935. *The Nature of the Internal Hydrogen Bond. Part I. Tautomerism of 1-Arylazo-2-naphthols.*

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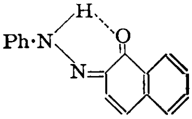
The spectra of 1-phenylazo-2-naphthol and its derivatives in various solvents have been examined. The solutions are shown to contain equilibria of the phenylhydrazone and azo-tautomers, and the effect of substituents and solvents on these equilibria is discussed. Formulation of substances containing an internal hydrogen bond as resonance hybrids or by means of any other structure based on the valency conception of non-localised bonds is excluded—these bonds are of an essentially electrostatic nature. For the first time the existence of two molecules of almost identical energy and atomic arrangement is unambiguously established. This emphasises the highly speculative character of the numerous interpretations of structures based on the valency conception of non-localised bonds.

Numerous investigations have been carried out to elucidate the structure of *o*-hydroxyazo-compounds which may exist as true azo-compounds or as *o*-quinone phenylhydrazones. Burawoy and Markowitsch (*Annalen*, 1933, **503**, 180; 1934, **504**, 71; 1933, **509**, 60) showed that the properties discussed in the earlier literature did not allow unambiguous conclusions. However, investigation of the electronic spectra established that " 1-phenylazo-2-naphthol " and " 2-phenylazo-1-naphthol " exist in solution as 1 : 2-naphthaquinone phenylhydrazones (cf. I). Their spectra are very different from those of the corresponding *O*-methyl ethers (cf. II), whereas the spectrum of (I) is almost identical with that of its *N*-phenyl derivative (III) (cf. also Kuhn and Bär, *Annalen*, 1935, **516**, 143).



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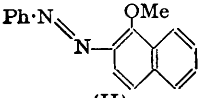

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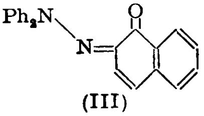


(III)

The presence of an internal hydrogen bond in *o*-hydroxyazo-compounds, suggested by their low degree of association in organic solvents when compared with *p*-hydroxyazo-compounds (Auwers and Orton, *Z. physikal. Chem.*, 1896, **21**, 355), and their ability to form complex salts (Mason, *J. Soc. Dyers and Col.*, 1932, **48**, 293), has been established by investigatons of their parachors, densities, and surface tensions (Burawoy and Markowitsch-Burawoy, *J.*, 1936, 36) and their infra-red spectra (Hendricks, Wulf, Hilbert, and Liddell, *J. Amer. Chem. Soc.*, 1936, **58**, 1991).

Sidgwick (*Ann. Reports*, 1934, **31**, 40) suggested that, since they have never been observed to exhibit tautomerism, substances containing internal hydrogen bonds should be represented as resonance hybrids, *i.e.*, should contain a non-localised bond. This logical application of the conception of resonance among several valence-bond structures has been generally accepted. Thus, it has been repeatedly claimed that a distinction between the azo- or phenylhydrazone structures of *o*-hydroxyazo-compounds is not justified (Hendricks *et al.*, *loc. cit.*; Shingu, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1938, **35**, 78; Fierz-David, Blangey, and Streif, *Helv. Chim. Acta*, 1946, **29**, 1718, where other references are given).

On the other hand, Burawoy and Markowitsch-Burawoy (*loc. cit.*) pointed out that this view cannot be reconciled with the normally small effect of an internal hydrogen bond on the ultra-violet and visible spectra, although these are known to be very sensitive to changes in the electronic structure of a molecule. Thus, the spectra of salicylaldehyde and its methyl ether or 2-phenylazo-1-naphthol (I) and its *N*-phenyl derivative (III) are very similar (cf. also Burawoy and Chamberlain, *J.*, 1952, 2310). Similar conclusions have recently been drawn from a comparison of the spectra of porphyrins and tropolones with those of their methyl ethers by Corwin and Erdman (*J. Amer. Chem. Soc.*, 1946, **68**, 1885) and by Cook, Gibb, Raphael, and Somerville (*J.*, 1951, 508) respectively. Koch

(*J.*, 1951, 514) also concluded that the infra-red spectra of tropolones disagreed with the interpretation of these substances as resonance hybrids.

