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The Effects of Cyclic Terminal Groups in 4-Aminoazobenzene and Related Azo Dyes: Part 2†—pK_a Values of Some Monoazo Dyes Derived from *N*-Phenylpyrrolidine and *N*-Phenylpiperidine

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SUMMARY

Basicity values have been determined for series of monoazo dyes incorporating a pyrrolidino or a piperidino moiety. In general, the pK_a *value is found to decrease as the donor capacity of the terminal nitrogen atom decreases.*

The basicities of the 4'-substituted piperidinoazobenzenes decrease as the electron withdrawing strength of the 4'-substituent increases. However, the pK_a *values of the related pyrrolidino compounds appear to be insensitive to the substituent.*

1. INTRODUCTION

Many *p*-aminoazobenzene dyes undergo a pronounced colour change on addition of acid, the generally observed shift of the absorption band to

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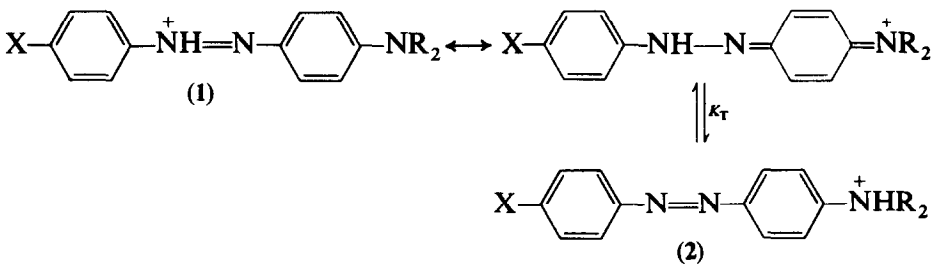
longer wavelength being attributed to resonance stabilisation of the resulting cation. This phenomenon of halochromism has been reviewed.[2] Solutions of the mono-acid salts of derivatives of 4-aminoazobenzene generally show two absorption bands associated with an equilibrium between two tautomeric forms.[3] In the azonium cation (**1**) the β-azo nitrogen atom is protonated,[4] whereas it is the terminal nitrogen atom which is protonated in the ammonium ion (**2**).[5] In the latter species, protonation prevents mesomeric interaction of the terminal lone pair of electrons with the π-system and absorption occurs at about 320 nm, some 200 nm below that of the azonium ion, but close to that of azobenzene itself.



The tautomeric equilibrium, K_T, defined as [azonium]/[ammonium][6] (though the inverse relationship has also been used[7]), is dependent on steric effects and it appears that the basicities of the β-azo and terminal nitrogen atoms are largely determined by the extent of conjugation between the amino group and the rest of the molecule.[8]

An increase in acid concentration also affects the equilibrium, leading to a shift towards the azonium ion. Although this behaviour has been attributed to differences in solvation of the cations derived from 4-aminoazobenzenes through hydrogen bonding,[9] the hybridisation of the terminal nitrogen atom may be more relevant in *NN*-disubstituted aminoazobenzenes. In the ammonium ion, the tetrahedral configuration of the terminal nitrogen atom restricts access of the counter ions to a greater extent than does the planar arrangement about the sp^2 hybridised atom in the azonium form, which is consequently stabilised more effectively.

An indication of the position of the tautomeric equilibrium can be obtained from measurements of ε_{max} values at the wavelength maxima of the azonium (C band) and ammonium (A band) forms. The ratio $C_\varepsilon/A_\varepsilon$ is roughly proportional to K_T if the absorption of the azonium ion at λ_{max}

(ammonium ion) is assumed to be zero, and vice versa, although doubt has been cast on the validity of this assumption.[9] An allowance has to be made for the fact that the absolute values of ε_{max} for the two species are not equal. Data from the work of Yamamoto[8] and Hallas[10] suggest an absolute ε_{max} value (ε^0) of 20 000–25 000 for the ammonium tautomer and 55 000–65 000 for the azonium species, giving a factor (k) of $0{\cdot}38 \pm 0{\cdot}07$ for $A_{\varepsilon^0}/C_{\varepsilon^0}$.

Although as a consequence of the equilibrium it is impossible to measure the individual basicity of each nitrogen atom, the overall basicity of the molecule (pK_a) can be determined[11] from the absorbances of the non-protonated and mono-protonated forms of the dye.

The relationships between protonation equilibria in monoazo dyes and properties of the individual tautomers are summarised in eqn (1).

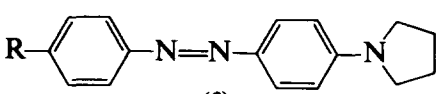
$$K_T = \frac{[\text{azonium}]}{[\text{ammonium}]} = k\frac{C_\varepsilon}{A_\varepsilon} \propto \frac{pK_2}{pK_1} \propto \frac{\text{Basicity at } \beta\text{-N}}{\text{Basicity at terminal N}} \qquad (1)$$

It was of interest to investigate the influence of saturated heterocyclic terminal groups on the properties of monoazo dyes. In this paper, the effects of terminal piperidino and pyrrolidino groups and of substituents in the aromatic moiety on the pK_a values of the dyes and the tautomeric equilibria are described.

