
834. *Dipole Moments of a Series of Substituted Phenols in Benzene.*

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Apparent dipole moments of a series of substituted phenols have been determined from measurements on dilute solutions in benzene. Interaction moments (μ_{int}) along the O—C bond necessary to correlate the observed and calculated moments of the *para*-substituted compounds have been evaluated, and show a trend parallel with acid dissociation constants, OH bond stretching frequencies, and Hammett σ values of the aromatic substituents. Moments of mesitol, durenol, and 2,4,6-tri-*t*-butylphenol are explained by inhibition of mesomerism, hyperconjugation of the *ortho*-methyl groups with the aromatic nucleus occurring in mesitol, and steric inhibition in 2,4,6-tri-*t*-butylphenol. In durenol, owing to the close approach of the *o*-methyl groups to the hydroxyl group, both effects are important. Moments of 2,4,6-trihalogenophenols are explained by intramolecular hydrogen bonding. A comparison of dipole moments in cyclohexane and in benzene indicates some solute-solvent interaction in the latter solvent.

WHEN two different *ortho* : *para*-directing groups other than methyl are substituted *para* to each other in benzene, the observed dipole moment of the compound is generally found to be greater than that calculated vectorially. This difference is explained by a moment arising from interaction between the mesomeric effects of the two groups, being positive relative to the group having the greater *ortho* : *para*-directing power. The negative values in *p*-halogenophenols¹ appear anomalous therefore.

¹ Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, p. 209.

Also, the moment of mesitol² (1.39 D) is reported to be lower, and that of durenol³ (1.68 D) to be much higher, than that of phenol⁴ (1.45 D). The value for durenol, approximating to that of an aliphatic alcohol, was interpreted as indicating steric inhibition of mesomerism, but such does not appear to be the case in mesitol.

In an attempt to resolve these anomalies, the dipole moments in benzene of a series of *para*-substituted and 2,4,6-trisubstituted phenols have been determined. The results, calculated as described previously,⁵ are summarised in Table 1, where α and ν are the

TABLE 1. Polarisation data for solutions in benzene at 25°.

Compound	10 ³ α	10 ² ν	$P_{2\infty}$ (c.c.)	μ_B (D)	μ_C (D)	Previous values *	
						μ (D)	
Phenol	2904	15	48.7	1.54	1.43	1.53(4), ^a	1.45
<i>p</i> -Cresol	2630	16	50.1	1.57	1.44	1.64, ^b	1.57 ^b
<i>p</i> -t-Butylphenol	1950	6	53.4	1.62	1.48		
<i>p</i> -Fluorophenol	4614	4	96.5	2.17	—	2.08 ^c	
<i>p</i> -Chlorophenol	4524	15	105.7	2.27	2.25	2.68, ^b	2.22
<i>p</i> -Bromophenol	3411	17	105.4	2.27	2.15	2.25, ^b	2.12 ^b
<i>p</i> -Iodophenol	2633	23	99.5	2.21	—		
<i>p</i> -Nitrophenol	20,430	28	526.4	5.07	—	5.05, ^b	5.01 ^b
<i>p</i> -Cyanophenol	22,600	21	501.4	4.95	—		
Mesitol	1690	6	41.7	1.43	1.30	1.36, ^b	1.39 ^c
2,4,6-Trichlorophenol	1275	15	41.7	1.43	1.38	1.62 ^b	
2,4,6-Tribromophenol	973	18	49.2	1.55	1.44	1.56 ^b	
2,4,6-Tri-t-butylphenol	1095	-1	54.4	1.63	1.55		

* Values in benzene.

^a Hulett, Pegg, and Sutton, *J.*, 1955, 3901. ^b Various measurements from Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948. ^c Ref. 1. ^d Ref. 4. ^e Ref. 2.

limiting values of $d\epsilon/dw$ and dn^2/dw , respectively, and the other symbols have their usual significance. Dipole moments determined in benzene (μ_B) are all greater than corresponding values determined previously in cyclohexane⁵ (μ_C) indicating some solute-solvent interaction in benzene.

