296. *The Effect of Solvents on the Tautomeric Equilibria of 4-Arylazo-1-Naphthols and the* ortho-*Effect.*

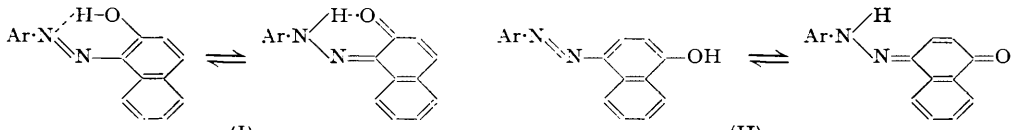
By A. Burawoy and A. R. Thompson.

The electronic spectra of 4-arylazo-1- and 1-arylazo-2-naphthols in various solvents have been determined. The differences in the effects of solvents and of *ortho*-substituents on the tautomeric equilibria observed in these two series are discussed. They originate mainly in the ability of both tautomers of the 4-arylazo-1-naphthols (in contrast to those of the 1-arylazo-2-naphthols) to form external hydrogen bonds with suitable solvents. The different strength of these bonds in the azo- and phenylhydrazone tautomers is shown to influence considerably the equilibrium constants. The inhibition of external hydrogen-bond formation by *ortho*-substituents in the phenylhydrazone tautomers is mainly responsible for their surprisingly small concentrations in solvents such as water, ethyl alcohol and acetic acid.

Investigation of the electronic spectra of 1-arylazo-2-naphthols has shown that they exist in solution as tautomeric equilibria (I) (Burawoy, Salem, and Thompson, *J.*, 1952, 4793). The phenylhydrazone concentration in all the solvents investigated increased in the order of substituents 4-MeO $<$ 4-Me $<$ 3-Me $\sim$ H $\sim$ 4-Cl $<$ 3-MeO $<$ 2-Me $<$ 3-Cl $<$ 2-Cl $<$ 2-MeO. It was noted that this was similar to the findings of Shingu (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1938, **35**, 78) for the tautomeric equilibria of the 1-arylazo-4-naphthols (II) in ethyl alcohol except that, in the latter series, *ortho*-substituents are responsible for unexpectedly small concentrations of the phenylhydrazone tautomer.

Burawoy and Chamberlain (*J.*, 1952, 2310), extending an earlier investigation by Morton and Stubbs (*J.*, 1940, 1347), found that, in absence of internal hydrogen bonding

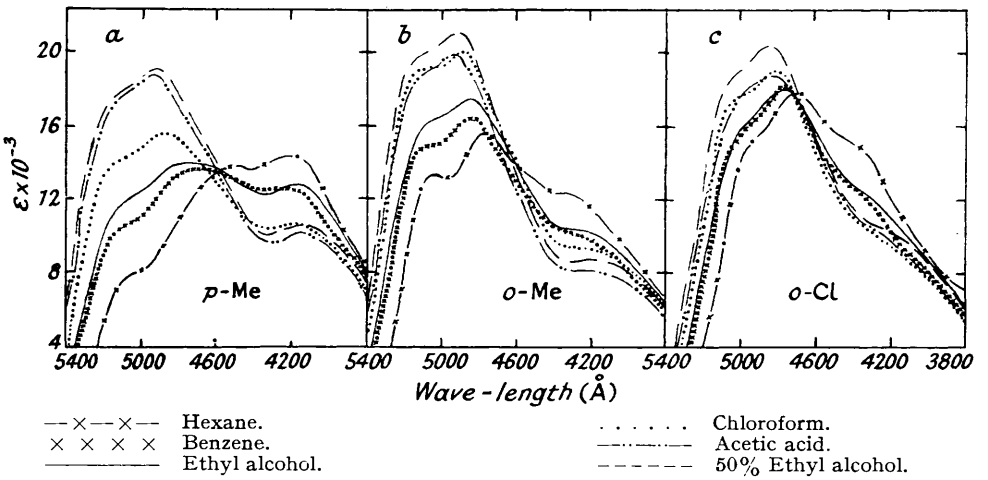
in the phenols and intramolecular steric effects in the methyl ethers, phenols absorb in hexane at shorter wave-lengths, but in ethyl alcohol and to a smaller degree in chloroform at longer wave-lengths, than the corresponding methyl ethers. This reversal of the normal effect of hydroxy- and methoxy-groups is due to the formation of hydrogen bonds by phenols with the latter solvents, the hydroxy-groups becoming more electron-repelling