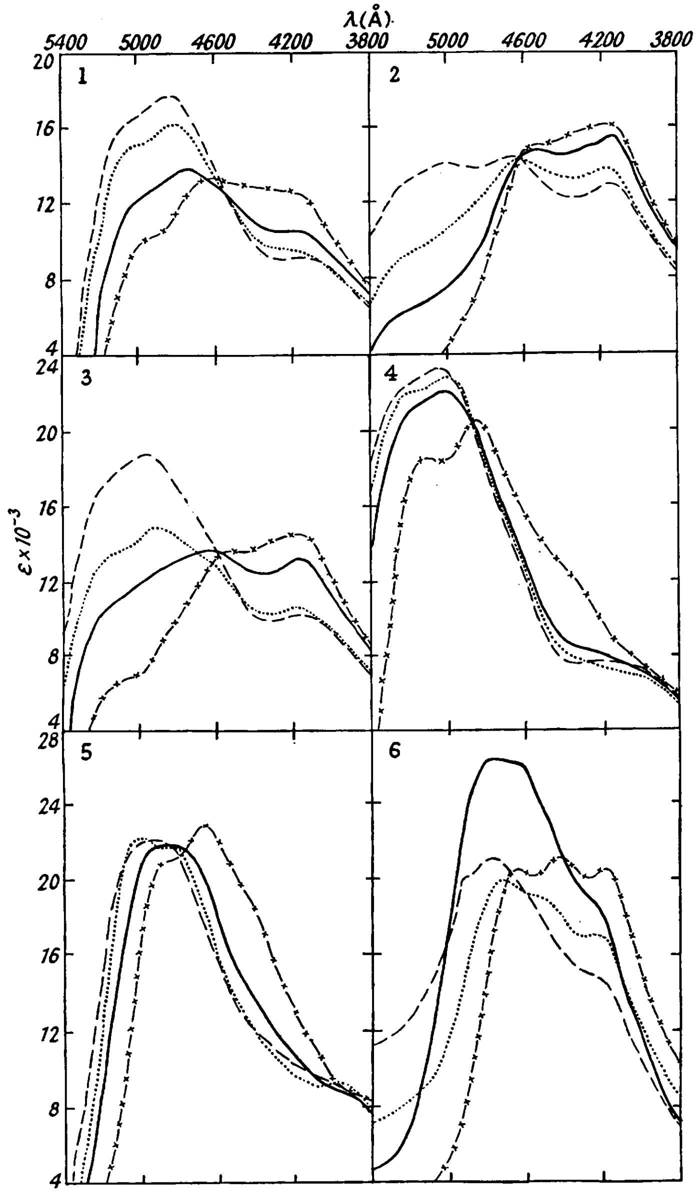
An unambiguous solution of the problem of the nature of the internal hydrogen bond would be obtained if tautomers of substances containing such bonds could be shown to exist. Burawoy and Chamberlain (*J.*, 1952, 3734) recently found that *o*-hydroxyazo-compounds of the benzene series such as 2-phenylazophenol and 4-phenylazoresorcinol exist in solution as true azo-compounds, and that their spectra in various solvents were very similar, giving no indication of the presence of equilibria. Simultaneously, we observed that 1-*p*-hydroxyphenylazo-2-naphthol absorbs in ethyl alcohol at much shorter wave-lengths (4150 Å) than the quinonoid 1-phenylazo-2-naphthol (4750 Å), although a hydroxyl group as terminal group of an absorbing conjugated system is known to displace the absorption band (*K*-band) to longer wave-lengths; it was obviously present as true azo-compound. Recently, Fierz-David, Blangey, and Merian (*Helv. Chim. Acta*, 1951, **34**, 846) showed this to be the case also for 3-phenylazo-2-naphthol. The recognition that the structure of *o*-hydroxyazo-compounds can vary suggested that a systematic investigation of suitably chosen derivatives would permit a decision whether equilibria exist or not. We have, therefore, extended the earlier limited spectroscopic examinations to numerous derivatives of 1-phenylazo-2-naphthol and to various solvents, and have now established the existence of tautomeric equilibria in solution, varying considerably with the solvent and the nature of substituents in the phenyl group. We shall discuss the spectra of these substances in hexane, ethyl alcohol, chloroform, and 50% ethyl alcohol, hexane and water being found to contain the highest proportions of the azo- and phenylhydrazone tautomers respectively.