Moments of the *para*-substituted phenols have been calculated from equation (1), the angle which the C-OH group moment in phenol makes with the C-O bond (87° 47') being determined vectorially from the moments of phenol (1.54 D), *p*-cresol (1.57 D), and toluene (0.37 D):

$$\mu_{\text{calc}}^2 = 1.54^2 + \mu_{\text{PhX}}^2 + 2(1.54)\mu_{\text{PhX}} \cos 87^\circ 47' \quad . \quad . \quad . \quad (1)$$

The following values have been taken for the moments of the parent monosubstituted benzenes (μ_{PhX}): *t*-butylbenzene — 0.53, chlorobenzene 1.58, bromobenzene 1.56, fluorobenzene 1.48, iodobenzene 1.40, nitrobenzene 4.01, and cyanobenzene 4.03. Interaction moments (μ_{int}) along the O-C bond, necessary to explain the observed dipole moments, have been calculated from equation 2 (Fig. 1):

$$\mu_B^2 = 1.54^2 + (\mu_{\text{int}} + \mu_{\text{PhX}})^2 + 2(1.54)(\mu_{\text{int}} + \mu_{\text{PhX}}) \cos 87^\circ 47' \quad . \quad . \quad (2)$$

The results, together with acid dissociation constants (K_a), infrared spectral data, and Hammett substituent constants (σ), are summarised in Table 2. Values of μ_{int} for the *para*-halogenophenols, now reported to be positive, increase in the order F < Cl < Br < I, in accordance with the view that the mesomeric effects of the halogen atoms, which oppose the mesomeric effect of the hydroxyl group, follow the order F > Cl > Br > I. The negligibly small values of μ_{int} for *p*-fluoro-, *p*-chloro-, and *p*-t-butyl-phenol, in comparison with values reported for similarly substituted anilines and dimethylanilines,¹ are considered to be due to the greater *ortho*:*para*-directing power of the amino- and dimethylamino-groups. The value of μ_{int} increases with the acid dissociation constant, and the large

² Suetaka and Sanesi, *Ann. Chim. (Italy)*, 1956, **46**, 1133.

³ Ingham and Hampson, *J.*, 1939, 981.

⁴ Boud, Cleverdon, Collins, and Smith, *J.*, 1955, 3793.

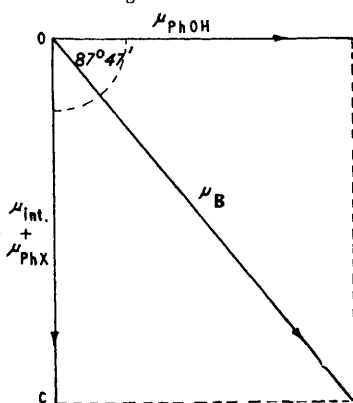
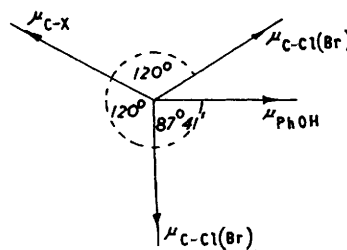
⁵ Erić, Goode, and Ibbitson, *J.*, 1960, 55.

TABLE 2.

	μ_B (D)	μ_{calc} (D)	μ_{int} (D)	σ^c	$10^{10}K_a$	OH frequencies in CCl_4 (cm^{-1})
<i>p</i> -t-Butylphenol	1.62	1.61	-0.03	-0.197	—	3612.1
<i>p</i> -Fluorophenol	2.17	2.18	-0.01	0.062	0.26 ^a	—
<i>p</i> -Cresol	1.57	1.57	0	-0.170	—	3612.8
Phenol	1.54	1.54	0	0	0.32 ^a	3610.1
<i>p</i> -Chlorophenol	2.27	2.25	0.03	0.227	1.32 ^a	3608.5
<i>p</i> -Bromophenol	2.27	2.23	0.05	0.232	1.55 ^a	3607.4
<i>p</i> -Iodophenol	2.21	2.12	0.13	0.276	2.19 ^a	—
<i>p</i> -Cyanophenol	4.95	4.37	0.62	1.000	112.2 ^b	—
<i>p</i> -Nitrophenol	5.07	4.35	0.76	1.270	724.5 ^b	3594.5

^a Bennett, Brooks, and Glasstone, *J.*, 1935, 1821. ^b Judson and Kilpatrick, *J. Amer. Chem. Soc.*, 1949, **71**, 3110. ^c Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.

values for *p*-nitrophenol and *p*-cyanophenol are in accord with the powerful acid strengthening character of the nitro- and cyano-groups. Ingraham, Corse, Bailey, and Stitt⁶ have related the OH bond-stretching frequencies of substituted phenols to the Hammett σ

FIG. 1. Calculation of μ_{int} directed along the O-C bond.FIG. 2. Calculation of $\mu_{\text{C-X}}$ for 2,4,6-trihalogenophenols.

values of the aromatic substituents, and Goulden⁷ has shown that they can also be related to the $\text{p}K_a$ values. The values of μ_{int} provide contributory evidence of the extent of change of electrical character of the C-OH group effected by *para*-substituent groups.

