

432. *Effect of Methylation on the Light Absorption of Phenols.*  
*Part I.*

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The spectra of numerous substituted phenols and of the corresponding anisoles in ethyl alcohol are compared. Methylation displaces both the *B*- and the *K*-bands to shorter wave-lengths and reduces their intensity. If both *ortho*-positions to the hydroxyl group are occupied by Cl, Br, I, CH<sub>3</sub>, CHO, or NO<sub>2</sub>, this effect is considerably enhanced owing to the intramolecular steric hindrance involving one of these substituents and the methoxyl group. The cause of the steric inhibition of conjugation is briefly discussed.

THE electronic spectra of organic molecules above 2000 Å consist of two types of absorption bands (Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 464, 1635; 1932, **65**, 941; *J.*, 1939, 1177): (i) *R*-bands of low intensity ( $\epsilon < 2000$ ) which are due to electronic transitions originating in individual multiple linkages; and (ii) *K*-bands of a comparatively high intensity ( $\epsilon > 5000$ ) which are connected with systems represented by A·[CH:CH]<sub>n</sub>·CH:B, where A = R, Hal, OR, SR, NR<sub>2</sub>, O<sup>-</sup>, S<sup>-</sup>, or NR<sup>-</sup>, and B = CR<sub>2</sub>, NR, O, S, <sup>+</sup>NR<sub>2</sub>, <sup>+</sup>OR, or <sup>+</sup>SR; these are the so-called conjugated systems. It is now accepted that the electronic transitions involved correspond *qualitatively* to electron displacements along the axis of these systems (McMurry and Mulliken, *Proc. Nat. Acad. Sci.*, 1940, **26**, 312, and earlier

papers; Calvin and Lewis, *Chem. Reviews*, 1939, **25**, 303). These investigations led also to an early recognition of two factors: (a) the distinct nature of the characteristic long-wave bands appearing in the spectra of benzene and many of its homologues and derivatives; such bands have comparatively low intensities ( $\epsilon$  generally  $<5000$ ) similar to those of the *R*-bands, but obey very different optical rules (Burawoy, *Ber.*, 1930, **63**, 3157; 1931, **64**, 489; *Discuss. Faraday Soc.*, 1950, **9**, 70); and (b) the influence of intramolecular steric inhibition of conjugation on the position and intensity of the *B*- (benzene) and *K*-bands (Burawoy, *J.*, 1939, 1186; cf. also Calvin, *J. Org. Chem.*, 1939, **4**, 256), now well-established.

We have compared the spectra of numerous substituted phenols and the corresponding anisoles (in ethyl alcoholic solution). The data obtained for the *B*-bands appearing in the near ultra-violet spectra of phenols and anisoles substituted by Me, Cl, Br, or I are collected in Table I.

TABLE I.

Substituents	Fig.	Phenol		Anisole		Substituents	Fig.	Phenol		Anisole	
		$\lambda$ (Å)	$\epsilon$	$\lambda$ (Å)	$\epsilon$			$\lambda$ (Å)	$\epsilon$	$\lambda$ (Å)	$\epsilon$
None .....	1	2719	1875	2770	1400	2 : 6-(CH <sub>2</sub> :OH) <sub>2</sub> -4-Me	11	2826	2850	2748	1050
<i>p</i> -Me .....	2	2802	2100	2700	1580	<i>p</i> -Cl .....	12	2828	1850	2880	1600
<i>m</i> -Me .....	3	2747	1850	2775	2100	<i>o</i> -Cl .....	13	2784	2400	2813	1850
<i>o</i> -Me .....	4	2746	2025	2780	1650	2 : 4 : 6-Cl <sub>3</sub> .....	14	2941	2900	2810	2100
3 : 5-Me <sub>2</sub> .....	5	2780	1900	2720	1700	<i>p</i> -Br .....	15	2845	1650	2740	2100
2 : 6-Me <sub>2</sub> .....	6	2725	1800	2770	1725	<i>o</i> -Br .....	16	2789	2800	2874	875
2 : 4 : 6-Me <sub>3</sub> .....	7	2785	1800	2712	1725	2 : 4 : 6-Br <sub>3</sub> .....	17	2949	3200	2805	875
2 : 3 : 5 : 6-Me <sub>4</sub> ...	8	2760	1200	2795	1700	<i>p</i> -I .....	18	2820	1700	2880	1300
2 : 3 : 4 : 6-Me <sub>4</sub> ...	9	2802	1700	2715	1700	<i>o</i> -I .....	19	2870	3000	2812	1500
Me <sub>5</sub> .....	10	2807	1600	2650	600	2 : 4 : 6-I <sub>3</sub> .....	20	2800	3450	2810	2100
				2772	500			2944	3600	2764	2400
				2686	575					2893	1000
				2665	300					2818	1000
				2782	525					2850	2750
				2705	525					2780	3250
				2710	450					2770	980*