(I) (II)

than the methoxy-groups in the methyl ethers. It was also pointed out that the same phenomenon would explain the fact that the dissociation constants of *m*- and *p*-methoxybenzoic and *m*-methoxycinnamic acid are higher than those of the corresponding hydroxy-derivatives in aqueous or alcoholic solution. Similarly, Bell and Bailey (*J.*, 1952, 1518), investigating the effect of substituents on the basicity of amines in chlorobenzene and

FIG. 1. *1-Arylazo-2-naphthols.*



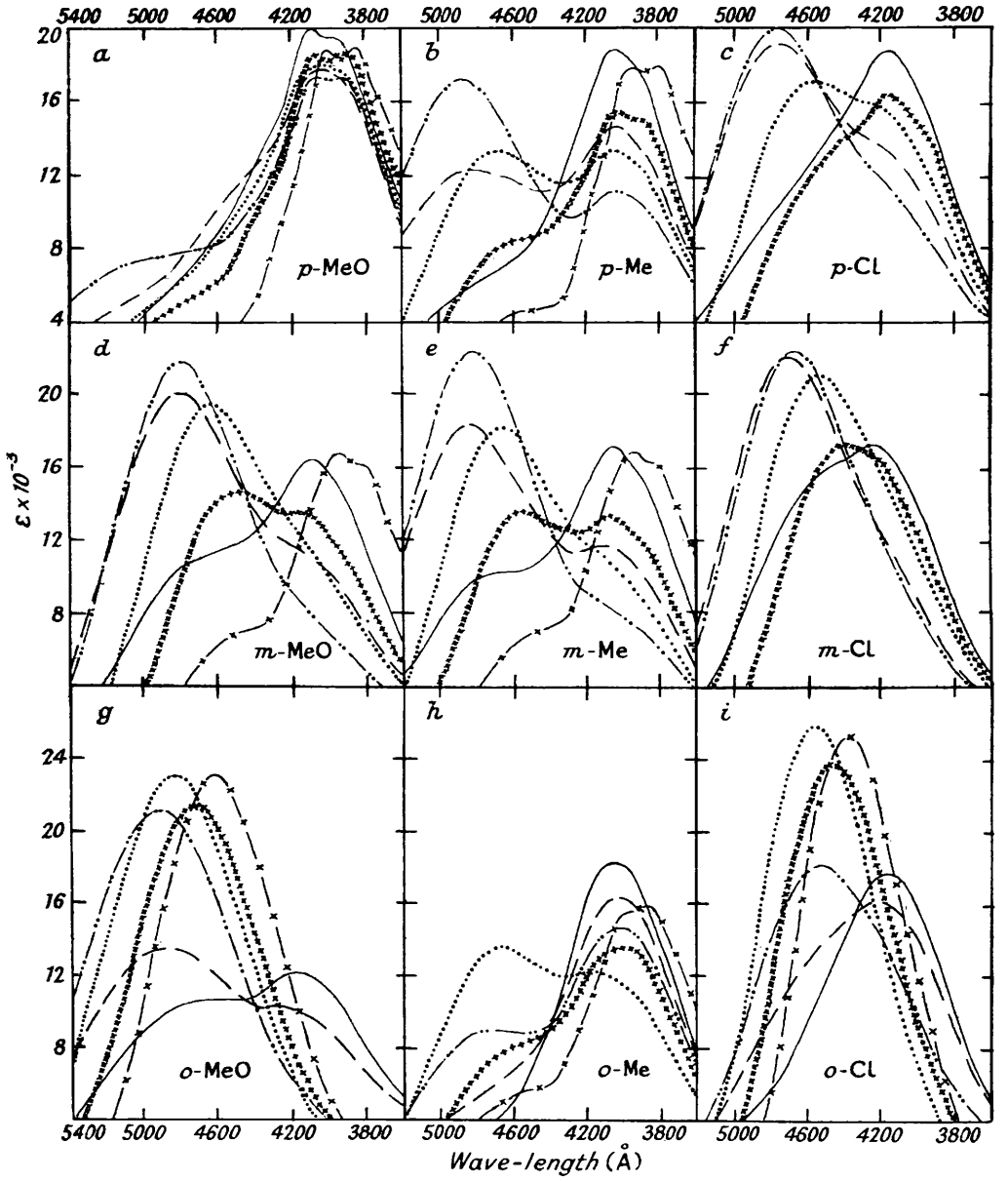
anisole, concluded that external hydrogen bonding is responsible for numerous anomalies of the dissociation constants observed in aqueous solution.

