715. *Effect of Methylation on the Light Absorption of Phenols. Part II.* Monophenylazophenols.*

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The spectra of monophenylazophenols and of the corresponding nitrophenol derivatives are reported and compared with those of their methyl ethers. It is confirmed that the normal effect of methylation (in absence of hydrogen-bond formation and steric effects) is a displacement of the *B*- and *K*-bands to longer wave-lengths. The generally observed displacements to shorter wave-lengths may be due to a reversal of the effect of hydrogen-bond formation and also, in phenols substituted in the *ortho*-position, to reduced conjugation caused by intramolecular steric effects. The electronic spectra can serve as a test for the presence of an internal hydrogen bond in phenolic substances. The investigated *o*-hydroxyazo-compounds (I, III, IV) exist in solution as true phenols.

Recently we reported an investigation of the effect of methylation on the absorption bands of phenols (Part I *). Whereas the normal effect of methylation (observed in hexane solution) is a displacement of the *B*- and *K*-bands to longer wave-lengths, in agreement with the greater electron-repelling power of the methyl group, displacements to shorter wave-lengths are generally observed. This is due partly to a reversal of the effect of hydrogen-bond formation involving the hydroxyl group (Morton and Stubbs, *J.*, 1940, 1347), and partly to a reduction of conjugation resulting from a repulsive interaction between the methoxyl group and substituents in the *ortho*-position.

We have extended this investigation to monophenylazophenols of the benzene series. In order to eliminate any difficulty arising from the hitherto uncertain structure of these

* Part I, *J.*, 1952, 2310.

substances, the spectra of the corresponding nitrophenols and their methyl ethers have been compared.

The data for the *B*- and *K*-bands of 4-methyl-2-phenylazophenol (I), *p*-phenylazophenol (II), and 4-phenylazoresorcinol (III), as well as of 2- and 4-nitrophenol (VI and VII), 4-nitroresorcinol (VIII), and their methyl ethers, in alcoholic solution, are listed in Table 1, together with those of the azo-compounds in hexane and chloroform solution (for method used, see Part I, *loc. cit.*).

TABLE 1.

			Phenol		Methyl ether	
Compound	Solvent	Band	λ, max.	$10^3\varepsilon$, max.	λ, max.	$10^3\varepsilon$, max.
I	C_6H_{14}	*B*	3935	9·8	3590	9·0
		K	3230	25·0	3090	13·5
	$CHCl_3$	*B*	3940	9·0	3615	8·5
		K	3240	24·0	3120	12·5
	EtOH	*B*	3935	9·6	3600	8·4
		K	3235	25·0	3110	12·5
II	C_6H_{14}	*K*	3365	28·5	3380	24·7 †
	$CHCl_3$	*K*	3480	28·5	—	—
	EtOH	*K*	3510	29·0	3415	24·0 †
III	C_6H_{14}	*K*	3680	23·0	—	—
	$CHCl_3$	*K*	3765	26·0	—	—
	EtOH	*K*	3800	26·0	—	—
IV	C_6H_{14}	*K*	3765	23·0	3590	17·0
	$CHCl_3$	*K*	3740	24·0	3625	19·0
	EtOH	*K*	3745	25·0	3617	19·0
V	C_6H_{14}	*K*	3565	23·0	3590	17·0
	$CHCl_3$	*K*	3690	23·0	3625	19·0
	EtOH	*K*	3720	24·0	3617	19·0
VI	,,	*B*	3435	3·6 *	3172	2·85 *
		K	2730	6·6	2585	3·45
VII	,,	*K*	3140	13·0 *	3050	13·0 *
VIII	,,	*K*	3450	14·0	—	—
IX	,,	*K*	3345	10·5	3225	8·0
X	,,	*K*	3295	9·5	3225	8·0

(I) = 4-Methyl-2-phenylazophenol. (VI) = *o*-Nitrophenol.
(II) = *p*-Phenylazophenol. (VII) = *p*- ,,
(III) = 4-Phenylazoresorcinol. (VIII) = 4-Nitroresorcinol.
(IV) = 4- ,, 1-methyl ether. (IX) = 4- ,, 1-methyl ether.
(V) = 4- ,, 3- ,, (X) = 4- ,, 3- ,,

* Part I. † Burawoy, *J.*, 1937, 1865.