\* Inflexion.

Methylation displaces the *B*-bands of phenol and its derivatives substituted in *meta*- or *para*-positions slightly to shorter wave-lengths (10—20 Å), the intensity being also decreased by about 5—10%. Since the bands of most methyl ethers, in contrast to those of the corresponding phenols, show in our measurements two peaks, this is more apparent by comparing their graphs (Figs. 1—20).

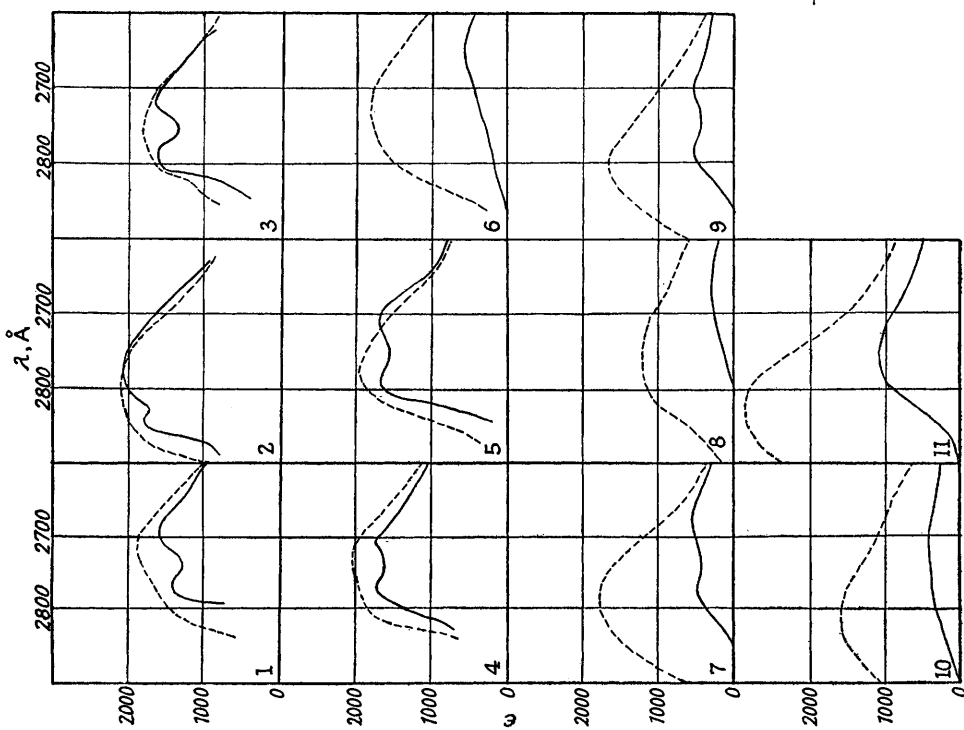
The same effect is observed in the case of the anisole derivatives with only one *ortho*-substituent. Undoubtedly, the methyl group of OMe is able to turn away from the large substituent in *ortho*-position and, thus, evade steric interaction.