Evidence for intramolecular hydrogen bonding in *ortho*-substituted chlorophenols is provided by Wulf, Liddel, and Hendricks from an analysis of infrared spectra in the overtone region. *cis*- and *trans*-Forms of *o*-chlorophenol are distinguished, a considerably higher proportion of the *cis*-form being present, owing to hydrogen-bond stabilisation.⁹ From the observed moment of phenol (1.54 D) acting at an angle of $87^\circ 47'$ to the O-C bond, and a C-Cl bond moment of 1.58 D at an angle of 60° , we have calculated the dipole moments of the *cis*- and the *trans*-form of *o*-chlorophenol to be 0.75 D and 2.99 D, respectively. The reported moment of *o*-chlorophenol¹⁰ is 1.33 D, indicating preference for the *cis*-configuration, and providing further evidence for intramolecular hydrogen bonding. In order to interpret the measured moments of the 2,4,6-trihalogenophenols, intramolecular hydrogen bonding is recognised. It is considered that changes in the moments of the C-O, O-H, C-X (X = Cl, Br) bonds will occur, and in addition the $\text{H} \cdots \text{X}$ bond will contribute to the resultant moment of the molecule. These changes being assumed to reside in a single vector directed along the C-X bond in the *ortho*-position, and coupling

⁶ Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.

⁷ Goulden, *Spectrochim. Acta*, 1954, **6**, 129.

⁸ Wheland, Brownell, and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 2492.

⁹ Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287.

¹⁰ Anzilotti and Curran, *J. Amer. Chem. Soc.*, 1943, **65**, 607.

this vector (μ_{C-X}) with the moment of phenol, and the moments of the C-X bonds ($\mu_{C-Cl} = 1.58$ D, $\mu_{C-Br} = 1.56$ D) in the *para*- and remaining *ortho*-positions μ_{C-X} is calculated to be 1.71 and 1.55 for 2,4,6-trichlorophenol and 2,4,6-tribromophenol, respectively (Fig. 2). The observed dipole moments of these two compounds are, therefore, readily explained by small polar changes in one of the *ortho*-substituted groups, brought about by intramolecular hydrogen bonding.

Infrared studies by Sears and Kitchen¹¹ indicate close proximity of alkyl to hydroxyl groups in *o*-alkylphenols, *e.g.*, hindrance to intermolecular hydrogen bonding is partial in *o*-cresol, much greater in mesitol, and almost complete in 2,6-di-*t*-butylphenol. Mesitol undergoes hydrogen bonding to a greater extent than does durenol, and in explanation the above authors suggest that a *meta*-methyl group forces an adjacent *ortho*-methyl group closer to the hydroxyl group. We have calculated the dipole moments of the *cis* (1.88 D)

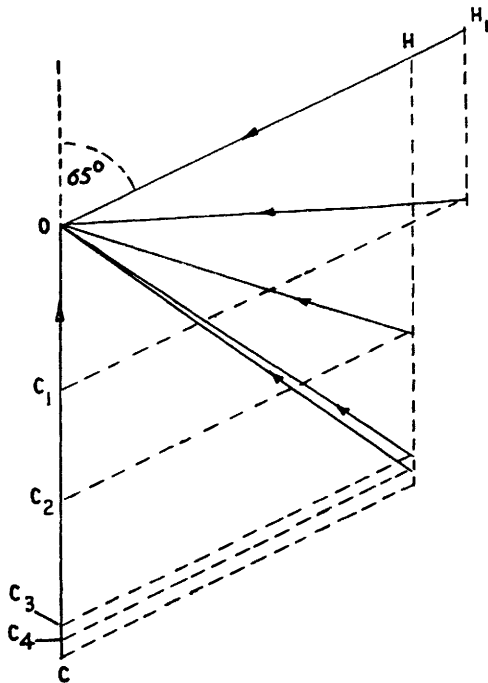


FIG. 3. Calculation of μ_{O-C} for mesitol, durenol, and 2,4,6-tri-*t*-butylphenol.

