^{-1} l cm^{-2} [a]	θ (°) [b]
(I)	3 533.3	2.26	
(II)	3 556.9	1.48	~60
(III)	3 565.8	1.35	
(IV)	3 526.5	2.49	
(V)	3 550.7	1.83	~70
(VI)	3 560.7	1.62	

[a] Integrated intensity; maximum error <5%. [b] The dihedral angle θ was estimated from the K band maximum in the u.v. spectrum (H. Suzuki, *Bull. Chem. Soc. Japan*, 1959, **32**, 1340, 1350, 1357; M. Oki and Iwamura, *J. Amer. Chem. Soc.*, 1967, **89**, 576) [(II) $\lambda_{max.}$ 241; (V) 236 nm (heptane)].

When a cyanide is added to phenols (I)—(VI) in CCl_4 solution, an intermolecular OH · · · N band appears on the lower frequency side of the intramolecular OH · · · π band, and intensities and frequencies of both bands change with the concentration of cyanide (Figure 1). In order to study the competitive interaction between the OH · · · π and OH · · · N systems the equilibrium constants *K* in dilute solutions of CCl_4 were determined (Table 2). Table 2 shows that the *K* values for different cyanides increase with the base strength of the cyanides. This suggests that the steric hindrance between the 2,6-aryl groups of the phenols and the alkyl group of the cyanide is small for the OH · · · N association and that the alkyl group is well removed from the point of association. Our results are consistent with those of White

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[1] (*a*) S. C. White and H. W. Thompson, *Proc. Roy. Soc.*, 1966, *A*, **291**, 460; (*b*) M. C. Sousa Lopes and H. W. Thompson, *Spectrochim. Acta*, 1968, **24A**, 1367.

[2] M. Horák, J. Poláková, M. Jakoubková, J. Moravec, and J. Plíva, *Coll. Czech. Chem. Comm.*, 1966, **31**, 622.

[3] Z. Yoshida and N. Ishibe, *Bull. Chem. Soc. Japan*, 1969, **42**, 3254.

[4] M. Ōki, H. Hosoya, and H. Iwamura, *Bull. Chem. Soc. Japan*, 1961, **34**, 1391.

and Thompson[1] who studied hydrogen bonding between 2,6-dialkylphenols and cyanides. For the phenyl (I)—(III) and tolyl series (IV)—(VI) the latter has the larger K values. This trend is interpreted in terms of a difference in the dihedral angle between tolyl and phenyl series (see Table 1). Since the steric hindrance between cyanide and aryl decreases with increase of dihedral angle, OH · · · N association is favoured for the tolyl series with larger dihedral angles, although the tolyl series has the stronger intramolecular OH · · · π bonds (see Table 1). Furthermore this angular dependence of the K values implies that the OH group is approximately coplanar with the phenol ring for OH · · · N association, because marked bending of the OH group out of the plane of the phenol ring should cause an increase in steric hindrance with an increase in the dihedral angle. Comparison of log K with ν_0(OH) (Table 2) reveals a linear relation for both the phenyl and tolyl series (Figure 2). This indicates that the ν_0(OH) is a convenient measure of the strength of OH · · · N association. The slopes of the lines are virtually the same and the difference in free energy change ($-\Delta F = RT\ln K$) between the two series is *ca.* 0.1 kcal mol^{-1}.

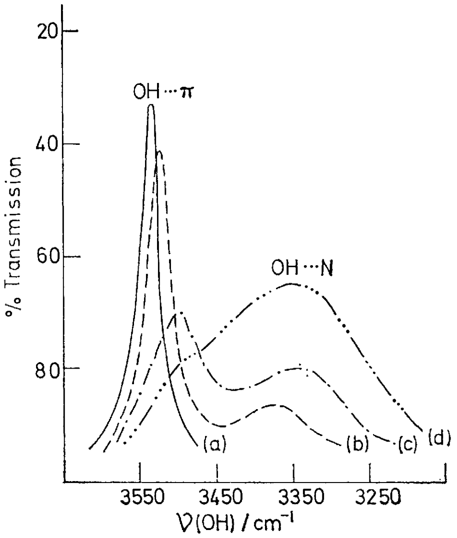

FIGURE 1 OH Stretching absorption spectrum of compound (I) in the presence of acetonitrile in CCl_4: relative concentrations of acetonitrile: (a), 0; (b), 5%; (c), 40%; (d), 100%

TABLE 2

Equilibrium constants K^a and $\nu_0(OH)^b$ band frequencies

Compound		CH_3CN	$(CH_3)_2CHCN$	$(CH_3)_3CCN$
(I)	K/l mol^{-1}	1.00	1.16	1.27
	ν_0(OH)/cm^{-1}	3 369	3 351	3 340
(II)	K/l mol^{-1}	0.37	0.40	0.49
	ν_0(OH)/cm^{-1}	3 436	3 423	3 416
(III)	K/l mol^{-1}	0.33	0.38	0.43
	ν_0(OH)/cm^{-1}	3 442	3 428	3.422
(IV)	K/l mol^{-1}	1.15	1.34	1.54
	ν_0(OH)/cm^{-1}	3 363	3 347	3 336
(V)	K/l mol^{-1}	0.49	0.50	0.54
	ν_0(OH)/cm^{-1}	3 434	3 419	3 416
	K/l mol^{-1}	0.48	0.39	0.54
	ν_0(OH)/cm^{-1}	3 440	3 431	3 419

[a] K Values were determined from calibration charts (absorbance as a function of concentration for each of the phenols used in CCl_4) and were used to determine the concentration of residual OH · · · π in phenol (0.003—0.007M)–cyanide (0.4—1.0M) mixtures in CCl_4. K Was calculated according to the equation K = [OH · · · N]/[OH · · · π] [RC≡N]. Maximum error is ±5%. [b] OH · · · N Band frequency at infinite dilution of CCl_4.