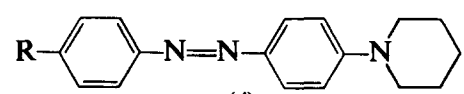
2. EXPERIMENTAL

The dyes (**3**) and (**4**) were prepared by coupling the appropriate diazonium ion with either *N*-phenylpyrrolidine or *N*-phenylpiperidine in buffered aqueous acetic acid. The purification and physical data have been described.[1]

Solutions containing constant dye concentration but varying amounts of sulphuric acid were prepared in 50 % v/v aqueous ethanol using a stock dye solution in ethanol. One strongly basic and a number of strongly acidic solutions were prepared for each dye. The solutions were thermostatted at 298 K before measuring their spectra in 4 cm silica cells



(3)

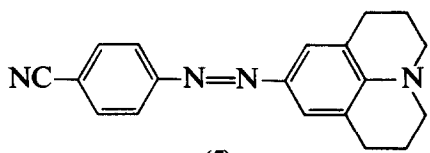


(4)

contained in the thermostatted cell block of a Pye–Unicam SP8-100 spectrophotometer.

The H_0 values of the solutions were taken from the data of White *et al.*[12] who used nitro- and chloro-substituted anilines as indicators. Despite the reservations expressed by Yamamoto,[7] the results of Safta[13] appear to justify the use of an acidity function based upon a mixture of different kinds of indicators. The H_0 values derived by White cover a larger range of acidities than the somewhat different figures obtained by Safta and were hence considered more appropriate. Tables of H_0 at varying temperatures[14] show that a change in temperature from 303 K, at which White's values are quoted, to 298 K will have negligible effect.

The pH values of solutions of 9-(4-cyanophenylazo)julolidine (**5**) were measured because the acidity range for protonation of this dye



(**5**)

was outside the available H_0 values. Standard buffer solutions[15] of 0·01 mol dm^{-3} lithium hydrogen oxinate/0·01 mol dm^{-3} oxalic acid and of 0·01 mol dm^{-3} lithium hydrogen succinate/0·01 mol dm^{-3} succinic acid in 50% ethanol were used to calibrate the pH meter (Philips PW 9410 Digital).

The concentrated solutions of sulphuric acid were standardised by accurate dilution and titration with sodium hydroxide solution, itself standardised with AR potassium hydrogen phthalate.

3. RESULTS AND DISCUSSION

Ionisation constants can be calculated from eqn (2),[16]

$$pK = pH - \log\left(\frac{\varepsilon - \varepsilon_{BH^+}}{\varepsilon_B - \varepsilon}\right) - \log\left(\frac{f_B}{f_{BH^+}}\right) \qquad (2)$$

where ε_B and ε_{BH^+} are the molar extinction coefficients of the non-protonated (base) and the mono-protonated forms of the dye, respectively, and ε is the apparent molar extinction at a given pH. In the

present work, the range of acidities is such that the activity coefficient ratio can not be assumed to be unity despite the very low dye concentrations. Furthermore, the calculations are based on H_0 values and the basicities, referred to as pK_a' values, were obtained from eqn (3), a modified form of eqn (2),

$$pK_a' = H_0 - \log \frac{A - A_{BH^+}}{A_B - A} \tag{3}$$

in which A_B and A_{BH^+} are the absorbances of solutions containing 100% non-protonated dye and 100% protonated dye, respectively, and A is the absorbance of the solution at the appropriate acid concentration and at the same wavelength.

For the calculations, λ_{max} for BH^+ was usually chosen. However, there was considerable overlap of the absorption bands of the two species B and BH^+ for several of the piperidinoazobenzenes. For these dyes, λ_{max} for B was used because it gave a better spread of absorbance values. The insensitivity of such measurements to any changes in A_{BH^+} arising from a shift in the tautomeric equilibrium in favour of the azonium ion with increasing acid concentration is not important. The pK_a' measures the overall basicity of the azo dye and does not distinguish between the two sites of protonation, the β-azo and the terminal nitrogen atoms. Changing the wavelength at which the results were calculated did not change the value of pK_a' within standard error (s.e.) limits.

The determination of A_{BH^+} required special consideration. Carpentier and Dominique[9] showed that a solution containing 100% BH^+ cannot be obtained for 4-aminoazobenzene because the pK values for mono- and di-protonation are too similar. For each dye in the present study, the diprotonated species, BH_2^{2+}, can be obtained in concentrated sulphuric acid, but could not be obtained for most of the dyes in 50% ethanol and hence Carpentier's procedure could not be used. For all of the dyes in the present study, the constancy of the absorbance values over an appreciable range of acidities ($\sim$1–5 M), together with the excellent isobestic point obtained, shows that the pK values for the mono- and di-protonated forms are sufficiently separated for 100% BH^+ to be obtained over this range and this absorbance was taken as A_{BH^+}.