Analysis of Spectra.—The spectrum of azobenzene in hexane (Burawoy, *J.*, 1937, 1865) shows in addition to the characteristic low-intensity *R*-band of the azo-group (λ 4480 Å; ε 425) a *K*-band of high intensity (λ 3130 Å; ε 20,000) due to an electronic transition along the conjugated system Ph·N=NPh (Fig. 1). The *B*(enzene)-band is not observed, being masked by the *K*-band. Similarly, nitrobenzene in alcohol exhibits the *K*-band (λ 2590 Å; ε 9500) associated with the conjugated system O=NO·Ph (Fig. 2), in addition to a broad inflexion of low intensity (cf. Scheibe, *Ber.*, 1926, **59**, 2622).

Examination of the spectra of the monophenylazophenols (I—III) in hexane (Fig. 1) and the nitrophenols (VI—VIII) in alcohol (Fig. 2) reveals that the *K*-band is displaced appreciably to longer wave-lengths by a terminal (*p*-)hydroxyl group, whereas the effect of a hydroxyl group in the branching *ortho*-position is only slight (cf. Burawoy, *Ber.*, 1930, **63**, 3155; *J.*, 1937, 1865; 1939, 1177).

4-Methyl-2-phenylazophenol (I) and *o*-nitrophenol (VI) also show the *B*-band of lower intensity at longer wave-lengths which in the spectra of *p*-phenylazophenol (II), 4-phenylazoresorcinol (III), and the corresponding nitrophenols (VII and VIII) is again masked by the *K*-band of higher intensity. Its presence in the spectrum of (III) in a position similar to that observed for (I) is clearly indicated by a considerable extension of the *K*-band to longer wave-lengths. Thus, in contrast to the *K*-bands the (masked) *B*-bands of azo-

benzene and nitrobenzene are displaced to considerably longer wave-lengths by a hydroxyl group in the *ortho*-position and not at all by a hydroxyl group in the *para*-position.

The *R*-band of the azo-group is also observed in the spectrum of *p*-phenylazophenol in hexane solution (λ 4410 Å; ε 780), but is completely masked by the *B*-band in the spectra of 4-methyl-2-phenylazophenol and 4-phenylazoresorcinol.

Effect of Methylation on B- and K-*Bands.*—Methylation of a hydroxyl group in the *para*-position to the azo-group in (II), (III), and (V) is responsible in hexane for a slight shift of the *K*-band to longer, but in chloroform and alcohol to shorter, wave-lengths (<100 Å) and for a slight change of intensity (Figs. 3—8). Obviously, the position of the *K*-bands is much more dependent on the solvent in the spectra of the phenols than in those of their methyl ethers. This lends additional support to the view that the normal effect of methylation (in hexane) is a displacement to longer wave-lengths and that the observed shifts to shorter wave-lengths are due to a reversal of the bathochromic effect of hydrogen bond formation involving the solvent (solvation). The corresponding nitrophenols (VII), (VIII), and (X) and their methyl ethers in alcoholic solution show analogous spectral relations (Figs. 4, 6, 8).

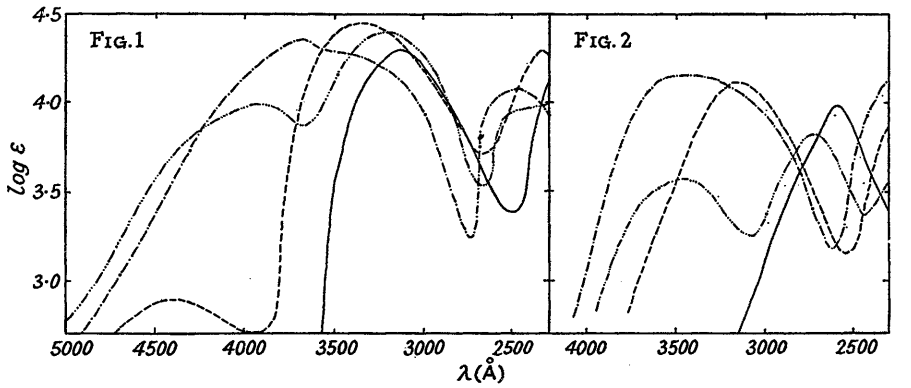


FIG. 1.