Aliphatic alcohol: $\mu_{(O-H)} = 1.5$ D, $\mu_{(O-C)} = 1.7$ D.
 Phenol: $\mu_{(O-H_1)} = 1.7$ D, $\mu_{(O-C_1)} = 0.66$ D.
 Mesitol: $\mu_{(O-C_2)} = 1.08$ D.
 Durenol: $\mu_{(O-C_4)} = 1.62$ D.
 2,4,6-Tri-*t*-butylphenol: $\mu_{(O-C_3)} = 1.53$ D.

and the *trans* (1.24 D) form of *o*-cresol in the same way as previously described for *o*-chlorophenol. Comparison with the reported moment of *o*-cresol, 1.41 D (Table I, ref. b), indicated preference for the *trans*-form, and suggests that the closeness of approach of the groups in the *ortho*-positions causes repulsion. With mesitol and durenol, repulsion will occur between the hydroxyl group and two *ortho*-methyl groups. The vector diagram (Fig. 3) illustrates how a decrease in the mesomeric moment due to the hydroxyl group can explain the high moment of durenol (1.68 D),³ and the low moment of mesitol (1.43 D), relative to that of phenol (1.54 D). A C-O-H valency angle of 115° in phenol,¹⁰ and a value of $87^\circ 47'$ for the angle which the C-OH group moment in phenol makes with the C-O bond being assumed, the moments μ_{O-H} and μ_{O-C} associated with the O-H and O-C bonds are calculated, by a method previously described,⁵ to be 1.70 D and 0.66 D, respectively. Approximate bond moments for aliphatic alcohols are μ_{O-H} , 1.5 D and μ_{O-C} , 1.7 D (ref. 1, p. 92). A decrease in mesomeric moment along the O-C bond in mesitol and durenol would increase μ_{O-C} from 0.66 D towards a value of 1.7 D, and reduce μ_{O-H} from 1.7 D towards a value of 1.5 D. Taking the minimum value of μ_{O-H} (1.5 D), we have

¹¹ Sears and Kitchen, *J. Amer. Chem. Soc.*, 1949, **71**, 4110.

calculated from equation 3 the values of μ_{O-C} for mesitol, durenol, and 2,4,6-tri-*t*-butylphenol necessary to explain the observed moments of these compounds (Fig. 3). These are 1.08 D, 1.62 D, and 1.53 D, respectively.

$$\mu_B^2 = 1.5^2 + \mu_{O-C}^2 + 2(1.5)(\mu_{O-C}) \cos 115^\circ \quad . \quad . \quad . \quad (3)$$

Because of the small steric requirements of the hydroxyl group, we consider that the increase in the C-O bond dipole from 0.66 D in phenol to 1.08 D in mesitol results from hyperconjugation of the *ortho*-methyl groups, rather than from steric inhibition of mesomerism. Supporting evidence for this suggestion is provided by data on acid dissociation constants. Phenol, *p*-cresol, *o*-cresol, 2,6-dimethylphenol, and mesitol have pK_a values of 9.94, 10.19, 10.28, 10.60, and 10.88, respectively.^{8,12} The effect of methyl substituents on the ionisation of phenol being assumed to be additive, calculated pK_a values of 2,6-dimethylphenol and mesitol are 10.62 and 10.87, respectively, in close agreement with the observed values. Such agreement would be unlikely if steric inhibition of mesomerism, absent in phenol, *p*-cresol, and *o*-cresol, were an additional explanatory factor of the decreased acidity of 2,6-dimethylphenol and mesitol.

TABLE 3.