The effect of solvents on the tautomeric equilibria of 1-arylazo-2-naphthols is similar to that observed by Meyer (*Ber.*, 1912, **45**, 2843) on the keto-enol equilibria of ethyl acetoacetate and acetylacetone (Burawoy, Salem, and Thompson, *loc. cit.*). Since both tautomers in each of these systems are unable to form external hydrogen bonds, the concentration of the more polar ketonic structures increases in the order of solvents hexane < benzene ~ ethyl alcohol < chloroform < acetic acid < water, approximately in line with their increasing dielectric constant. It is important for the following discussion that this order is observed in all the 1-arylazo-2-naphthols investigated, including those substituted in the *ortho*-position. This is illustrated in Fig. 1 by the examples of 1-*p*-tolylazo-, 1-*o*-tolylazo-, and 1-*o*-chlorophenylazo-2-naphthol.

On the other hand, in the 4-arylazo-1-naphthol series the NH and the OH groups respectively of the tautomers are able to form hydrogen bonds with suitable solvents. We considered that the tautomers might be stabilised to a different degree by such bonds, and, in particular, that substituents in the *ortho*-position to the amino-group in the phenylhydrazone tautomers would inhibit sterically the formation of such bonds and be responsible for their observed anomalously low concentrations in ethyl alcohol. Investigation of the effect of solvents on the equilibria of 4-phenylazo-1-naphthol and its chloro-, methyl, and methoxy-derivatives confirms this view.

Figs. 2*a*—*f* show the spectra of the *meta*- and *para*-derivatives. The spectra of 4-phenylazo-1-naphthol itself are not reproduced, since they are almost identical with those of its *meta*-methyl derivative. The phenylhydrazone concentration increases in the order of

FIG. 2. 4-*Arylazo*-1-*naphthols*.



substituents 4-MeO < 4-Me < 4-Cl < H ~3-Me < 3-MeO < 3-Cl and in the order of solvents hexane < ethyl alcohol < benzene < chloroform ~50% ethyl alcohol < acetic acid. In contrast to the observations in the 1-arylazo-2-naphthol series, the phenylhydrazone concentration is considerably smaller in ethyl alcohol and 50% ethyl alcohol

than in benzene and acetic acid respectively. In the light of the following observations this is due to the formation of stronger hydrogen-bonds by the former solvents and the resulting greater stabilisation of the azo-tautomer, the hydrogen atom of the hydroxy-group forming stronger bonds than that of the NH group in the phenylhydrazone tautomer as expected.

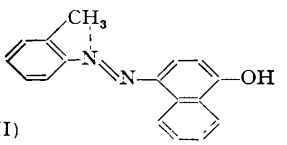
This effect is considerably enhanced by *ortho*-substituents, which sterically inhibit the formation of external hydrogen bonds in the phenylhydrazone tautomers. Both 4-*o*-chloro- and 4-*o*-methoxy-phenylazo-1-naphthol (Figs. 2*i* and *g*) exist almost exclusively as phenylhydrazones in hexane, benzene, and chloroform, and to a slightly smaller degree in acetic acid, whereas in ethyl alcohol and also in 50% ethyl alcohol which contains normally the highest phenylhydrazone concentration, a considerable amount of the azo-tautomer is present. It is estimated to be 50% in the aqueous-alcoholic solution of the *o*-methoxy-derivative and considerably more in the other three solutions. The surprisingly small increase of the phenylhydrazone concentration on addition of water to ethyl alcohol is due to the superposition of two strong, but opposing, effects : a relative increase of the stability of the azo-tautomer due to the formation of stronger hydrogen bonds with water, and a slightly greater one of the more polar phenylhydrazone tautomer due to the increased dielectric properties of this solvent.

The spectra also show that acetic acid contains a smaller phenylhydrazone concentration than chloroform, indicating that the former solvent forms stronger hydrogen bonds. The effect is similar to, but smaller than, that shown by ethyl alcohol and water (50% ethyl alcohol). The strength of the hydrogen bonds increases in the order of solvents chloroform < acetic acid < ethyl alcohol < water.

The rather small phenylhydrazone concentration of the *o*-substituted 4-phenylazo-1-naphthols which led to the present investigation is limited to solvents forming comparatively strong hydrogen bonds, such as water, ethyl alcohol, and acetic acid. In hexane, benzene, and chloroform it is in agreement with the observations made for all solvents in the 1-arylazo-2-naphthol series, *i.e.*, considerably greater in the *ortho*- than in the corresponding *para*- and *meta*-derivatives.