——— *Azobenzene.*
— — — 4-*Phenylazophenol.*
— · · · — 4-*Methyl-2-phenylazophenol.*
— · — · 4-*Phenylazoresorcinol in hexane.*

FIG. 2.

——— *Nitrobenzene.*
— — — 4-*Nitrophenol.*
— · · · — 2-*Nitrophenol.*
— · — · 4-*Nitroresorcinol in alcohol.*

On the other hand, methylation of a hydroxyl group in the *ortho*-position to the azo-group in (I), (III), and (IV) results in a more considerable displacement of the *K*-bands to shorter wave-lengths in all three solvents (100—200 Å). The effect of solvents on the position of the bands of both the phenols and their methyl ethers is very similar. Again, analogous effects are observed for the corresponding nitrophenol derivatives (VI), (VIII), and (IX) in alcoholic solution (Figs. 9—14). Two factors appear to contribute to these spectral changes.

(i) A reversal of the bathochromic effect of the internal hydrogen bond, known to be present in these substances (cf. Hendricks, Wulf, Hilbert, and Liddel, *J. Amer. Chem. Soc.*, 1936, **58**, 1991; Burawoy and Markowitsch-Burawoy, *J.*, 1936, 36). This contribution is comparatively small. Thus, the methylation of salicylaldehyde displaces the *K*-band in hexane and alcohol by 85 and 20 Å respectively to shorter wave-lengths, the intensity being also only slightly changed (cf. XI, Table 2). We have ascertained that this effect is not associated with the presence in itself of a hydroxyl group in the *ortho*-position. As already noted by Friedel, Orchin, and Reggel (*ibid.*, 1948, **70**, 199), the displacement of the *K*-band in hexane solution of 2-hydroxydiphenyl, which does not contain an internal hydrogen bond, is normal, *i.e.*, to longer wave-lengths on methylation (cf. XII, Table 2). Undoubtedly, a comparison of the spectra of a phenol and its methyl ether in hexane provides a method for the detection of an internal hydrogen bond.

(ii) A steric repulsion between the nitro-group or azo-group and the oxygen atom of

the methoxyl group in the *ortho*-position, which accounts for the considerably greater displacements to shorter wave-lengths of the *K*-bands on methylation of the 4-nitro- and 4-phenylazoresorcinols and their 1-methyl ethers as well as of *o*-nitrophenol and 4-methyl-

