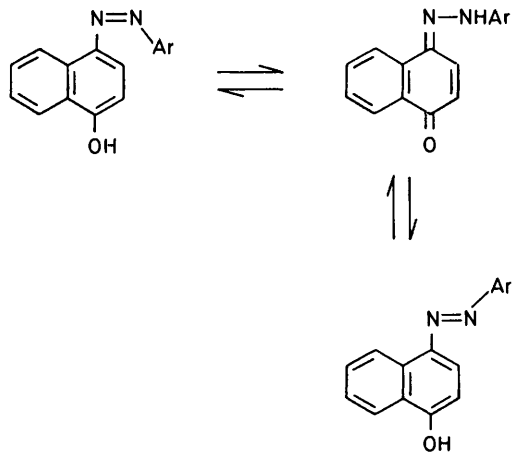
Protonation Equilibria of 1-Arylazo-4-naphthols and 1-Arylazo-4-Methoxynaphthalenes

By **Lorenzo Abate, Maria Luisa Longo, Emanuele Maccarone,* and Michele Torre,** Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

The spectroscopic behaviour of substituted 1-arylazo-4-naphthols and 1-arylazo-4-methoxynaphthalenes has been investigated in a solvent system consisting of 20% v/v ethanol and 80% v/v sulphuric acid–water in order to measure the protonation equilibrium constants. Some naphthols (I; X = H, *o*-OCH_3, *p*-OCH_3, *o*-CH_3, *p*-Cl) and all the methoxynaphthalenes (II) show two absorption bands due to the free base and the conjugate acid, with a characteristic isosbestic point. For these compounds, pK_{BH^+} values have been calculated using Jaffé's acidity function. Other naphthols (I; X = *m*-OCH_3, *m*-CH_3, *p*-CH_3, *o*-Cl, *m*-Cl) show a single absorption band which shifts on changing the acidity of the medium. The lack of an isosbestic point has been ascribed to the overlap of the azo–hydrazone equilibrium with the protonation equilibrium of the azo-group. For methoxynaphthalenes, separate correlations of pK_{BH^+} values with σ_m and σ_p of the substituents are found, owing to the presence in the molecules of two distinct basic centres.

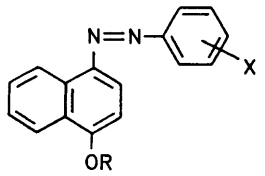
It is generally accepted that azo-derivatives exist exclusively in the *trans*-form in solution, and that the *cis*-form is too short-lived at room temperature (except under conditions of intense irradiation or in a few highly fluorinated derivatives) to effect spectra measurably.[1] In particular, hydroxyazo-compounds isomerize *via* a tautomeric hydrazone [2-5] (Scheme), the azo–hydrazone equilibrium depending on structural effects and on the medium polarity, as shown by spectroscopic methods [6] or by dipole moments.[7]

Azo-derivatives in aqueous acid solution show basic properties, protonation occurring at the azo-group. Basicity constants of substituted azobenzenes in 20% aqueous ethanol were measured by Jaffé and his co-workers who defined an acidity function in this medium [8] and studied the substituent effects.[9] More recently, Reeves investigated the effect of ionic solubilizing groups [such as SO_3^- and $\overset{+}{N}H(CH_3)_2$] on the spectroscopic behaviour of azobenzenes and 1-arylazo-2-naphthols.[10]



Scheme

A spectroscopic study on the protonation equilibria of 1-arylazo-4-naphthols (I) can provide evidence of their structures and also whether the azo–hydrazone equilibria takes place, as observed for 1-arylazo-2-naphthols.[11] The evaluation of pK_{BH^+} for the corresponding methyl ethers (II), where no azo–hydrazone equilibrium is possible, is useful for the study of substituent effects.



X = H, OCH_3, CH_3, Cl.

(I) R = H

(II) R = CH_3

In this paper we also contribute evidence on the protonation site of the azo-group.[12]

Results and Discussion

The spectral behaviour of 1-arylazo-4-naphthols (I) and 1-arylazo-4-methoxynaphthalenes (II) was studied in a solvent system consisting of 20% v/v ethanol and 80% v/v sulphuric acid–water. Some naphthols (I; X = H, *o*-OCH_3, *p*-OCH_3, *o*-CH_3, *p*-Cl) and all the methoxynaphthalenes showed two absorption bands, one at 405—422 nm due to the free base and the other at 550—580 nm due to the conjugate acid. An isosbestic point at 470—495 nm is also present.

