The Effects of Cyclic Terminal Groups in 4-Aminoazobenzene and Related Azo Dyes. Part 1. Electronic Absorption Spectra of Some Monoazo Dyes derived from *N*-Phenylpyrrolidine and *N*-Phenylpiperidine

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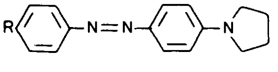
Monoazo dyes containing a terminal piperidino group absorb hypsochromically when compared with their pyrrolidinyl counterparts. In acid solution, the pyrrolidinyl dyes protonate almost exclusively at the β-azo nitrogen atom (azonium tautomer), whereas the analogous piperidino compounds protonate very largely at the terminal nitrogen atom (ammonium tautomer). These effects are related to differences in the conjugative capacity of the lone pair of electrons on the terminal nitrogen atom brought about by a change in size of the saturated heterocyclic ring.

It is well established that terminal bridging in analogues of 4-aminoazobenzene leads to notable bathochromic displacements of the first absorption band together with increased intensities, relative to appropriate 4-dialkylaminoazobenzenes.[1] Derivatives of 9-phenylazojulolidine,[2] 8-phenylazolilolidine,[3] 9-phenylazo-1-ketojulolidine,[4] 6-phenylazo-1,2,3,4-tetrahydroquinoline,[5,6] and 5-phenylazoindoline [7] have been studied, but the influence of saturated heterocyclic terminal groups in derivatives of 4-aminoazobenzene has not been examined systematically. It is therefore of interest to investigate the effects of changes in ring size and content on the properties of dyes of this type. In this paper a comparison is made between monoazo dyes derived from *N*-phenylpyrrolidine (I) and their *N*-phenylpiperidine analogues (II).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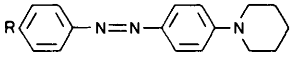
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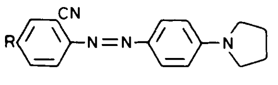
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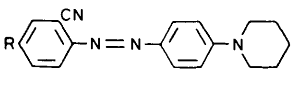
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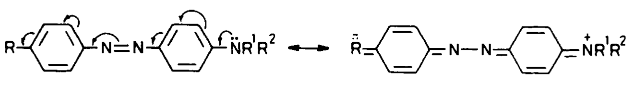

(V) (VI)

The effects of *para*-substituents on the spectroscopic properties of 4-dialkylaminoazobenzene dyes can be accounted for qualitatively in terms of the valence-bond resonance approach.[1] The parent dye system may be regarded as a resonance hybrid of two extreme canonical structures, (V) ⟷ (VI), of different energies. Structure (V) is a fairly close approximation to the ground state of the molecule since dipole-moment measurements on a series of *para*-substituted 4-dimethylaminoazobenzene dyes [8] suggest that the contribution of charge-separated structures to the ground state does not exceed 7%. The high-energy dipolar structure (VI) can be taken as a reasonable approximation to the excited state and this arrangement will be stabilised when R is an electron-withdrawing group, so that such substituents exert a bathochromic effect, since ΔE becomes smaller. In general, the visible absorption band is shifted by an amount that is approximately proportional to the appropriate Hammett σ-constant.[9] This relationship is illustrated by the data in Table 1 for representative groups of monoazo dyes derived from *N*-phenylpyrrolidine and *N*-phenylpiperidine.

The positive solvatochromism of the monoazo dyes (Table 1) can also be explained qualitatively in terms of resonance canonicals. Thus, an increase in solvent polarity will tend to stabilise the dipolar excited state more than the neutral ground state, resulting in a bathochromic shift of the first absorption band. In both series, the positive solvatochromism increases gradually as the electron-withdrawing capacity of the *para*-substituent increases, due to a progressive stabilisation of the excited state (VI) by the polar solvent. For dyes containing powerful electron-withdrawing groups, it is found that the pyrrolidinylazo derivatives are more sensitive to the change of solvent than are the less polar piperidino analogues, in keeping with greater stabilisation of the excited state in the former case.

In aminoazobenzene dyes of this type, the visible electronic transition involves a migration of electron density from the terminal nitrogen atom towards the azo group. Hence, alkylation of the terminal amino group increases the electron-donating strength of the substituent and leads to bathochromic shifts.[1] It is clear from Table 1 that, in neutral solution, the dyes derived from *N*-phenylpyrrolidine (I) are more bathochromic than their counterparts obtained from *N*-phenylpiperidine (II). Comparison with the $\lambda_{max.}$ values of some 4-dimethylaminoazobenzenes [10] and analogous 4-diethylaminoazobenzenes [11] reveals that the electron-donor power decreases in the order pyrrolidinyl ~ diethylamino > dimethylamino > piperidino. This overall trend is supported by other experimental data. Thus, the ^{13}C n.m.r. spectra of *N*-phenylpyrrolidine and *NN*-diethylaniline are very similar, whereas the *para*-carbon shielding in the case of *N*-phenylpiperidine reflects a decreased resonance interaction between the terminal nitrogen atom and the benzene ring.[12] Measurements of pK_a for the parent amines [12] and their *p*-carboxy-[13] and *p*-nitro-derivatives [14] give the same sequence, apart from variations in the position of diethylamino, attributable to solvation effects.[12] Values of the exaltation of molar refraction (ΔR_D) increase for the series *N*-phenylpiperidine < *NN*-dimethylaniline < *NN*-diethylaniline < *N*-phenylpyrrolidine in accordance with increasing resonance interaction.[12] It is interesting to note that this parameter suggests rather more effective conjugation by the pyrrolidinyl group than the diethylamino group, an observation that is supported by the results of ^{1}H n.m.r. studies [15] and by dipole-moment values of some aminoazobenzene derivatives.[16] This situation, however, is not clearly reflected in the $\lambda_{max.}$ values of the dyes (I) and (V) ($R^1 = R^2 =$ Et) which are very similar in both polar and non-polar solvents. It is possible that the ground state of