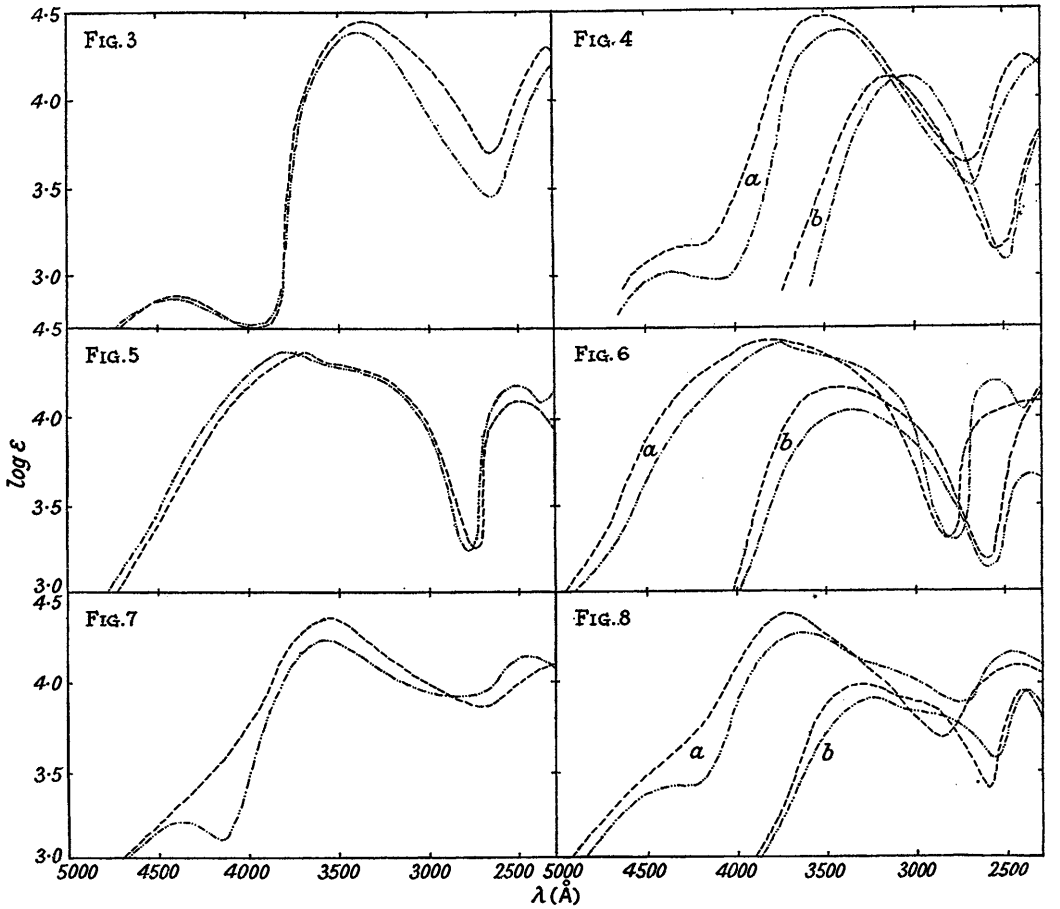


FIG. 3.

— — — 4-*Phenylazophenol.*
— · — 4-*Phenylazoanisole in hexane.*

FIG. 4.

a — — — 4-*Phenylazophenol.*
a — · — 4-*Phenylazoanisole.*
b — — — 4-*Nitrophenol.*
b — · — 4-*Nitroanisole in alcohol.*

FIG. 5.

— — — 4-*Phenylazoresorcinol.*
— · — 4-*Phenylazoresorcinol* 1-*methyl ether in hexane.*

FIG. 6.

a — — — 4-*Phenylazoresorcinol.*
a — · — 4-*Phenylazoresorcinol* 1-*methyl ether.*
b — — — 4-*Nitroresorcinol.*
b — · — 4-*Nitroresorcinol* 1-*methyl ether in alcohol.*

FIG. 7.

— — — 4-*Phenylazoresorcinol* 3-*methyl ether.*
— · — 4-*Phenylazoresorcinol dimethyl ether in hexane.*

FIG. 8.

a — — — 4-*Phenylazoresorcinol* 3-*methyl ether.*
a — · — 4-*Phenylazoresorcinol dimethyl ether.*
b — — — 4-*Nitroresorcinol* 3-*methyl ether.*
b — · — 4-*Nitroresorcinol dimethyl ether in alcohol.*

2-phenylazophenol. The resulting reduction of conjugation of these groups is clearly shown by the intensities of the *K*-bands in the spectra of *o*-nitroanisole and 4-methyl-2-phenylazoanisole (ε 3450 and 13,500, respectively) which are considerably lower than those

TABLE 2.

Compound	Solvent	Band	Phenol λ, max.	Phenol $10^3\varepsilon$, max.	Methyl ether λ, max.	Methyl ether $10^3\varepsilon$, max.
(XI)	C_6H_{14} †	*B*	3285	3·23	3100	5·62
		K	2550	10·0	2465	12·0
	EtOH †	*B*	3250	3·0	3195	4·26
			* (3244	4·35	3210	4·55)
		K	2550	10·0	2530	11·7
			* (2540	12·5	2528	10·5)
(XII)	C_6H_{14}	*B*	2825	5·75	2835	6·2
		K	2442	12·5	2460	15·5
	EtOH	*B*	2880	5·5	2850	5·50
		K	2470	13·5	2464	13·0

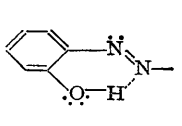
* Part I. † Morton and Stubbs, *loc. cit.*

observed in the spectra not only of the corresponding phenols, but also of nitrobenzene and azobenzene (ε 9500 and 20,000, respectively).