On increasing the acidity of the medium the absorbance of the first band decreases and that of the latter increases. Figure 1 reports the absorption curves for 1-*o*-tolylazo-4-naphthol at various sulphuric acid concentrations.

Other naphthols (I; X = *m*-OCH_3, *m*-CH_3, *p*-CH_3, *o*-Cl, *m*-Cl) show only one absorption band which, on increasing the medium acidity, is shifted towards higher wavelengths (Figure 2).

In the Table we report the maximum absorption wavelengths of the free base (λ_B) and of the conjugate acid (λ_{BH^+}) for the compounds which show an isosbestic point (λ_i). For the other naphthols only the $\lambda_{max.}$ values of the bands at lowest and highest acidities are reported.

For these compounds the absence of an isosbestic point can be ascribed to medium effects and probably to

Maximum absorption wavelengths (nm) of the free base (λ_B), the conjugate acid (λ_{BH^+}), and the isosbestic point (λ_i) and the pK_{BH^+} values at 25 °C of 1-arylazo-4-naphthols (I) and 1-arylazo-4-methoxynaphthalenes (II)

X	λ_B	λ_i	λ_{HH^+}	pK_{BH^+}[a]
Arylazonaphthols				
H	415	478	550	0.12
o-OCH_3	412	495	580	−0.05
m-OCH_3	472[b]		564[c]	
p-OCH_3	405	480	567	0.46
o-CH_3	410	480	550	−0.74
m-CH_3	470[b]		553[c]	
p-CH_3	490[b]		565[c]	
o-Cl	440[b]		564[c]	
m-Cl	432[b]		556[c]	
p-Cl	420	492	572	−1.08
Arylazomethoxynaphthalenes				
H	410	477	550	−0.50
o-OCH_3	412	478	554	−0.33
m-OCH_3	410	470	550	−0.81
p-OCH_3	420	482	565	−0.30
o-CH_3	408	486	560	−1.21
m-CH_3	416	478	558	−0.10
p-CH_3	415	487	568	−0.55
o-Cl	410	482	580	−2.21
m-Cl	422	480	568	−1.08
p-Cl	405	487	470	−1.20

[a] Standard error of the estimated value is 0.05 pK units. [b] Measured for a solution of 0.04% sulphuric acid. [c] Measured for a solution of 61% sulphuric acid.

the azo–hydrazone equilibrium. This hypothesis is supported by the λ_B and λ_{BH^+} values for the naphthols and methoxynaphthalenes (Table).

The close similarity between λ_B and λ_{BH^+} for the naphthols with the isosbestic point and the corresponding methoxynaphthalenes, in which the hydrazone form is not possible, suggests a structural analogy between them. For the naphthols where the isosbestic point is absent, λ_{BH^+} values are still similar to those of the corresponding methoxynaphthalenes, while the λ_B values are remarkably shifted towards higher wavelengths, indicating the presence of the hydrazone structure.[2,5] Hence these compounds exist mainly in the hydrazone form (less basic than the azo-form) at low acidities, and in the azo-protonated form at high acidities.

Therefore, it is difficult to choose a wavelength for the measurement of pK_{BH^+} values. Available methods,[13] including vectorial analysis for the calculation of the isosbestic point,[14] can be applied to band shifts caused by medium effects; these methods, however, do not take into account the presence of another equilibrium also influenced by medium effects.

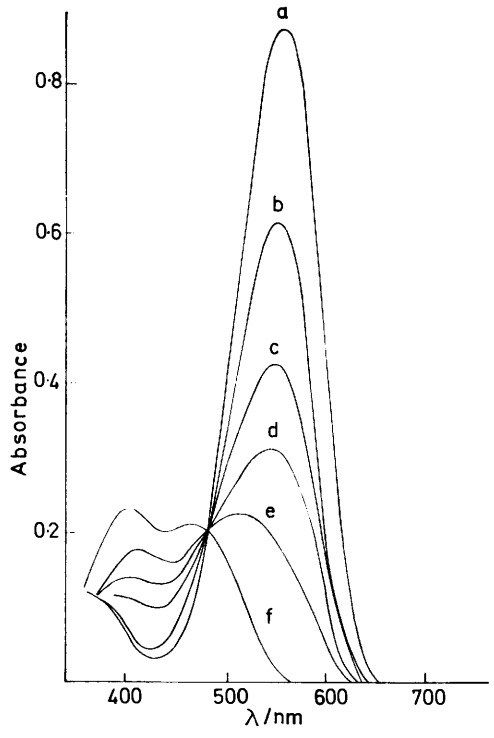


FIGURE 1 Absorption curves of 1-*o*-tolylazo-4-naphthol at various concentrations of sulphuric acid (wt %); a, 61%; b, 25%; c, 16%; d, 12%; e, 7%; f, 0.04%