The spectrum of 1-phenylazo-2-naphthol in hexane shows an absorption region consisting of two coalescent bands at about 4200 and 4600 Å, whereas in ethyl alcohol, chloroform, and 50% ethyl alcohol the intensity of the former band is reduced and that of the latter (appearing now at slightly longer wave-length) increases (Fig. 1). Although a small solvent effect could be expected, the absorption curves almost pass through an isosbestic point characteristic of equilibria. It may be pointed out that the effect of solvents on the absorption bands of an individual substance consists of slight displacements and does not involve a fundamental change of general form of a spectrum. This has been already shown, *e.g.*, for the quinonoid "4-phenylazo-1-anthranol" (Shingu, *loc. cit.*) and for the phenolic hydroxyazo-compounds of the benzene series (Kuhn and Bär, *loc. cit.*; Burawoy and Chamberlain, *loc. cit.*, p. 3734). In the light of the following observations the two bands are held to correspond to the azo- and the phenylhydrazone tautomer respectively, the former being present in appreciable quantity only in hexane solution.

The spectra of 1-*p*-methoxy- (Fig. 2) and 1-*p*-hydroxy-phenylazo-2-naphthol in the four solvents show the other extreme, the phenylhydrazone tautomer being slightly preponderant only in dilute alcohol. Obviously, the introduction of the *p*-methoxy- or *p*-hydroxy-group has increased considerably the relative stability of the azo-tautomer. The spectra also illustrate the negligible effect of solvents on the position of the band of the azo-tautomer.

Burawoy and Chamberlain (*loc. cit.*, p. 2310) recently showed that two methyl groups in the *ortho*-position to a methoxy-group are responsible for intramolecular steric hindrance resulting in appreciable reduction of conjugation between the methoxy-group and the aromatic nucleus. We therefore prepared 1-(4-methoxy-3 : 5-dimethylphenylazo)-2-naphthol, expecting that the two methyl groups would reduce the effect of the methoxy-group and the difference in the stability of the tautomers and that this substance would show an intermediate behaviour. Indeed the opposing intensity changes of the two bands in the four solvents are more pronounced, and the long-wave band corresponding to the phenylhydrazone becomes preponderant already in chloroform solution (Fig. 3). The effect of the two methyl groups in absence of steric repulsive interaction is negligible. The spectral changes of 1-(4-hydroxy-3 : 5-dimethylphenylazo)-2-naphthol are almost identical with those observed for 1-*p*-hydroxy- and 1-*p*-methoxy-phenylazo-2-naphthol. The equilibrium of 1-*m*-methoxyphenylazo-2-naphthol, in contrast to its *para*-isomer, is similar to that of its parent substance, whereas 1-*o*-methoxyphenylazo-2-naphthol exists in all solvents almost exclusively as phenylhydrazone, its spectra indicating only slight variations of the equilibrium (Fig. 4). They also illustrate the negligible effect of solvents on the absorption of the phenylhydrazone tautomer, only hexane being responsible

FIG. 1, Ph. FIG. 2, *p*-MeO·C_6H_4. FIG. 3, 4 : 3 : 5 : 1-MeO·$C_6H_2Me_2$. FIG. 4, *o*-MeO·C_6H_4. FIG. 5, *o*-NO_2·C_6H_4. FIG. 6, *p*-NH_2·C_6H_4.



1-Arylazo-2-naphthols in — × — × — *hexane,* . . . . . *chloroform,* —— *ethyl alcohol, and* - - - - - 50% *ethyl alcohol.*

for a moderate displacement to shorter wave-lengths, as could be expected. Comparison of the spectra of the discussed substances in the same solvent confirms that the concentration of the phenylhydrazone tautomer increases in the order

p-MeO < 4-MeO- 3 : 5-Me_2 < H < m-MeO < o-MeO.

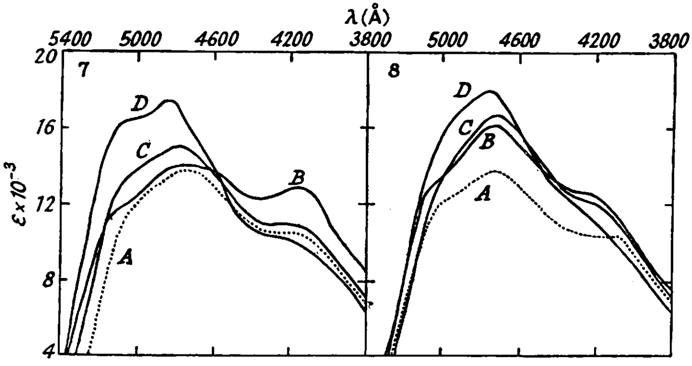
The presence of equilibria is also clearly observed for the three isomeric 1-tolylazo-2-naphthols and the 1-chlorophenylazo-2-naphthols. The concentration of the phenylhydrazone tautomers increases in the order of solvents, hexane < ethyl alcohol < chloroform < 50% ethyl alcohol, and of substituents, *p*-Me < *m*-Me $\sim$ H < *o*-Me and H $\lesssim$ *p*-Cl < *m*-Cl < *o*-Cl (cf. as examples Figs. 7 and 8 for the spectra in ethyl-alcoholic solution).