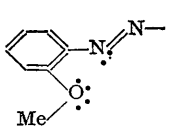
The effect of methylation on the *B*-bands is similar. A moderate shift to shorter wave-lengths of the *B*-band of salicylaldehyde is observed in both hexane and alcohol (185 and 55 Å, respectively), whereas the *B*-band of 2-hydroxydiphenyl, containing no hydrogen bond, undergoes a slight displacement in hexane to longer wave-lengths and in alcohol in the opposite direction (Table 2). Again, the *B*-bands in the spectra of *o*-nitrophenol and 4-methyl-2-phenylazophenol (in all solvents) are much more strongly displaced to shorter wave-lengths (270—340 Å). This change is also greater than that observed for the *K*-bands. The reduction of conjugation of the methoxyl group in *o*-nitroanisole and 4-methyl-2-phenylazoanisole results in a reversal of the considerable bathochromic effect of a hydroxyl group in the *ortho*-position on the *B*-bands (cf. above).

This appreciable displacement of the *B*-bands to shorter wave-lengths is also responsible for (*a*) the absence in the spectra of the 3-methyl ether and the dimethyl ether of 4-phenylazoresorcinol of the extension to longer wave-lengths of the *K*-bands observed in the spectra of 4-phenylazoresorcinol and its 1-methyl ether due to superposition by the *B*-band (cf. Figs. 7, 8, 11—14), and (*b*) the appearance of the low-intensity *R*-band characteristic of the azo-group in the spectra of 4-methyl-2-phenylazoanisole and 4-phenylazoresorcinol dimethyl ether which, being masked by the *B*-band in the spectra of the corresponding phenols, now becomes evident (cf. Figs. 7—10, 13, 14).

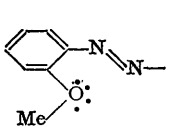
The steric interaction of the methoxyl group with an azo- or nitro-group in the *ortho*-position may be accounted for as follows. In *o*-phenylazophenol (XIII), *o*-nitrophenol, and salicylaldehyde the orbitals of the unshared electrons of the oxygen atom of the hydroxyl group will extend (mainly) to the outside of the six-membered ring formed, as illustrated for (XIII). Their steric repulsive interaction with the unshared electrons of the nitrogen atom of the azo-group (also extending outwards), or the electrons of the N=O and C–H linkages respectively, will be at a minimum. On the other hand, for steric reasons the most stable configurations of the methyl ethers are probably as shown in (XIV)—(XVI), in which the orbitals of the oxygen atom of the methoxyl group extend inwards and are involved in appreciable steric repulsion with the unshared electrons of the nitrogen atom in (XIV*a*) or the electrons of the N=N or N=O linkage in (XIV*b*) and (XV) respectively, whereas in *o*-methoxybenzaldehyde (XVI) repulsion with the C–H linkage will be too small to allow unambiguous spectroscopic detection. Finally, the most stable configurations of both 2-hydroxydiphenyl and its methyl ether being undoubtedly similar, methylation is not responsible for an (enhanced) steric effect, in agreement with the negligible displacements observed for both the *B*- and *K*-bands.



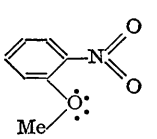
(XIII)



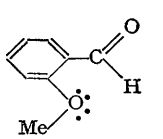
(XIV*a*)



(XIV*b*)



(XV)



(XVI)

Structure of o-*Hydroxyazobenzenes.*—Numerous investigations have been carried out to elucidate the structure of *o*-hydroxyazo-compounds which may be true phenols or *o*-quinone phenylhydrazones. Burawoy and Markowitsch (*Annalen*, 1933, **504**, 180), having un-