Table 1. Absorption bands of some dyes derived from *N*-phenylpyrrolidine and *N*-phenylpiperidine and halochromism in ethanol–hydrochloric acid

Dye	$\lambda_{max.}$/nm (Cyclohexane)	$10^{-4}\varepsilon_{max.}$ (Cyclohexane)	$\lambda_{max.}$/nm (Ethanol)	$10^{-4}\varepsilon_{max.}$ (Ethanol)	$\Delta\lambda$ (ethanol − cyclohexane)/nm	$\Delta\lambda$ [relative to (I) or (II)]/nm	$\lambda_{max.}$/nm (EtOH + HCl)	$10^{-4}\varepsilon_{max.}$ (EtOH + HCl)	($\lambda_{azonium} - \lambda_{neutral}$)/nm
(I) (R = OMe)	407	3.44	411	2.98	4	−2[a]	559	5.90	148
(I) (R = Me)	407	3.45	412	3.02	5	−1[a]	540	5.98	128
(I) (R = H)	407	3.48	413	2.86	6		530	5.77	117
(I) (R = Cl)	416	3.40	423	3.08	7	10[a]	534	5.88	111
(I) (R = Br)	418	3.86	425	3.32	7	12[a]	535	6.23	110
(I) (R = CF_3)	424	3.45	434	3.14	10	21[a]	514	5.82	80
(I) (R = COMe)	434	3.75	454	3.25	20	41[a]	531	6.34	77
(I) (R = CN)	438	3.70	460	3.52	22	47[a]	518	6.19	58
(I) (R = NO_2)	459	3.50	488	3.43	29	75[a]	518	6.82	30
(III) (R = H)	438	3.32	458	3.08	20	45[a]	505	3.40	47
(III) (R = NO_2)	503	4.03	536	4.44	33	123[a]	498	6.47	−38
(II) (R = OMe)	392	2.69	398	2.80	6	−2[b]	558	0.12	160
(II) (R = Me)	391	2.82	398	2.47	7	−2[b]	541	0.28	143
(II) (R = H)	392	2.63	400	2.49	8		528	0.35	128
(II) (R = Cl)	403	2.80	412	2.85	9	12[b]	534	0.26	122
(II) (R = Br)	404	3.01	413	2.60	9	13[b]	534	0.29	121
(II) (R = CF_3)	411	2.71	423	2.69	12	23[b]	515	0.64	92
(II) (R = COMe)	420	2.76	436	3.08	16	36[b]	530	0.96	94
(II) (R = CN)	427	3.11	442	2.89	15	42[b]	521	0.99	79
(II) (R = NO_2)	444	2.95	470	2.76	26	70[b]	522	1.33	52
(IV) (R = H)	428	2.77	442	2.83	14	42[b]	498		56
(IV) (R = NO_2)	499	3.27	529	3.83	30	129[b]	498	0.39	−31

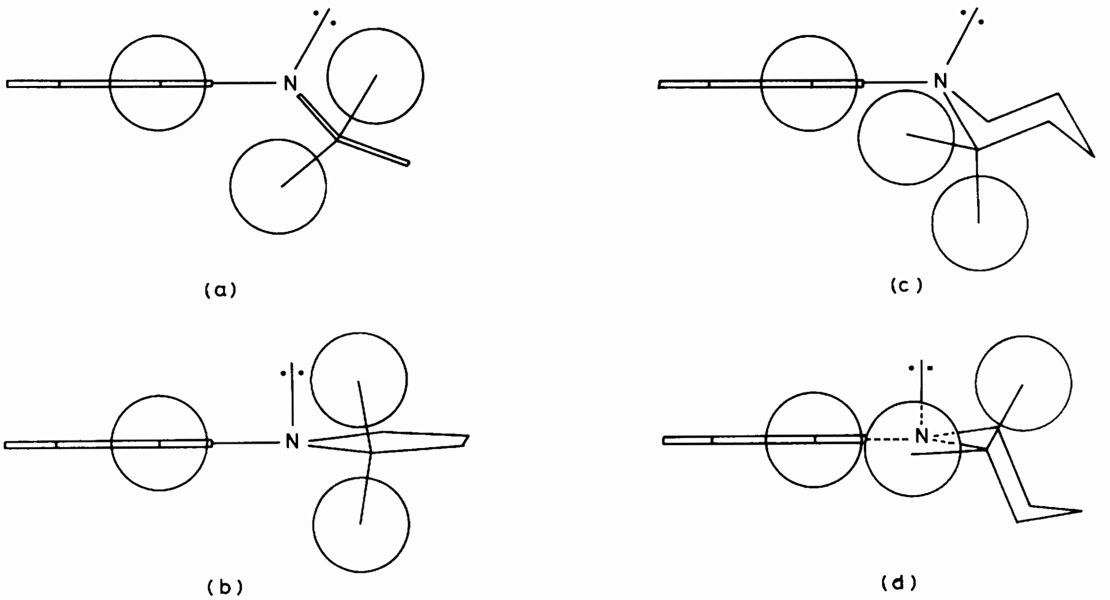
[a] Relative to (I) (R = H). [b] Relative to (II) (R = H).