This is not possible if both *ortho*-positions are occupied. Owing to the resulting reduction of conjugation, methylation of such phenols is responsible for much greater displacements to shorter wave-lengths (70—100 Å) and, in particular, for a reduction of the intensity by 70—80%.

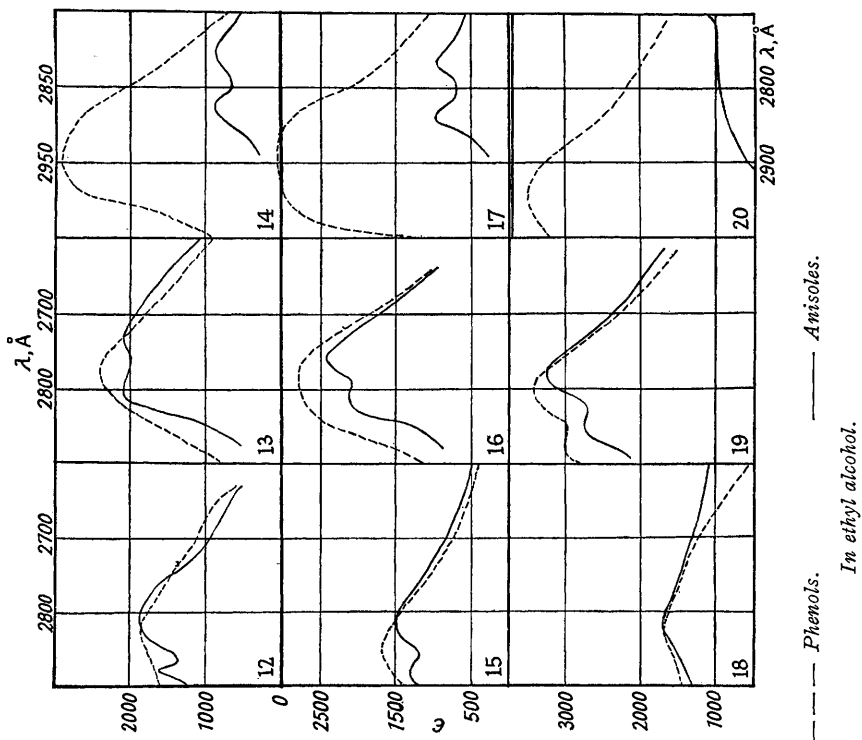
We had no facilities for measuring the *K*-bands of these simple molecules which have maxima below 2200 Å. However, these bands are displaced considerably to longer wave-lengths on the introduction of a nitro- or formyl-group in the *para*-position of phenol. We have, therefore, investigated these bands in the spectra of *p*-nitrophenol, *p*-hydroxybenzaldehyde, and a few derivatives substituted by methyl groups (Table 2; Figs. 21—23), and established that they behave similarly to the *B*-bands of lower intensity discussed above. The latter are not observed in the spectra of these substances since they are covered by the more intense *K*-bands.

Again, methylation of *p*-nitrophenol, *p*-hydroxybenzaldehyde, and 4-hydroxy-2 : 6-dimethylbenzaldehyde displaces the *K*-bands slightly to shorter wave-lengths (20—90 Å), their intensity being almost unaffected. The spectra of 3 : 5-dimethyl-4-nitrophenol and

Figs. 1-11.



Figs. 12-20.



--- Phenols.  
 — Anisoles.

In ethyl alcohol.

its methyl ether are rather complicated owing to the known steric interaction between the methyl groups and the nitro-group, but they behave similarly.

In contrast, the *K*-bands are strongly displaced on methylation of 4-hydroxy-3 : 5-dimethylbenzaldehyde and 2 : 6-dimethyl-4-nitrophenol (250 and 350 Å respectively) owing to the considerable steric interaction of the OMe group with one of the two methyl groups in the *ortho*-position and the resulting reduction of conjugation between the methoxyl group and the benzene ring.