The three 1-nitrophenylazo-2-naphthols exist almost exclusively as phenylhydrazones, only the spectra of the *meta*-derivative giving a possible slight indication of the presence of an equilibrium. In spite of the introduction of the strongly polar nitro-group, the effect of solvents on the position of the phenylhydrazone band is small. As example, the spectra of the *o*-nitro-derivative are shown in Fig. 5.

The spectra of 1-*p*-aminophenylazo-2-naphthol (Fig. 6) are complicated by the appreciable effect of an amino-group and of solvents on the position and intensity of the absorption bands, particularly of that of the azo-tautomer. This is similar to the displacement of the *K*-band of azobenzene (3130 Å in hexane) to longer wave-lengths in *p*-aminoazobenzene (3620 Å in hexane) and the appreciable solvent effect on the band of the more polar substance (Burawoy, *Ber.*, 1930, **63**, 3170; *J.*, 1937, 1865). The observed band, undoubtedly, belongs to the azo-tautomer. The presence of an equilibrium is indicated by the appreciably lower intensity of this band in dilute alcohol compared with that in alcohol and, in particular, by the increasing intensity of an inflexion at about 5300 Å (belonging to the phenylhydrazone tautomer) in the order hexane < ethyl alcohol < chloroform < 50% ethyl alcohol. The concentration of the azo-tautomer is greater than in all other investigated 1-phenylazo-2-naphthol derivatives.

FIG. 7. *A*, Ph. *B*, *p*-C_6H_4Me. *C*, *m*-C_6H_4Me. *D*, *o*-C_6H_4Me.

FIG. 8. *A*, Ph. *B*, *p*-C_6H_4Cl. *C*, *m*-C_6H_4Cl. *D*, *o*-C_6H_4Cl.



1-*Arylazo*-2-*naphthols in ethyl alcohol.*

Effect of Substituents on the Equilibria.—A quantitative analysis of the equilibria is not possible, since the true maxima and intensities of the bands of the individual tautomers are unknown, and the observed data are to a varying degree modified by the overlap of the two absorbing systems. This is particularly the case for the absorption band of the azo-tautomer situated at shorter wave-lengths and accounts for its generally smaller intensity changes. As the intensity of the phenylhydrazone band increases, its short-wave slope and secondary absorption overlapping the azo-band reduce the simultaneous intensity decrease of the latter. In a few spectra the overlap of the absorption systems is responsible for an additional absorption maximum, which is however only apparent.

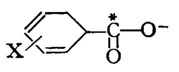
However, the values of the ratio $\varepsilon_{Ph}/\varepsilon_{Az}$ of the molecular extinction coefficients at the maxima of the observed two bands (sometimes estimated from broad inflexions) may give an approximate measure of the relative changes of the equilibrium caused by solvents and substituents. The values for the ethyl-alcoholic solutions of the 1-phenylazo-2-naphthol derivatives investigated are listed in the first line of Table 1. Since the phenylhydrazone band is less affected by the azo-band, an alternative and more satisfactory measure is the ratio of the extinction coefficients of this band in different solvents, the variations decreasing with the increasing relative stability of the phenylhydrazone. The second line shows the values of the ratios for ethyl alcohol and 50% ethyl alcohol.