4-*o*-Tolylazo-1-naphthol (Fig. 2*h*) behaves similarly, but the concentration of the azo-tautomer is appreciably higher, resulting in a greater differentiation of the effect of solvents on the equilibrium. Again, the phenylhydrazone concentration is smallest in ethyl alcohol, no band corresponding to the phenylhydrazone tautomer being actually observed, and only slightly higher in 50% ethyl alcohol which is now similar to that in hexane. It increases in the order hexane < benzene < acetic acid < chloroform. The reversal of the effects of chloroform and acetic acid is even more pronounced than for the *o*-chloro- and *o*-methoxy-derivatives.

In contrast to the corresponding 1-arylazo-2-naphthol derivatives, 4-*o*-tolylazo-1-naphthol contains, not only in water and ethyl alcohol, but to a lesser degree also in hexane and benzene, a smaller phenylhydrazone concentration than its *meta*-isomer. This observation indicates the contribution of an alternative factor in addition to the steric inhibition of external hydrogen-bond formation in the phenylhydrazone tautomer. It is generally recognised that a different degree of intramolecular steric (repulsive or attractive) interaction involving *ortho*-substituents in the two entities forming an equilibrium can have an appreciable effect on equilibrium constants. The formation of a weak hydrogen bond (attraction) between the methyl group and the azo-group in the azo-tautomer of



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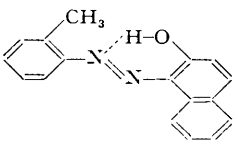


(IV)

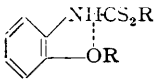
4-*o*-tolylazo-1-naphthol (III) might be responsible for its increased stability. This would be prevented in the azo-tautomer of the isomeric 1-*o*-tolylazo-2-naphthol by the presence of the much stronger hydrogen bond involving the hydroxy-group (IV). The absence of

this anomaly in the *o*-chloro- and *o*-methoxy-derivatives respectively would also be accounted for.

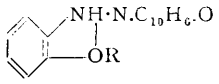
Our observations as regards the effect of solvents on the tautomeric equilibria of the *ortho*-substituted 4-arylazo-1-naphthols are analogous to those just reported by Russell (*J. Amer. Chem. Soc.*, 1952, **74**, 2654) for the keto–enol equilibria of cyanodeoxybenzoin (V) and α-2-furoyl-α-phenylacetonitrile (VI), the concentrations of the enolic tautomers increasing in the order of solvents hexane < water < ethyl alcohol. This is not surprising, since in both series the enolic (phenolic), but not the ketonic, tautomers are able to form external hydrogen bonds with suitable solvents. This results in a superposition of the stabilising effect of external hydrogen-bond formation in the enolic (phenolic) tautomers on the normal, probably non-stoicheiometric dielectric effect of the solvents.

NC·CHPh·COR ⇌ NC·CPh:CR·OH

(V; R = Ph)
(VI; R = 2-furoyl)



(VII)



(VIII)

After submission of this paper, Burrows and Hunter (*J.*, 1952, 4118) reported that *o*-alkoxyphenyl-thion- and -dithio-carbamic and *o*-bromophenyldithiocarbamic esters are not (appreciably) associated in benzene, in contrast to the *o*-methyl derivatives (and all *m*- and *p*-isomers). They, therefore, suggest that this may be mainly due to the formation of internal hydrogen bonds (cf., *e.g.*, VII), rather than to steric influences. It is possible that the presence of such bonds will somewhat stabilise the phenylhydrazone tautomers of 4-*o*-methoxy- and 4-*o*-chlorophenylazo-1-naphthol (cf., *e.g.*, VIII), but, since these substances are, even in absence of such bonds, expected to exist almost exclusively as phenylhydrazones in solvents such as hexane and benzene, our observations cannot afford any evidence for this effect. We can also not exclude a partial contribution of this factor to the inhibition of external hydrogen-bond formation by these phenylhydrazones, but the analogous behaviour of 4-*o*-tolylazo-1-naphthol shows that steric influences are mainly responsible in this series.

Our investigation shows that the ability of molecules to form external hydrogen bonds with suitable solvents is an important factor determining equilibrium constants and, in particular, contributing to the qualitative anomalies often observed to be caused by *ortho*-substituents.

Experimental.—Spectra were determined with a Hilger Uvispek Photoelectric Spectrophotometer. The concentrations used varied between 0·000025M and 0·000125M, Beer's law being valid within these limits and the experimental error of this method. The light absorption of 4-*p*- and 4-*m*-chlorophenylazo-1-naphthol in hexane could not be measured owing to the low solubilities.

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