The values of pK_a' given in Table 1 were determined from plots of H_0 vs $\log (A - A_{BH^+})/(A_B - A)$. The graphs were observed to be linear in each case and the best value of pK_a' and its s.e. limits were obtained from a least-squares computer program. Only data within the range $pK_a' \pm 1$

TABLE 1
pK'_a Values of Some Derivatives of Piperidinoazobenzene and Pyrrolidinoazobenzene in 50% Aqueous Ethanol at 298 K

Substituent	σ_p[a]	pK'_a	
		Pyrrolidinoazobenzene (3)	*Piperidinoazobenzene* (4)
4-OCH_3	−0·28	1·94 ± 0·02	3·15 ± 0·01
4-CH_3	−0·14	2·18 ± 0·01[b]	2·99 ± 0·01
H	0·00	2·16 ± 0·02[c]	2·68 ± 0·02
4-Br	0·26	1·85 ± 0·01	2·67 ± 0·01
4-Cl	0·27	1·84 ± 0·01[d]	2·72 ± 0·01
4-$COCH_3$	0·47	2·13 ± 0·01	2·48 ± 0·01
4-CF_3	0·53	1·95 ± 0·01	2·46 ± 0·01
4-CN	0·69	1·98 ± 0·01	2·31 ± 0·01
4-NO_2	0·82	1·96 ± 0·01	2·27 ± 0·01

[a] Values taken from O. Exner, *Advances in linear free energy relationships*, eds N. B. Chapman and J. Shorter, p. 439. London, Plenum, 1972.
[b] Literature[8] value 2·43.
[c] Literature[8] value 2·38.
[d] Literature[8] value 2·15.

were used. The slopes of these graphs were very close to the expected value of unity.

In acid solution, the pyrrolidinoazobenzene dyes (3) exist mainly (*ca* 95%) as the azonium cation, whereas the corresponding piperidino derivatives are present predominantly (*ca* 85%) in the ammonium form. Thus, although pK'_a measures the overall basicity of the dye, in the present work the pK'_a value can be related to protonation at a specific site.

Examination of the data in the Table shows that the piperidinoazobenzenes have larger pK'_a values than the correspondingly substituted pyrrolidino analogues, reflecting the greater electron density at the terminal nitrogen than at the azonium nitrogen atom. The different behaviour of the two series of dyes is attributable to the loss of conjugation experienced by the piperidino group arising from steric interaction between the *ortho* hydrogen atoms of the benzene ring and the α-methylene groups of the piperidine moiety.[1] It has also been noted that an *exo* double bond will stabilise a five-membered ring but destabilise a six-membered ring.[17]

By way of comparison, 9-(4-cyanophenyl)azojulolidine (5), which

forms the azonium ion exclusively in acid solution,[10] is even more basic ($pK_a' = 3{\cdot}55$) than the piperidino analogue. This finding indicates more efficient delocalisation of the lone pair of electrons on the terminal nitrogen atom than in the case of the analogous pyrrolidine dye and provides further evidence for a near planar disposition of the nitrogen atom in the julolidine dyes.[18] It is also of interest to compare the present results with the published pK_a values for 4-diethylaminoazobenzenes.[19] Their higher basicities have been attributed to a loss of solvation as a result of the congested situation in the vicinity of the nitrogen atom which destabilises the base relative to the ammonium ion.[20] It is also clear that the acyclic diethylamino compounds show much less bias towards the azonium ion than do the pyrrolidino dyes.[8]

The response of the two series of dyes towards substituents is also different. The pyrrolidinoazobenzenes (**3**) show very little variation in pK_a' despite the introduction of *p*-substituents of such divergent electronic properties as nitro and methoxy groups, all values falling in the range $2{\cdot}0 \pm 0{\cdot}16$. The dyes derived from *NN*-diethylaminoazobenzene show a drop in basicity as the electron withdrawing strength of the *p*-substituent increases[19] and the different behaviour of the pyrrolidino compounds must be linked with their almost exclusive protonation at the *β*-azo nitrogen atom, the electron density at which must remain almost constant. A balance between the loss of electron density brought about by the electron withdrawing substituent and the increased conjugation of the lone-pair on the terminal nitrogen atom caused by the substituent can be envisaged.

The dominance of the ammonium tautomer for the piperidinoazobenzenes (**4**) leads to a situation where the electron density at the terminal nitrogen atom should directly influence the pK_a' and indeed a decrease in basicity is observed as the electron withdrawing nature of the substituent increases. Furthermore, a good linear correlation (r 0·967) is found between pK_a' and σ_p. The relatively small value of the reaction constant ρ ($0{\cdot}76 \pm 0{\cdot}08$) implies that the pK_a' of the dyes shows only a small dependence on the *p*-substituent. This value is not dissimilar from that observed for a series of *p*-substituted dimethylaminoazobenzenes ($\rho = 0{\cdot}55$),[21] although in this case it is considered that the initial protonation occurs at the azo nitrogen atom. It is of interest to note that the use of σ_p^- for groups capable of mesomeric interaction with the piperidino nitrogen atom does not significantly alter the goodness of fit (r 0·952).

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