The effect of substituents is similar to that known for other equilibria. For comparison, the dissociation constants of benzoic acids are listed in Table 1. Acid-strengthening groups increase also the phenylhydrazone concentration, as expected. Electron-attracting substituents will increase the positive charge at the C* atoms, which will be responsible for a greater stabilisation (accompanied by a change of polarity and shortening) of the more strongly polarisable C*–O⁻ and C*–NH linkages in the benzoate ion (IV) and the phenylhydrazone (V) respectively than of the C*–OH and C*–N:N linkages in the benzoic acid (VI) and the azo-tautomer (VII) respectively; both the dissociation constants of the benzoic acids and the phenylhydrazone concentrations will thus increase. A more detailed analysis would require the consideration of a second factor. The replacement of the charged O⁻ atom and the nitrogen atom of the (substituted) amino-group respectively in (IV) and (V) by the more strongly electron-attracting OH and N:N groups in (VI) and (VII) will increase the positive charge at the carbon atoms of the benzene nucleus, which will *in both cases* result in qualitatively similar stabilisations (changes of polarity and shortening) of the attached linkages. This effect is negligible for the C–H linkages, but will be greater and variable for the more strongly polarisable linkages C–X involving other substituents (cf. Burawoy, " Contribution à l'Étude de la Structure Moléculaire," Liège, 1947/48, p. 73).

TABLE 1.

	p-NH$_2$	p-HO	p-MeO	4-HO-3 : 5-Me$_2$	p-Me	4-MeO-3 : 5-Me$_2$	m-Me	H
a, $\epsilon_{Ph}/\epsilon_{Az}$, 1-arylazo-2-naphthol	0·17	0·40	0·45	0·46	1·08	1·02	1·37	1·31
b, $\epsilon_{Ph}^{EtOH}/\epsilon_{Ph}^{aq.\ EtOH}$, ,,	0·39	0·50	0·50	0·52	0·73	0·74	0·77	0·78
c, $\epsilon_{Ph}/\epsilon_{Az}$, 4-arylazo-1-naphthol	—	—	0·22	—	0·39	—	0·72	0·63
d, 10^5K, Ar·CO$_2$H	—	2·9	3·38	—	4·24	—	5·35	6·27

	m-MeO	p-Cl	o-Me	m-Cl	o-Cl	m-NO$_2$	o-MeO	p-NO$_2$	o-NO$_2$
a, $\epsilon_{Ph}/\epsilon_{Az}$. 1-arylazo-2-naphthol	1·41	1·26	1·71	—	—	>2·0	>2·0	>2·0	>2·0
b, $\epsilon_{Ph}^{EtOH}/\epsilon_{Ph}^{aq.\ EtOH}$, ,,	0·81	0·82	0·83	0·88	0·89	0·93	0·95	—	0·99
c, $\epsilon_{Ph}/\epsilon_{Az}$, 4-arylazo-1-naphthol	0·89	0·84	0·23	1·5	0·5	1·9	0·9	>2·0	>2·0
d, 10^5K, Ar·CO$_2$H	8·17	10·5	12·35	14·8	114·0	32·1	8·06	37·6	671·0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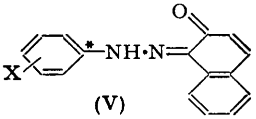
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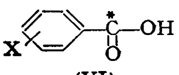
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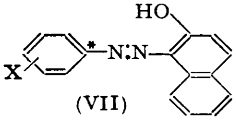

(VII)

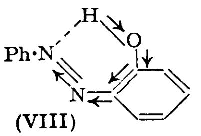
Following the discovery of the existence of a tautomeric equilibrium in solutions of 4-phenylazo-1-naphthol by Kuhn and Bär (*loc. cit.*), Shingu (*loc. cit.*) examined the spectra of numerous derivatives in ethyl alcohol. The values of the ratio $\varepsilon_{Ph}/\varepsilon_{Az}$ obtained or estimated by this author are shown in the third row of Table 1. As expected, the effect of substituents is similar in both series. It is, however, noteworthy that in the 4-phenylazo-1-naphthol series a methyl or chlorine substituent in the *o*-position decreases the phenylhydrazone concentration in ethyl-alcoholic solution, in contrast to the considerable increase observed in the 1-phenylazo-2-naphthol series and of the dissociation constants of the corresponding benzoic acids. The cause of these and other discrepancies involving *ortho*-substituents will be discussed elsewhere.