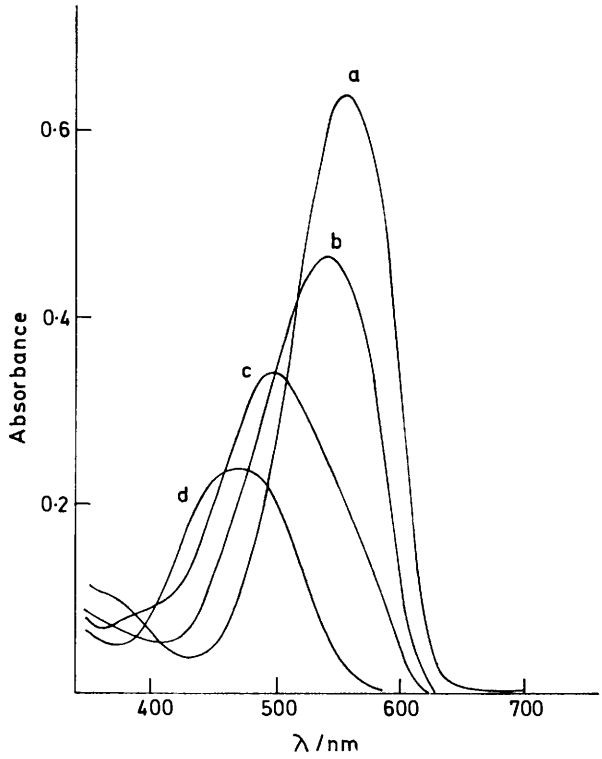


FIGURE 2 Absorption curves of 1-*m*-methoxyphenylazo-4-naphthol at various concentrations of sulphuric acid (wt %): a, 61%; b, 12%; c, 6%; d, 0.04%

The protonation equilibrium constants (Table) were calculated using the H_0 acidity function measured by Jaffé and his co-workers [equation (1)].[8] This function

$$H_0 = pK_{BH^+} - \log([BH^+]/[B]) \qquad (1)$$

is suitable for these equilibria, which are specific to the 20% ethanol-containing acid system and which refer to structurally similar indicators (azobenzenes). The Hammett H_0 acidity function [15] cannot be used, since the pK values are strongly dependent on the aqueous ethanol solvent system.[16] Moreover, plots of log $[BH^+]/[B]$ against H_0 values are linear with a slope close to unity,

as required to apply the acidity functions correctly and to deduce thermodynamic equilibrium constants.[17]

The substituent effects on the basicity of the naphthols cannot be assessed owing to the few data available; however, useful information can be drawn from the

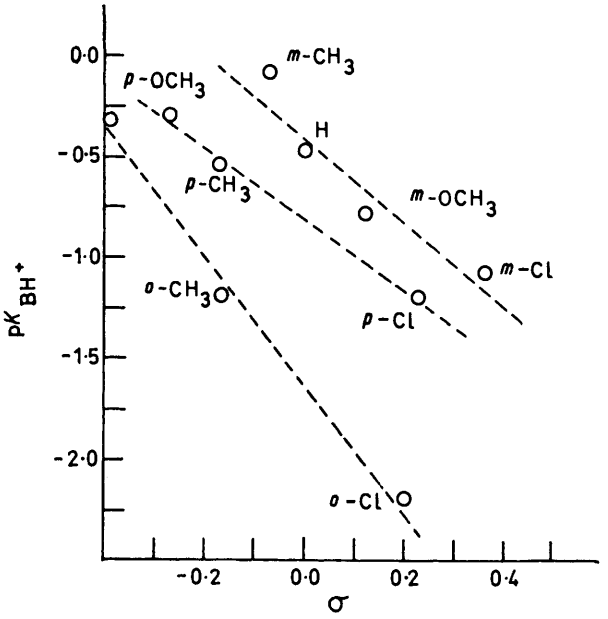
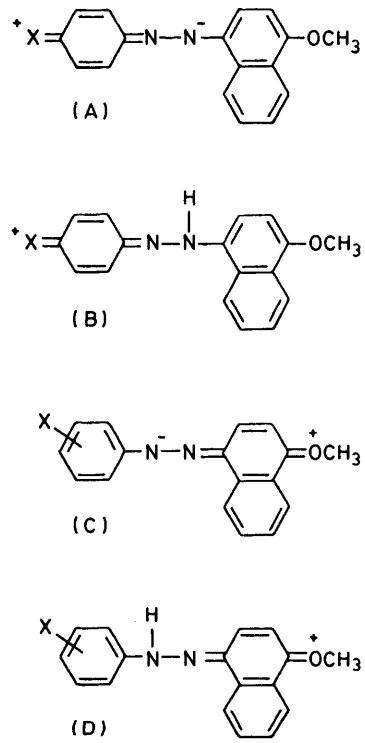