FIGS. 21—26.

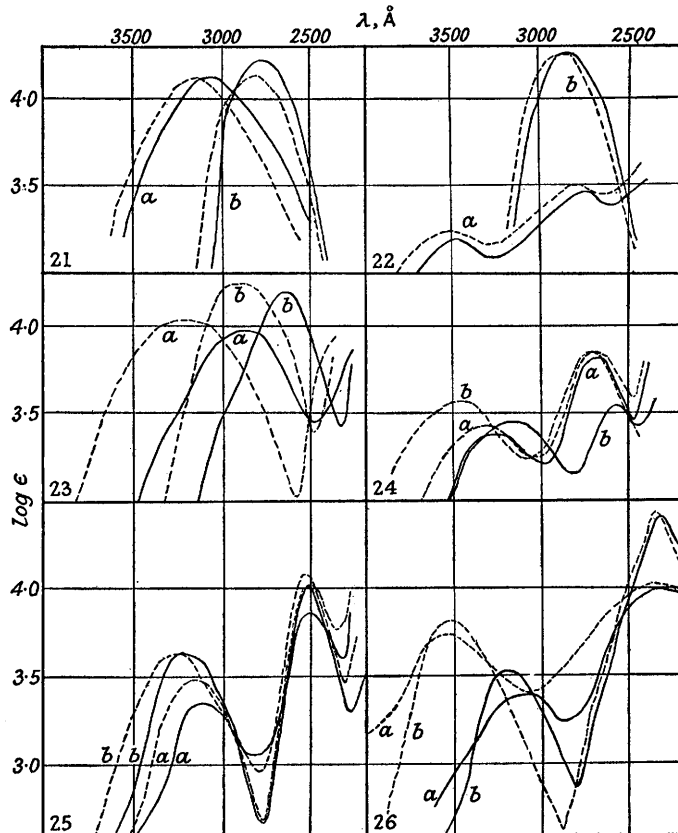
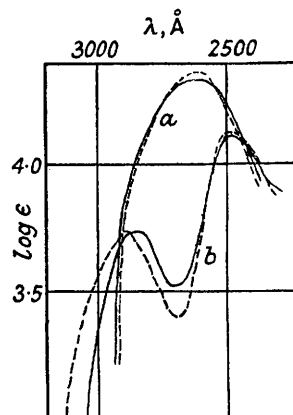


FIG. 27.



(N.B. Because of a drafting error, the lowest curve in Fig. 25 should be displaced upwards by 0.3 unit.)

It is noteworthy that in the case of the *B*-bands steric interaction is responsible for a considerable decrease in intensity, but a comparatively small displacement to shorter wavelengths, whereas the much greater shift of the *K*-bands is accompanied by only a small decrease in intensity (about 10%). This was expected since it is just the reversal of the effects resulting from the introduction of the hydroxyl group, as may be illustrated by the examples (*a*) of benzene ( $\lambda$  2543 Å;  $\epsilon$  300) and phenol ( $\lambda$  2719 Å;  $\epsilon$  1875) for the *B*-bands and

TABLE 2.

Substance	Fig.	Phenol		Anisole	
		$\lambda$ (Å)	$\epsilon$	$\lambda$ (Å)	$\epsilon$
<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·OH	21 <i>a</i>	3140	13,000	3050	13,000
<i>p</i> -OH·C <sub>6</sub> H <sub>4</sub> ·CHO	21 <i>b</i>	2815	14,000	2765	15,500
4 : 3 : 5 : 1-NO <sub>2</sub> ·C <sub>6</sub> H <sub>2</sub> Me <sub>2</sub> ·OH	22 <i>a</i>	3507	1,750	3492	1,600
		2813	3,150	2763	3,000
4 : 2 : 6 : 1-OH·C <sub>6</sub> H <sub>2</sub> Me <sub>2</sub> ·CHO	22 <i>b</i>	2863	18,000	2840	18,000
4 : 2 : 6 : 1-NO <sub>2</sub> ·C <sub>6</sub> H <sub>2</sub> Me <sub>2</sub> ·OH	23 <i>a</i>	3227	11,000	2886	9,500
4 : 3 : 5 : 1-OH·C <sub>6</sub> H <sub>2</sub> Me <sub>2</sub> ·CHO	23 <i>b</i>	2901	17,000	2647	15,500

