

867. *Dipole Moments and Near-infrared Spectra of a Series of p-Substituted Phenols.*

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The hydroxyl-group stretching frequencies for a series of *p*-substituted phenols have been determined in a cyclohexane–dioxan solvent mixture of dioxan weight fraction 0.0131. The frequency shifts with respect to phenol in cyclohexane, considered to be a measure of the strength of the hydrogen bond to dioxan, ΔH , are found to be linearly related to the O–H bond-moment increment necessary to explain the observed dipole moments of the phenols in dioxan. A parallelism between these increments and the acid strength of the phenol, pK_a , is also observed.

CHANGES in dielectric properties and shifts in near-infrared frequencies are two of the many modifications in physical properties that are associated with hydrogen bonding in solution. That the dipole moments of phenols¹ and amines² in dioxan are greater than

¹ Erić, Goode, and Ibbotson, *J.*, 1960, 55.

² Few and Smith, *J.*, 1949, 753, 2781; Smith, *J.*, 1953, 109.

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those in benzene or cyclohexane, has been attributed to hydrogen bonding to dioxan. Badger³ observed a relation between hydrogen-bond energy, ΔH , and the shift in stretching frequency of the O-H bonds, $\Delta\nu_s$, and Fox and Martin⁴ used the Morse curve to show that $\Delta\nu_s/\nu_s$ should be related to ΔH . There has been general acceptance of the suggestion that $\Delta\nu_s/\nu_s$ provides an index of ΔH for hydrogen-bond formation.⁵

The present investigation was carried out in order to assess the effect of *p*-substituents on the O-H bond-moment of phenols hydrogen bonded to dioxan, and to ascertain the relationship between these bond moments and the strength of the hydrogen bond, ΔH , as given by the shift in O-H stretching frequency.

EXPERIMENTAL

Dipole Moments.—Materials. "Spectrosol" carbon tetrachloride was dried over phosphorus pentoxide in a desiccator. Cyclohexane and dioxan, dried and then refluxed with sodium wire, were distilled and the fractions of b. p. 80.8°/760 mm. and 101.4°/760 mm., respectively, were collected. AnalaR *p*-nitrophenol, m. p. 114°, *p*-hydroxybenzaldehyde, m. p. 115–116°, and *p*-hydroxyacetophenone, m. p. 109°, were recrystallised from benzene. Phenol, m. p. 41.5°, was distilled and then recrystallised from light petroleum (b. p. 40–60°).

Apparatus and methods. Dielectric constants and refractive indices of solutions of graded concentrations of each compound in dioxan or cyclohexane were determined at 25.0°.

The dielectric constants, accurate to 0.0001, were measured with an internally thermostated, heterodyne-beat dipolemeter, type DM.01, manufactured by the Wissenschaftlich-Technische Werkstätten, G.m.b.H. The thermostated dielectric cell, type D.F.L.1., of 20-ml. capacity, had gold-coated interior plates. The linear condenser was calibrated by making measurements on benzene (ϵ 2.2725), cyclohexane (ϵ 2.0139), and carbon tetrachloride (ϵ 2.2274). The refractive indices, measured with an Abbé refractometer, were of high accuracy.

The densities of cyclohexane and dioxan were determined with a 25-ml. capacity Warden's density bottle. In order to prevent vapour losses, the bottle was fitted with a cap which was ground on over the capillary stopper.

The results are summarised in Table 1, where the symbols have their usual significance.

TABLE I.

100 <i>w</i>	ϵ	n_D	100 <i>w</i>	ϵ	n_D
Phenol in cyclohexane			<i>p</i> -Nitrophenol in dioxan		
0.000	2.0150	1.42358	0.000	2.2079	1.41984
0.361	2.0225	—	0.102	2.2348	1.42003
0.558	2.0273	—	0.172	2.2530	1.42014
0.744	2.0315	1.42417	0.292	2.2845	1.42035
0.949	2.0357	1.42436	0.397	2.3122	1.42045
1.425	2.0457	1.42472	0.504	2.3403	1.42068
$10^3\alpha = 2172$; $10^2\nu = 23$; $P_{2\infty} = 43.9$; $\mu_D = 1.46$.			$10^3\alpha = 26,250$; $10^2\nu = 48$; $P_{2\infty} = 589.8$; $\mu_D = 5.37$.		
<i>p</i> -Hydroxybenzaldehyde in dioxan			<i>p</i> -Hydroxyacetophenone in dioxan		
0.000	2.2112	1.42031	0.000	2.2107	1.42013
0.379	2.2186	—	0.205	2.2141	—
0.566	2.2218	—	0.338	2.2161	—
0.728	2.2252	—	0.736	2.2218	—
0.964	2.2298	—	1.262	2.2305	—
1.173	2.2334	—	1.542	2.2350	—
2.280	—	1.42068	2.110	—	1.42068
2.679	—	1.42092	6.702	—	1.42125
7.366	—	1.42150	18.980	—	1.42332
$10^3\alpha = 19,100$; $10^2\nu = 46$; $P_{2\infty} = 373.9$; $\mu_D = 4.28$.			$10^3\alpha = 15,680$; $10^2\nu = 47$; $P_{2\infty} = 339.7$; $\mu_D = 4.08$.		