Effect of Solvents on the Equilibrium.—In Table 2 the intensities of the phenylhydrazone and azo-bands (or inflexions) at their approximate maxima 5050 and 4200 Å respectively and the values of the ratio $\varepsilon_{Az}/\varepsilon_{Ph}$ for the most sensitive 1-(4-methoxy-3 : 5-dimethylphenylazo)-2-naphthol in different solvents are listed. Comparison with the equilibrium constants C_{enol}/C_{keto} for keto-enol tautomers such as ethyl acetoacetate and acetylacetone as determined by Meyer (*Ber.*, 1912, **45**, 2843; cf. Table 2), shows that in both series the more polar ketonic structures increase in the same order of solvents. It appears that they are more strongly polarised and stabilised than the corresponding tautomers, approximately in line with the increasing dielectric constant of the solvent.

TABLE 2.

Solvent	Azo-compound ϵ_{Ph}^{5050}	ϵ_{Az}^{4200}	$\frac{\epsilon^{4200}}{\epsilon^{5050}}$	$CH_2Ac{\cdot}CO_2Et$ $\frac{C_{enol}}{C_{keto}}$	CH_2Ac_2 $\frac{C_{enol}}{C_{keto}}$
Water	—	—	—	0·004	0·24
50% AcOH	20,900	9,300	0·445	—	—
50% EtOH	18,500	10,300	0·556	—	—
AcOH	17,900	10,200	0·570	0·061	2·8
75% EtOH	16,500	11,300	0·684	—	—
$CHCl_3$	14,000	10,700	0·764	0·089	3·8
87·5% EtOH	15,100	12,000	0·795	—	—
$PhNO_2$	11,000	11,500	1·04	—	—
EtOH	11,600	13,100	1·13	0·15	5·3
Pyridine	11,100	12,800	1·15	—	—
C_6H_6	11,300	13,100	1·16	0·22	5·7
CCl_4	9,600	13,000	1·35	—	—
C_6H_{14}	6,900	14,600	2·12	0·9	12·0

Conclusions.—The existence of tautomeric equilibria in the 1-phenylazo-2-naphthol series excludes the interpretation of substances containing an internal hydrogen bond as "resonance hybrids" or any other structure based on the valency conception of non-localised bonds. Internal hydrogen bonds are essentially electrostatic, as is already generally accepted for intermolecular hydrogen bonds (cf. Davies, *Ann. Reports*, 1946, **43**, 5). This, of course, includes a polarisation of the molecule as, *e.g.*, indicated by arrows in (VIII). It is responsible for small displacements to longer wave-lengths of the *B*- and the *K*-bands of phenolic substances containing an internal hydrogen bond, such as salicylaldehyde and *o*-phenylazophenol (Morton and Stubbs, *J.*, 1940, 1347; Burawoy and Chamberlain, *locc. cit.*), the hydroxy-groups becoming more electron-repelling than the methoxy-groups in the methyl ethers.



(VIII)

The results of this investigation have wider implications. They show for the first time unambiguously that two molecules can exist which possess identical energies and atomic arrangements distinguished by only small changes of the bond-distances (<0·1 Å), although these conditions are generally accepted to be ideal for delocalisation of orbitals resulting in an increased stability. A weakness of this view has always been the inability to predict the interaction (resonance integral) of such structures which has been arbitrarily assumed always to occur. Our observations remove the justification for such an axiom and at least emphasise the highly speculative character of the numerous interpretations of structures based on the valency conception of non-localised bonds, which have already been shown to be in disagreement with numerous observations and 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.*, to changes of the repulsive interactions of electrons and nuclei (Burawoy, *Trans. Faraday Soc.*, 1944, **40**, 537; *Discus. Faraday Soc.*, Hydrocarbons, 1951, 104; *Chem. and Ind.*, 1944, 434; *op. cit.*, p. 73).

EXPERIMENTAL

Spectra were determined with a Hilger Uvispek Photoelectric Spectrophotometer. The concentrations used varied between 0·00025 and 0·000025M, Beer's law being valid within these limits. Numerous earlier determinations with a Hilger E3 quartz spectrograph fitted with a Spekker photometer showed that the spectral region below 3800 Å made no contribution to the elucidation of the problem under discussion, owing to a considerable overlap of band systems.

1-(4-*Hydroxy*-, dark purple needles (from aqueous ethyl alcohol), m. p. 209·5° (Found: N, 9·65. $C_{18}H_{16}O_2N_2$ requires N, 9·67%), and 1-(4-*methoxy*-3 : 5-*dimethylphenylazo*)-2-*naphthol*, dark red leaves (from ethyl alcohol), m. p. 128° (Found: N, 9·25. $C_{19}H_{18}O_2N_2$ requires N, 9·15%), are new.

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