(*b*) of benzaldehyde ( $\lambda$  2442 Å;  $\epsilon$  13,000) and *p*-hydroxybenzaldehyde ( $\lambda$  2815 Å;  $\epsilon$  14,000) or nitrobenzene ( $\lambda$  2590 Å;  $\epsilon$  9500) and *p*-nitrophenol ( $\lambda$  3140 Å;  $\epsilon$  13,000) for the *K*-bands.

In Table 3 the maxima of *B*- and/or *K*-bands of hydroxydiphenyls, nitrophenols, and hydroxybenzaldehydes, and their methyl ethers are listed. Again, anisoles substituted in the *meta*- or *para*-position by a phenyl, nitro-, or formyl group absorb at slightly shorter wave-lengths than do the corresponding phenols, the change of intensity being only negligible and almost within experimental error (5%).

TABLE 3.

Substance	Fig.	Phenol				Anisole			
		<i>B</i> -band		<i>K</i> -band		<i>B</i> -band		<i>K</i> -band	
		$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Ph·OH	27a	—	—	2612	22,500	—	—	2610	21,000
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Ph·OH	27b	2880	5500	2470	13,500	2850	5500	2464	13,000
<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·OH	21a	—	—	3140	13,000	—	—	3050	13,000
<i>m</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·OH	24a	3322	2700	2705	6,900	3252	2400	2680	6,400
<i>o</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·OH	24b	3435	3600	2730	6,600	3172	2850	2585	3,450
<i>p</i> -HO·C <sub>6</sub> H <sub>4</sub> ·CHO	21b	—	—	2815	14,000	—	—	2765	15,500
<i>m</i> -HO·C <sub>6</sub> H <sub>4</sub> ·CHO	25a	3155	3000	2537	9,500	3087	3000	2525	9,500
<i>o</i> -HO·C <sub>6</sub> H <sub>4</sub> ·CHO	25b	3244	4350	2540	12,500	3210	4550	2528	10,500
2 : 6 : 4 : 1-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>2</sub> Me·OH	26a	3542	5250	2410	10,500	3116	2600	2360	10,000
2 : 5 : 1 : 3-HO·C <sub>6</sub> H <sub>2</sub> Me(CHO) <sub>2</sub>	26b	3503	6800	2356	28,000	3190	3500	2326	26,000

The effect of one phenyl or formyl group in *ortho*-position is similar. It is noteworthy that formation of a hydrogen bond in *o*-hydroxybenzaldehyde has in itself only a small effect on the light absorption which, as Burawoy and Burawoy (*J.*, 1936, 38) have already pointed out, is incompatible with the interpretation of the internal hydrogen bond in terms of a resonance hybrid.

In contrast, both the *B*- and the *K*-band in the spectrum of *o*-nitroanisole are at considerably shorter wave-lengths (260 and 145 Å respectively) and have much lower intensities than those of *o*-nitrophenol. This is explained as follows. It is already known that methyl groups in the *ortho*-position to a formyl group reduce its conjugation only to a very small extent, if at all. Thus, the C:O Raman frequencies and dipole moments observed for benzaldehyde and 2 : 4 : 6-trimethylbenzaldehyde are very similar, showing the absence of any notable steric interaction (cf. Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310; Saunders, Murray, and Cleveland, *ibid.*, p. 3121; 1942, **64**, 1181; cf. also the spectra of *p*-hydroxybenzaldehyde and 4-hydroxy-2 : 6-dimethylbenzaldehyde, Table 2). On the other hand, intramolecular steric hindrance has been found to be very strong with the corresponding nitrobenzene derivatives, as comparison of the NO<sub>2</sub> Raman frequencies, dipole moments, electronic spectra, and molecular refractivities of nitrobenzene and nitromesitylene shows (cf. also Thomson, *J.*, 1944, 404, 408).