FIGURE 3 Dependence of pK_{BH^+} values of 1-arylazo-4-methoxynaphthalenes on Hammett σ values

results for the methoxynaphthalenes. In fact, separate Hammett correlations for *meta*-, *para*-, and *ortho*-derivatives are observed (Figure 3). This trend is unexpected, since no such effect was found in the original determination of the pK_{BH^+} values of *meta*- and *para*-substituted azobenzenes;[9] however, it can be ascribed to the presence of two distinct basic centres in the 1-arylazo-4-methoxynaphthalenes.



In fact, if we consider resonance structures (A)—(D), different sites of protonation, at the *N*-naphthyl and *N*-phenyl atoms, are possible. Protonation occurs mainly at the *N*-phenyl atom in the *meta*-derivatives, where structures (A) and (B) are less important, but, if electron-donating (+*M*) substituents in the *para*-position are present, structures (A) and (B) become competitive with (C) and (D), and protonation also occurs at the *N*-naphthyl atom. Thus, the lack of a single correlation for both *meta*- and *para*-substituents seems justified.

The higher basicities of the *meta*- with respect to the *para*-derivatives, assuming the same Hammett σ values, can be ascribed to the proximity of the *N*-phenyl basic centre to the substituents. Moreover, the lower basicities of the *ortho*- with respect to the *meta*- and *para*-derivatives, depends on resonance effects, as for *para*-derivatives, and, additionally, on steric effects.

EXPERIMENTAL

Materials.—1-Arylazo-4-naphthols (I) were prepared by usual diazotization of the corresponding anilines with 1-naphthol in alkaline solution. The compounds were purified by crystallization to constant m.p.:[5] (X, m.p.) H, 207°; *o*-OCH_3, 178°; *m*-OCH_3, 159°; *p*-OCH_3, 176°; *o*-CH_3, 160°; *m*-CH_3, 200°; *p*-CH_3, 210°; *o*-Cl, 189°; *m*-Cl, 226°; *p*-Cl, 231°.

1-Arylazo-4-methoxynaphthalenes (II) were obtained by methylation of the corresponding naphthols.[18] The compounds were crystallized from ethanol: [X, m.p., $\lambda_{max.}$ (95% ethanol) (log ε)]: H, 82°,[2] 398 nm (4.12); *o*-OCH_3, 121°,[18] 393 nm (4.11); *m*-OCH_3, 90°, 398 nm (4.04) (Found: C, 74.0; H, 5.55; N, 9.6. $C_{18}H_{16}N_2O_2$ requires C, 73.95; H, 5.5; N, 9.6%); *p*-OCH_3, 134°,[18] 393 nm (4.23); *o*-CH_3, 88°, 394 nm (4.13) (Found: C, 78.2; H, 5.75; N, 10.2. $C_{18}H_{16}N_2O$ requires C, 78.25; H, 5.85; N, 10.15%); *m*-CH_3, 152°, 397 nm (4.16) (Found: C, 78.25; H, 5.9; N, 10.1. $C_{18}H_{16}N_2O$ requires C, 78.25; H, 5.85; N, 10.15%); *p*-CH_3, 103°, 392 nm (4.16) (Found: C, 78.3; H, 5.8; N, 10.1. $C_{18}H_{16}N_2O$ requires C, 78.25; H, 5.84; N, 10.15%); *o*-Cl, 121°, 400 nm (4.04) (Found: C, 68.75; H, 4.34; N, 9.4. $C_{17}H_{13}ClN_2O$ requires C, 68.8; H, 4.4; N, 9.45%); *m*-Cl, 113°, 406 nm (4.04) (Found: C, 68.85; H, 4.45; N, 9.35. $C_{17}H_{13}ClN_2O$ requires C, 68.8; H, 4.4; N, 9.45%); *p*-Cl, 224°, 401 nm (4.10) (Found: C, 68.75; H, 4.45; N, 9.5. $C_{17}H_{13}ClN_2O$ requires C, 68.8; H, 4.4; N, 9.45%).