³ Badger, *J. Chem. Phys.*, 1940, **8**, 288.

⁴ Fox and Martin, *Proc. Roy. Soc., A*, **162**, 419.

⁵ Pimental and McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco and London, 1960, p. 83.

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The molar orientation polarisation at infinite dilution, $P_{2\infty}$, of each phenol was calculated from the equation:

$$P_{2\infty} = 3M_2v_1\{\alpha/(\epsilon_1 + 2)^2 - \nu/(n_1^2 + 2)^2\} \quad (1)$$

in which M_2 = molecular weight of solute, v_1 , ϵ_1 , n_1 are specific volume, dielectric constant, and refractive index, respectively, of the solvent at 25.0°, $\alpha = (d\epsilon/dw)_{w=0}$, and $\nu = (dn^2/dw)_{w=0}$. The values of the specific volume, v_1 , were 0.97163 ml. g.⁻¹ (dioxan) and 1.29226 ml. g.⁻¹ (cyclohexane). α and ν were determined from the equations $\alpha = \Sigma(\epsilon - \epsilon_1)/\Sigma w$ and $\nu = \Sigma(n^2 - n_1^2)/\Sigma w$, respectively.

Dipole moments (μ) were calculated from the equation:

$$\mu = 0.012812 (P_{2\infty} \times T)^{\frac{1}{2}} \quad (2)$$

Near-infrared Spectra.—Materials. *p*-Cresol and *p*-chloro-, *p*-bromo-, *p*-fluoro-, and *p*-cyano-phenol were prepared as previously described.^{1,6}

Apparatus and methods. Hydroxyl-group stretching frequencies, ν_s , in the near-infrared region were determined with a double-beam Unicam S.P. 700 recording spectrophotometer. By use of radiation from a tungsten-lamp source, the region 4300—2800 cm.⁻¹, covered by a Merton N.P.L. replica grating blazed at 3 μ , was investigated. Since cyclohexane and dioxan absorb strongly in this region, a 1-mm. path-length silica cell was used for cyclohexane solutions, and a variable path-length cell (0.5 to 1.0 mm.) with "infrasil" windows was used for dioxan solutions. At the solution concentrations chosen (to give 50% transmittance), solute-solute interactions proved to be negligible.

The results are recorded in Tables 2 and 3.

TABLE 2.

ν_s Values for phenol in cyclohexane-dioxan mixtures.

w_D	0	0.0131	0.0623	0.2087	0.5705	1.0000
ν_s (cm. ⁻¹)	3622	3400	3393	3385	3362	3340

TABLE 3.

O-H Stretching frequencies, dipole moments, and pK_a data for *p*-substituted phenols.

<i>p</i> -Substituent	σ^*	$\nu_1 \dagger$ (cm. ⁻¹)	$\Delta\nu_1$ (cm. ⁻¹)	pK_a (in water)	μ (D) (in dioxan)	y (D) (exptl.)	y (D) (calc.: eqn. 4)	y (D) (calc.: eqn. 5)
H	0.000	3400	222	9.95 ^a	1.86 ^g	0.42	0.38	0.40
Cl	0.227	3375	247	9.38 ^a	2.82 ^g	0.54	0.58	0.55
Br	0.232	3371	251	9.34 ^b	2.75 ^g	0.48	0.62	0.56
F	0.062	3391	231	9.95 ^c	2.67 ^h	0.43	0.45	0.40
NO ₂	1.270	3294	328	7.14 ^a	5.37	1.18	1.24	1.15
CN	1.000	3330	292	7.95 ^d	5.25 ^h	0.99	0.95	0.94
CHO	1.13	3338	284	7.66 ^e	4.28	0.99	0.88	1.01
CH ₃	-0.170	3407	215	10.19 ^f	1.83 ^g	0.35	0.32	0.33
CO·Me	0.874	3345	277	8.05 ^b	4.08	0.87	0.83	0.91

* Hammett substituent constant. $\dagger \nu_s$ values for the compounds in cyclohexane-dioxan solvent mixtures ($w_D = 0.0131$). ^a Judson and Kilpatrick, *J. Amer. Chem. Soc.*, 1949, **71**, 3110. ^b Bordwell and Cooper, *ibid.*, 1952, **74**, 1058. ^c Bennett, Brooks, and Glasstone, *J.*, 1935, 1821. ^d Wheland, Brownell, and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 2492. ^e Pauley, Schubel, and Lockemann, *Annalen*, 1911, **383**, 288. ^f Sprengling and Lewis, *J. Amer. Chem. Soc.*, 1953, **75**, 5709. ^g Ref. 1. ^h Colinese, Hall, and Ibbitson, *J.*, 1962, 983.

DISCUSSION

The studies of Hulett, Pegg, and Sutton on hydrogen bonding between a series of phenols and trimethylamine in cyclohexane solution⁷ indicated a linear relationship between $\ln K$ and $(\Delta\mu')^{\frac{1}{2}}$, where K is the association constant and $\Delta\mu'$ is the excess dipole moment for the complex over the sum of the moments for phenol and amine. A simple dependence of $\Delta\mu'$ on $\ln K$ is predictable from the equation $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$, if

⁶ Goode and Ibbitson, *J.*, 1960, 4265.