This effect is already appreciable in *o*-nitrotoluene and *o*-chloronitrobenzene which absorb at 2560 Å ( $\epsilon$  6000) and 2515 Å ( $\epsilon$  4500) respectively (cf. nitrobenzene :  $\lambda$  2590 Å;  $\epsilon$  9500). It can, therefore, be expected that the oxygen atom of the methoxyl group will already interact with the nitro-group in *o*-nitroanisole; this effect will be cancelled by the formation of the internal hydrogen bond in *o*-nitrophenols.

A comparison of the spectra of 4-methyl-2 : 6-dinitrophenol and 2-hydroxy-5-methylisophthalaldehyde with those of their methyl ethers shows that the steric effect is very strong in presence of *two* nitro- or formyl groups in the *ortho*-position. The *B*-bands in the spectra of the ethers are at much shorter wave-lengths (300 and 400 Å) and have considerably smaller intensities (about 50%). It is true that the *K*-bands remain almost unchanged, but this is not surprising since the influence of the hydroxyl group on the *K*-bands is only small.

Thus, in contrast to the *B*-bands, the observed *K*-bands of *m*-dinitrobenzene ( $\lambda$  2350 Å;  $\epsilon$  20,000) and isophthalaldehyde ( $\lambda$  2258 Å;  $\epsilon$  26,000) are only slightly displaced to longer wave-lengths in 4-methyl-2 : 6-dinitrophenol ( $\lambda$  2410 Å;  $\epsilon$  10,500) and 2-hydroxy-5-methylisophthalaldehyde ( $\lambda$  2356 Å;  $\epsilon$  28,000) respectively. Any small effect of the methyl group can be ignored. The reduced intensity of the *K*-band of 4-methyl-2 : 6-

dinitrophenol should be accounted for by the steric interaction of the oxygen atom of the hydroxyl group with the nitro-group not participating in the hydrogen bond (cf. above). It is not observed for the *K*-band of 2-hydroxy-5-methylisophthalaldehyde.

*Discussion.*—The interpretation of the reduction of conjugation due to a steric repulsive interaction of substituents is bound up with the coplanarity of unsaturated hydrocarbons and related systems, which is assumed to be due to the maximum orbital overlap or delocalisation of (classically non-bonded) electrons in this state. Any deviation from coplanarity would then cause a reduction of delocalisation and of the effects associated with conjugation.

However, a detailed empirical analysis of all known facts has shown that the hypothesis of non-localised bonds is in disagreement with numerous observations and is superfluous. All constitutive variations of linkages can be accounted for by changes of the effective nuclear charges (the screening) of the participating atoms, *i.e.*, by changes of the repulsive interactions of electrons and nuclei (A. Burawoy, *Trans. Faraday Soc.*, 1944, **40**, 537; *Discuss. Faraday Soc.*, 1951, **10**, 104; *Chem. and Ind.*, 1944, 434; Contribution à l'Etude de la Structure Moléculaire, Liège, 1948, p. 73; cf. also Lennard-Jones and Pople, *Discuss. Faraday Soc.*, 1951, **10**, 9).

This view leads to an alternative interpretation of the coplanarity and the reduction of conjugation by intramolecular steric effects, which may be illustrated by the simple example of butadiene. Two factors will be responsible for its stability in the coplanar state: (i) that the repulsive interaction between the two  $H_2C:CH$  groups is smallest in this state; and (ii) that, as is generally assumed, a bond orbital is cylindrically symmetrical. This simplification is scarcely justified for bonds involving asymmetrically substituted atoms since the orbital extension should depend on the repulsion arising from neighbouring orbitals.