Equilibrium Constants.—A stock solution of azo-compound (*ca.* 1×10^{-4}M) was prepared in absolute ethanol. Portions (5 ml) were pipetted into 25-ml volumetric flasks, placed in a thermostat at 25 ± 0.1 °C, and then diluted to the mark with aqueous sulphuric acid solutions of the appropriate concentration. A series of acid solutions, in which the content of ethanol was 20% v/v and the concentration of azo-compound *ca.* 2×10^{-5}M, was obtained. The ratio $[BH^+]/[B]$ at various acidities was determined by equation (2) where A_B, A_{BH^+}, and A are the absorbances of

$$[BH^+]/[B] = (A_B - A)/(A - A_{BH^+}) \qquad (2)$$

the free base, of the conjugate acid, and of the solution,

respectively, at the maximum absorption wavelengths of the protonated form. pK_{BH^+} Values were calculated by the least squares method from plots of log $[BH^+]/[B]$ against $-H_0$ [equation (1)].

Spectroscopic measurements were performed with Hitachi–Perkin-Elmer u.v. spectrophotometer.

We thank the C.N.R. (Rome) for financial support.

[9/964 *Received*, 21*st June*, 1979]

REFERENCES

[1] G. S. Hartley, *J. Chem. Soc.*, 1938, 633; E. Fischer, M. Frankel, and R. Wolovsky, *J. Chem. Phys.*, 1955, **23**, 1367; D. Schulte-Frohlinde, *Annalen*, 1958, **612**, 138.

[2] R. Kuhn and F. Bär, *Annalen*, 1935, **516**, 143.

[3] A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 1952, 4793; A. Burawoy and A. R. Thompson, *ibid.*, 1953, 1443.

[4] E. Fischer and Y. F. Frei, *J. Chem. Soc.*, 1959, 3159.

[5] K. J. Morgan, *J. Chem. Soc.*, 1961, 2151; J. Griffiths, *J. Soc. Dyers Colourists*, 1972, **88**, 106.

[6] E. Sawicki, *J. Org. Chem.*, 1957, **22**, 743; F. D. Saeva, *ibid.*, 1971, **36**, 3842; E. Manda, *Bull. Chem. Soc. Japan*, 1971, **44**, 1620.

[7] S. Millefiori, F. Zuccarello, A. Millefiori, and F. Guerrera, *Tetrahedron*, 1974, **30**, 735.

[8] S. J. Yeh and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1959, **81**, 3274.

[9] H. H. Jaffé and R. W. Gardner, *J. Amer. Chem. Soc.*, 1958, **80**, 319; S. J. Yeh and H. H. Jaffé, *ibid.*, 1959, **81**, 3279.

[10] R. L. Reeves, *J. Amer. Chem. Soc.*, 1966, **88**, 2240.

[11] L. Abate, *Boll. Acc. Gioenia* (*Catania*), 1978, 31.

[12] M. Liler, 'Reaction Mechanisms in Sulphuric Acid,' Academic Press, London, 1971, p. 100.

[13] L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103; C. T. Davis and T. A. Geismann, *ibid.*, 1954, **76**, 3507; K. Yates and R. A. McClelland, *ibid.*, 1967, **89**, 2686; G. C. Greig and C. D. Johnson, *ibid.*, 1968, **90**, 6453.

[14] J. T. Edwards and S. C. Wong, *J. Amer. Chem. Soc.*, 1977, **99**, 4229.

[15] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1; M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

[16] E. Grunwald and B. J. Berkowitz, *J. Amer. Chem. Soc.*, 1951, **73**, 4939; E. Gutbezahl and E. Grunwald, *ibid.*, 1953, **75**, 559, 565.

[17] K. Yates and J. B. Stevens, *Canad. J. Chem.*, 1965, **43**, 529.

[18] G. Charrier and L. Casale, *Gazzetta*, 1914, **44**, 607.