As for the effect of cyanide concentration on the frequency shifts arising from hydrogen bonding (*e.g.* phenol and cyanide),[2] it is known that the shifts are correlated by means of the well known Kirkwood–Bauer–Magat equation[5] $[\Delta\nu/\nu = C(\varepsilon - 1)/(2\varepsilon + 1)]$.* It is interesting that this relationship can be applied to the observed shifts (Figure 1) in the competitive interaction system. When the frequency shifts are plotted against $(\varepsilon - 1)/(2\,\varepsilon + 1)$, linear correlations are obtained for each series. This indicates that the bulk properties of solvent mixture (dielectric constant and refractive index) affect not only intermolecular OH · · · N bonding but also intramolecular OH · · · π bonding.

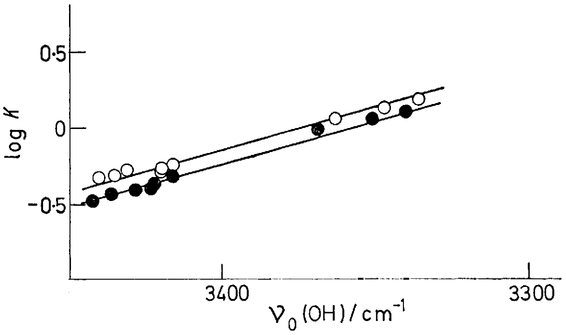

FIGURE 2 Relation between log K and ν_0(OH): ●, phenyl series; ○, tolyl series

EXPERIMENTAL

Spectral Measurements.—I.r. spectra were measured using a JASCO DS-402G grating spectrometer with a spectral slit width of 2 cm^{-1} at 29°. Frequencies were calibrated by the standard absorption lines of water vapour (3 568.5 and 3 447.2 cm^{-1}). The solvents for i.r. spectra were distilled and thoroughly dried before use, and sodium chloride cells of 0.2 or 2 mm thickness were employed. U.v. spectra were obtained with a Hitachi 124 automatic recording spectrophotometer. A quartz cell of 1.0 cm in length was employed.

Compounds (I),[6] (II),[7] and (IV)[8] are known.

4-*Methoxy*-2,6-*diphenylphenol* (III).—Methyl iodide (3 g) and anhydrous potassium carbonate (3 g) were added to a solution of 2,6-diphenylhydroquinone[8] (5.5 g) in acetone (40 ml) and the mixture was refluxed at 60—70° for *ca.* 6 h.

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* ε is the dielectric constant of the medium.

[5] E. Bauer and M. Magat, *J. Phys. Radium.*, 1938, **9**, 319.

[6] H. B. Hill, *Amer. Chem. J.*, 1900, **24**, 5.

[7] A. Luttringhans and D. Ambros, *Chem. Ber.*, 1956, **89**, 463.

[8] E. Charles, S. Jones, and J. Kenner, *J. Chem. Soc.*, 1931, 1842.

Work-up gave a viscous oil which was purified by chromatography on silica gel to give the *phenol* (III) (3.0 g) (Found: C, 82.45; H, 6.0. $C_{19}H_{16}O_2$ requires C, 82.6; H, 5.85%).

2,6-*Di*-o-*tolylphenol* (V).—Diazotization of 4-amino-2,6-di-*o*-tolylphenol[8] (2 g) in a mixture of glacial acetic acid (40 ml) and water (30 ml) at −5 to −10° afforded 2,6-di-*o*-tolylbenzoquinone 4-imine (1 g), m.p. 137° (decomp.) (from acetone). Reduction of the imine (1 g) in 2N-hydrochloric acid (40 ml) with hypophosphorous acid (50 ml) gave 2,6-*di*-o-*tolylphenol* (V) (0.7 g), m.p. 61—63° (from 70% ethanol) (Found: C, 87.4; H, 6.8. $C_{20}H_{18}O$ requires C, 87.5; H, 6.6%).

4-*Methoxy*-2,6-*di*-o-*tolylphenol* (VI).—Reduction of 2,6-di-*o*-tolylbenzoquinone[8] (2 g) in glacial acetic acid (120 ml) with zinc powder (4 g) afforded 2,6-di-*o*-tolylhydroquinone (1.4 g), m.p. 135—137° (from benzene). This hydroquinone (1.0 g) was treated as described for compound (III) to give 4-*methoxy*-2,6-*di*-o-*tolylphenol* (VI) (0.6 g), m.p. 64—66° (from hexane) (Found: C, 82.9; H, 6.55. $C_{21}H_{20}O_2$ requires C, 82.85; H, 6.6%).

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