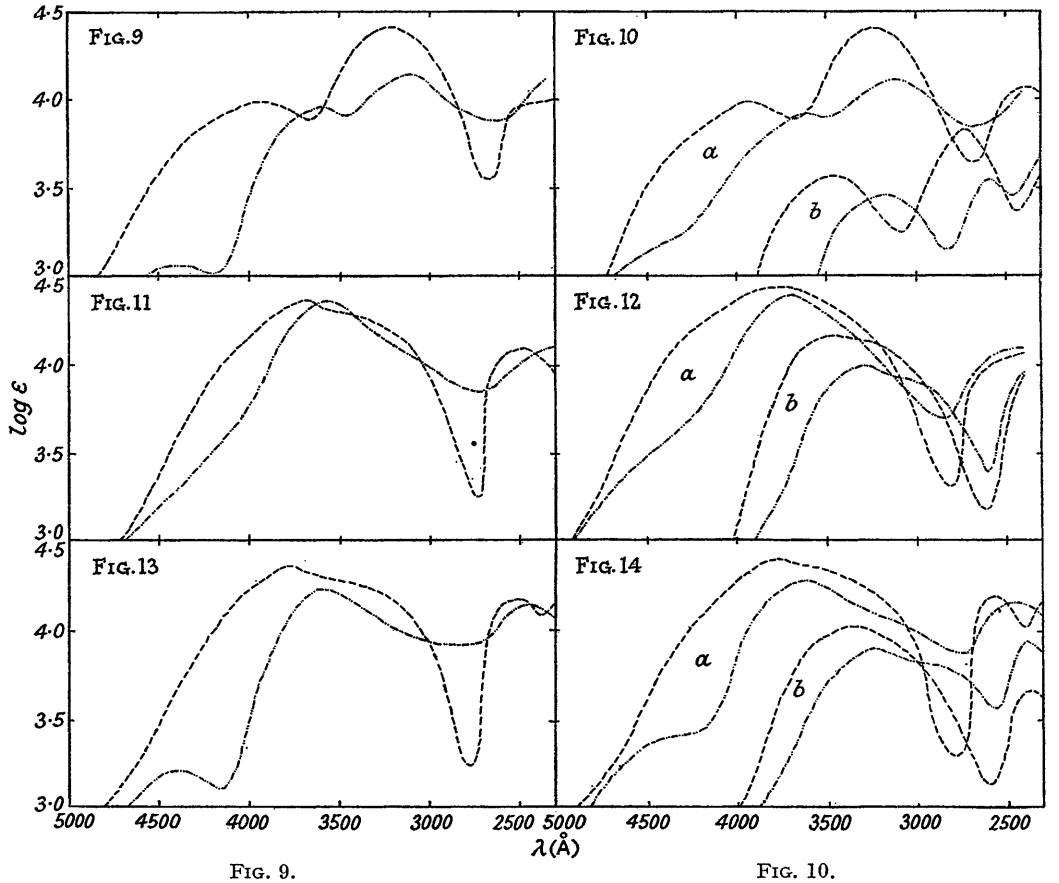


FIG. 9.

——— 4-*Methyl-2-phenylazophenol.*
— · · — 4-*Methyl-2-phenylazoanisole in hexane.*

FIG. 10.

a ——— 4-*Methyl-2-phenylazophenol.*
a — · · — 4-*Methyl-2-phenylazoanisole.*
b ——— 2-*Nitrophenol.*
b — · · — 2-*Nitroanisole in alcohol.*

FIG. 11.

——— 4-*Phenylazoresorcinol.*
— · · — 4-*Phenylazoresorcinol* 3-*methyl ether in hexane.*

FIG. 12.

a ——— 4-*Phenylazoresorcinol.*
a — · · — 4-*Phenylazoresorcinol* 3-*methyl ether.*
b ——— 4-*Nitroresorcinol.*
b — · · — 4-*Nitroresorcinol* 3-*methyl ether in alcohol.*

FIG. 13.