Thus, if the bond orbitals forming a double bond are assumed to be equivalent (cf. Burawoy, *loc. cit.*; Lennard-Jones and Pople, *loc. cit.*), they will strongly repel each other and be strained (bent). Each of these orbitals must be expected to extend more strongly in a plane parallel with that of the molecule. Similarly, the single C–C bond orbital in butadiene will not be cylindrically symmetrical, probably extending more strongly in a plane perpendicular to that of the molecule. The extension of the two atomic orbitals leading to the formation of the C–C bond will be similar and their overlap greatest in the coplanar configuration. Any deviation from coplanarity would cause an increased repulsion of the two bonding electrons (a reduced orbital overlap) resulting in a reduction of the exchange integral, of the bond energy in the ground state, and of the interaction of the absorbing electron system through this linkage in the excited state, causing the displacement of the absorption band to shorter wave-lengths. Similar considerations will apply to systems such as  $\bar{C}-OMe$  discussed in this paper.

The smaller displacements to shorter wave-lengths of the *B*- and the *K*-bands in ethyl alcoholic solution caused by the methylation of phenol and its derivatives in absence of steric effects appear to indicate a greater electron-attracting power of the methyl group as compared with a hydrogen atom, resulting in a reduced polarity of the absorbing conjugated systems. This rather surprising result is explained by the ability of the phenols to form internal or external hydrogen bonds.

Morton and Stubbs (*J.*, 1940, 1347) investigating the spectra of the hydroxy-benzaldehydes and their methyl ethers in hexane and ethyl alcohol solution arrived at this conclusion. They observed that both the *B*- and the *K*-bands of *m*-hydroxy-benzaldehyde in hexane solution, where there is a minimum possibility at least of solvent-solute interaction, are at shorter wave-lengths than those of its methyl ether. Although our absolute data for both these substances deviate somewhat from those reported by these authors, we have confirmed their findings in principle. Moreover, we have found that *p*-hydroxydiphenyl in hexane solution also absorbs at shorter wave-lengths than *p*-methoxydiphenyl (Table 4). These observations exclude the possibility that a slight steric interaction of the methyl group in OMe with a hydrogen atom in the *ortho*-position might reduce the conjugation between the methoxyl group and the benzene ring and contribute appreciably to the displacements under discussion.

Solvation would also account for the smaller resolution of the *B*-bands of the simple phenol derivatives in ethyl alcoholic solution as compared with the bands of the corresponding anisoles (cf. above) and for the well-known fact that the dissociation constants in aqueous or alcoholic solution of *m*- and *p*-methoxybenzoic acid and *m*-methoxycinnamic

TABLE 4.

Substance in hexane	Phenol				Anisole			
	<i>B</i> -band		<i>K</i> -band		<i>B</i> -band		<i>K</i> -band	
	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$
<i>m</i> -HO·C <sub>6</sub> H <sub>4</sub> ·CHO .....	3050	2700	2480	12,000	3050	3000	2488	10,000
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Ph·OH .....	—	—	2558	25,000	—	—	2596	27,000

acid are greater than those of the corresponding hydroxy-derivatives (Branch and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 2568; Dippy and Page, *J.*, 1938, 357). Obviously, solvation cannot always be neglected in discussions of the relative electronic effects of substituents on the strength of acids and other properties.

An interpretation of the influence of substituents on the position and intensity of the absorption bands of phenol is not relevant to the problem under discussion. It would require a consideration of other related systems and will be given elsewhere.

If not otherwise stated, all reported data are new determinations in ethyl alcoholic solution carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high-tension spark being employed as the source of light. A drop of concentrated hydrochloric acid was added to the solutions of all nitrophenols to inhibit dissociation.

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