100w	ϵ	n_D	100w	ϵ	n_D	100w	ϵ	n_D	100w	ϵ	n_D
Phenol			<i>p</i> -Cresol			<i>p</i> - <i>t</i> -Butylphenol			2,4,6-Tri- <i>t</i> -butylphenol		
0.000	2.2725	1.4981	0.000	2.2725	1.4981	0.000	2.2725	1.4981	0.000	2.2725	1.4981
0.274	2.2808	—	0.329	2.2813	—	0.225	2.2769	—	0.139	2.2742	—
0.395	2.2838	—	0.573	2.2877	—	0.451	2.2813	—	0.365	2.2768	—
0.519	2.2877	—	0.752	2.2923	—	0.676	2.2857	—	0.586	2.2790	—
0.769	2.2948	—	0.846	2.2947	—	0.898	2.2895	—	0.810	2.2811	—
0.903	—	1.4985	1.048	2.2999	—	1.121	2.2940	1.4983	1.055	2.2841	—
1.023	2.3023	—	1.318	—	1.4988	3.328	—	1.4988	4.190	—	1.4979
3.481	—	1.4998	2.045	—	1.4992	5.436	—	1.4992	8.000	—	1.4978
6.369	—	1.5013	3.224	—	1.4998				11.970	—	1.4977
<i>p</i> -Chlorophenol			<i>p</i> -Bromophenol			2,4,6-Trichlorophenol			2,4,6-Tribromophenol		
0.000	2.2725	1.4981	0.000	2.2725	1.4981	0.000	2.2725	1.4981	0.000	2.2725	1.4981
0.227	2.2826	—	0.339	2.2841	—	0.105	2.2738	—	0.115	2.2737	—
0.452	2.2927	—	0.451	2.2880	—	0.342	2.2768	—	0.230	2.2748	—
0.677	2.3033	—	0.564	2.2918	—	0.473	2.2786	—	0.445	2.2770	—
0.788	—	1.4985	0.675	2.2957	—	0.550	2.2796	—	0.580	2.2783	—
0.901	2.3133	—	0.787	2.2996	1.4985	0.792	2.2826	1.4985	0.680	2.2790	—
3.211	—	1.4997	3.692	—	1.5002	3.275	—	1.4997	1.057	—	1.4987
5.574	—	1.5009	5.434	—	1.5012	5.780	—	1.5010	3.226	—	1.5000
									5.314	—	1.5013
Mesitol			<i>p</i> -Iodophenol			<i>p</i> -Fluorophenol			<i>p</i> -Nitrophenol		
0.000	2.2725	1.4981	0.000	2.2725	1.4981	0.000	2.2725	1.4981	0.000	2.2725	1.4981
0.125	2.2748	—	0.117	2.2755	—	0.226	2.2830	—	0.057	2.2842	—
0.360	2.2787	—	0.386	2.2826	—	0.452	2.2938	—	0.114	2.2953	—
0.605	2.2828	—	0.575	2.2874	—	0.675	2.3038	—	0.163	2.3048	—
0.826	2.2868	—	0.794	2.2933	—	0.899	2.3133	—	0.223	2.3183	1.4983
1.034	2.2901	—	1.032	2.2999	1.4989	1.121	2.3238	1.4982	0.429	—	1.4985
2.331	—	1.4985	3.766	—	1.5010	3.435	—	1.4986	0.600	—	1.4987
4.406	—	1.4990	6.520	—	1.5031	5.370	—	1.4988			
7.219	—	1.4995									
			100w	ϵ	n_D	100w	ϵ	n_D			
			<i>p</i> -Cyanophenol			<i>p</i> -Cyanophenol					
			0.000	2.2725	1.4981	0.225	2.3238	1.4983			
			0.070	2.2880	—	0.412	—	1.4984			
			0.112	2.2975	—	0.870	—	1.4987			
			0.194	2.3165	—						

With 2,4,6-tri-*t*-butylphenol, mesomeric inhibition is reflected in the increase in C-O bond moment from 0.66 D in phenol to 1.53 D, and is readily explained by a steric effect caused by the large *ortho*-*t*-butyl groups.

¹² Sprengling and Lewis, *J. Amer. Chem. Soc.*, 1953, **75**, 5709.

Finally, we suggest that in the case of durenol, hyperconjugation, and steric inhibition of mesomerism caused by the closer approach of the *o*-methyl groups to the hydroxyl group than in mesitol,¹¹ may both contribute to the increase in C-O bond moment. A pK_a value for durenol would be of interest in this connection.

EXPERIMENTAL

Materials.—*p*-Iodophenol, m. p. 93·5°, and *p*-cyanophenol, m. p. 113°, prepared from *p*-aminophenol by the Sandmeyer reaction, were recrystallised from light petroleum (b. p. 80—100°) and water, respectively. *p*-Nitrophenol, m. p. 113—113·5°, was recrystallised from hydrochloric acid and then from benzene below 60°. *p*-Fluoroanisole, prepared from *p*-anisidine by the Bolz-Schiemann reaction, was heated with anhydrous aluminium chloride at 110° for 3 hr., and the product, *p*-fluorophenol, m. p. 46—48°, b. p. 77°/13 mm., purified by vacuum distillation. Other solutes were prepared and recrystallised, and benzene purified and dried, as described previously.⁵

Methods and Results.—Dielectric constants and refractive indices of solutions of graded concentration of each solute in benzene were determined at 25°, the methods and apparatus being the same as in a previous investigation.⁵ Dielectric constants were calculated relative to the value of 2·2725 at 25° for pure benzene. The results are recorded in Table 3, where the symbols have their usual significance.

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