——— 4-*Phenylazoresorcinol* 1-*methyl ether.*
— · · — 4-*Phenylazoresorcinol dimethyl ether in hexane.*

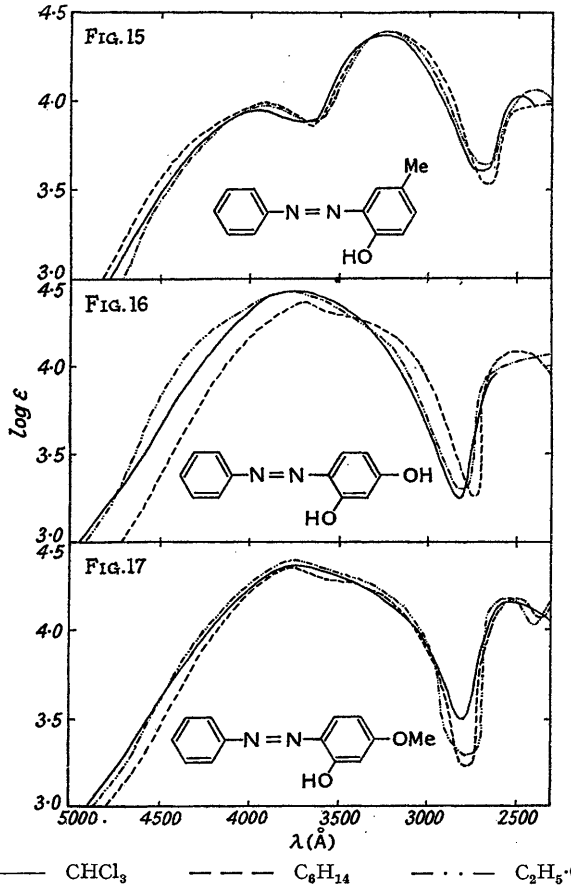
FIG. 14.

a ——— 4-*Phenylazoresorcinol* 1-*methyl ether.*
a — · · — 4-*Phenylazoresorcinol dimethyl ether.*
b ——— 4-*Nitroresorcinol* 1-*methyl ether.*
b — · · — 4-*Nitroresorcinol dimethyl ether in alcohol.*

ambiguously shown that 1-phenylazo-2-naphthol and 2-phenylazo-1-naphthol are present in solution as β-naphthaquinone phenylhydrazones, observed that the spectra of *o*-phenylazophenol and its methyl ether show differences which are considerably greater than could be expected at that time for true phenols. It was concluded that *o*-phenylazophenol also exists in solution as *o*-benzoquinone phenylhydrazone. Kuhn and Bär (*ibid.*, 1935, **516**, 73) questioned this interpretation, believing that the band of lower intensity at longer

wave-lengths in the spectrum of this substance might indicate the existence of an equilibrium. Burawoy (*ibid.*, 1936, **521**, 298) maintained the original view, pointing out that this is a *B*(enzene)-band also observed in *o*-benzoquinone, and that the very similar spectra of *o*-phenylazophenol in different solvents gave no experimental support for the possible existence of such an equilibrium.

The realisation that methylation may cause appreciable spectral changes due to steric repulsive interaction and a reversal of the effect of hydrogen-bonding necessitates a reconsideration of this problem, which has been one of the objects of this investigation. The similar changes undergone by the *B*- and *K*-bands in the spectra of azobenzene and



nitrobenzene on introduction of a hydroxyl group in the *ortho*-position and on its methylation show that the examined *o*-hydroxyazo-compounds exist in solution as true phenols. The spectral changes observed on methylation are not due to a qualitative change of structure and, as already pointed out by Burawoy and Markowitsch-Burawoy (*J.*, 1936, 36), cannot be reconciled with an interpretation of the internal hydrogen bond present by resonance hybrids involving both the azo- and the phenol structures (for similar conclusions reached more recently with regard to the related problems of the structure of the porphyrins and tropolones, see Erdman and Corwin, *J. Amer. Chem. Soc.*, 1946, **68**, 1886; Cook, Gibb, Raphael, and Somerville, *J.*, 1951, 508). Moreover, the very small variations of the spectra of (I), (III), and (IV) in different solvents (Figs. 15—17) do not give any experimental indication of tautomeric equilibria, the existence of which in more complicated *o*-hydroxyazo-compounds will, however, be shown elsewhere (cf. Burawoy, Salem, and Thompson, *Chem. and Ind.*, 1952, 410).

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