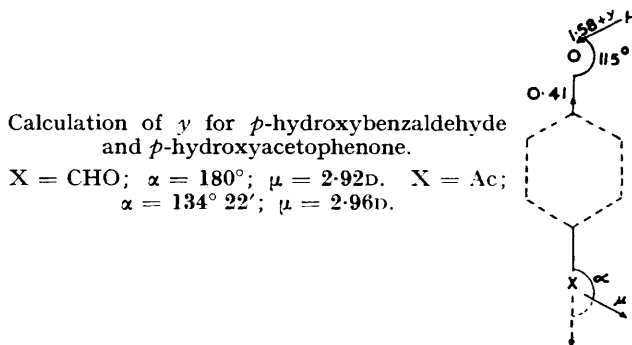
⁷ Hulett, Pegg, and Sutton, *J.*, 1955, 3901.

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$\Delta\mu'$, arising partly from the additional moment along the hydrogen bond, is determined by the enthalpy of formation of this bond, ΔH .

In the present investigation, O-H bond-moment increments, necessary to explain the observed moments in dioxan of a series of *p*-substituted phenols, are calculated and compared with the shifts in O-H stretching frequency.

In these bond-moment calculations, a C-O-H valency angle of 115° was assumed. The angle which the C-OH group moment in phenol makes with the C-O bond ($79^\circ 36'$) was calculated by Marsden and Sutton's method⁸ from the dipole moments, in cyclohexane, of phenol (1.46D), *p*-cresol (1.44D),¹ and toluene (0.37D). The moments $\mu_{\text{O-H}}$ and $\mu_{\text{O-C}}$, associated with the O-H and O-C bonds in phenol, were calculated by a method described previously,¹ to be 1.58 and 0.41D, respectively, the oxygen atom being at the



negative end of each dipole. The increases in O-H bond-moment (γ), necessary to explain the observed dipole moments in dioxan (Table 3), were calculated by means of eqn. 3.

$$\mu_{\text{D}}^2 = (1.58 + \gamma)^2 + (\mu_{\text{PhX}} - 0.41)^2 + 2(1.58 + \gamma)(\mu_{\text{PhX}} - 0.41)\cos 65 \quad (3)$$

where μ_{D} is the observed dipole moment in dioxan. The dipole moments of the mono-substituted benzene derivatives, μ_{PhX} , were taken as: toluene -0.37; chlorobenzene 1.58; bromobenzene 1.56; fluorobenzene 1.48; nitrobenzene 4.01; cyanobenzene 4.03; benzaldehyde 2.92; and acetophenone 2.96.

In the case of benzaldehyde and acetophenone, which have angular substituents, the angles, α , which the substituent-group moments make with a direction parallel to the C(ring)-O bond, were calculated vectorially from the dipole moments of benzaldehyde (2.92),⁹ 4-methylbenzaldehyde (3.30),¹⁰ toluene (0.37) ($\alpha = 180^\circ$), acetophenone (2.96),¹¹ 4-methylacetophenone (3.23),¹¹ and toluene (0.37) ($\alpha = 134^\circ 22'$). The values of γ for the two corresponding *p*-substituted phenols have been computed from the vector diagram (I), free rotation of the two vectors about the direction of the C(ring)-O bond being assumed.

The spectral data for phenol in cyclohexane-dioxan mixtures of varying composition (Table 2) show that as w_{D} , the weight fraction of dioxan, increases, the initial sharp drop in ν_{s} is followed by a smaller but continuous decrease. This suggests a change in ΔH with solvent composition. Since the dielectric constant of cyclohexane at 25° (2.0133) is almost equal to that of a cyclohexane-dioxan mixture of w_{D} 0.0131, *i.e.*, 2.0139, it was considered that $\Delta\nu_1$, the difference between the ν_{s} value for the compound in the latter solvent mixture and that for phenol in cyclohexane, would be indicative of the effect of a *p*-substituent on the strength of hydrogen bonding of phenol to dioxan. Values of $\Delta\nu_1$ and γ , recorded in Table 3, give a linear plot, as do those of γ and pK_{a} .

⁸ Marsden and Sutton, *J.*, 1936, 599.

⁹ Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 215.

¹⁰ Pearce and Berhenke, *J. Phys. Chem.*, 1935, **39**, 1005.

¹¹ Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957.

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Regression lines of y on $\Delta\nu_1$ and y on pK_a (eqns. 4 and 5) have been calculated, assuming no error in $\Delta\nu_1$ and pK_a .

$$y = 0.00814 \Delta\nu_1 - 1.43 \quad (4)$$

$$y = -0.269 pK_a + 3.07 \quad (5)$$

Values of y calculated from these equations (Table 3) compare favourably with the experimental values, thus illustrating the simple dependence of O-H bond-moment on strength of hydrogen bonding. That this variation is in accord with the known electrical effects of the p -substituents, is shown by comparing the Hammett substituent constant, σ , with $\Delta\nu_1$, pK_a , and y .

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