the pyrrolidinylazo dyes is more stable than that of the diethylamino types due to hybridisation differences at the terminal nitrogen atom. However, any stabilisation of the pyrrolidinylazo excited state, owing to increased conjugation of the lone pair, may be offset by the increase in energy associated with the eclipsed protons of the five-membered ring (see below).

The relative donating capacity of the pyrrolidinyl group compared with that of the piperidino group can be accounted for in terms of steric effects. By analogy with cyclopentane, the pyrrolidine ring can be regarded as a distorted pentagon, leading to the envelope [17] and the half-chair [18] conformations. Pseudorotation [19] ensures that departures from planarity are averaged around the ring so that the terminal nitrogen atom can be accommodated in an sp^3 arrangement with negligible angle strain. Mesomeric interaction with the phenyl ring will, however, increase the sp^2 character of the atom and will also obviate any steric crowding between the *ortho*-protons of the phenyl ring and the α-methylene protons of the five-membered ring (Figure), particularly in the excited state (b). Unfortunately, this interaction causes the pyrrolidine ring protons to become more nearly eclipsed, so that a balance must be achieved between steric and mesomeric interactions. In the case of the piperidine ring,[20] molecular models (Dreiding) suggest that the equatorial protons of the α-methylene groups in the chair conformation of the six-membered ring are directed towards the *ortho*-protons of the phenyl ring (Figure). The resulting steric hindrance is greater than that experienced in the pyrrolidinyl system and is accentuated in the excited state where the protons are essentially uniplanar, (d). Rotation about the ring–nitrogen bond to relieve this crowding will, of course, reduce the extent of the overlap between the nitrogen lone-pair orbital and the adjacent aromatic π-electron cloud, increase the sp^3 character of the terminal nitrogen atom and bring about a hypsochromic shift of $\lambda_{max.}$ together with a reduction in $\varepsilon_{max.}$.

The angle of rotation (θ) can be estimated by using the simple empirical relationship [21] $\cos^2\theta = \varepsilon/\varepsilon_0$, where ε and ε_0 are the molar absorption coefficients for the non-planar and planar molecules, respectively. Values of θ have been used recently as a test for the presence of electronic buttressing [22] in the 4-aminoazobenzene system.[23] Thus, in suitable systems typified by (VII) $\longleftrightarrow$ (VIII), the crowding effect of a bulky *ortho*-substituent (R) is resisted by an increasing contribution from (VIII) as the electron-withdrawing strength of the substituent X increases. Consequently, the calculated value of θ is smaller than that of the parent (X = H). Calculated θ values for some representative piperidinoazo derivatives are given in Table 2; the ε_0 values used are those of the pyrrolidinyl analogues. In this case, the steric interaction is between the α-methylene protons of the piperidino ring and the *ortho*-protons of the benzene ring, rather than with a bulky group, but similar arguments apply. In accord with recent findings,[23] θ does not decrease as the electron-withdrawing power of the *para*-substituent in (II) is increased, suggesting that the substituent is too far removed from the amino group to exert any significant buttressing effect. The phenylazo group itself does exert an appreciable buttressing effect, however, since u.v. spectroscopic data for the parent amine, *N*-phenylpiperidine, give a value of θ *ca.* 45° (in methanol),[14] whereas in the case of the 4-phenylazo analogues (II) θ falls within the range 21—28° (in ethanol).

For both series of dyes, the *o*-cyano derivative (III) and (IV) (R = H) have maximum absorbances at the same wavelength as the *para*-isomer (Table 1) in accordance with electrical equivalence between *o*- and *p*-cyano groups and the absence of steric hindrance.[24] The 2-cyano-4-nitro derivative (III) (R = NO_2) shows additivity of substituent effects,[4–7] but the analogous piperidino compound (IV) (R = NO_2) shows a bathochromic deviation of 17 nm (in ethanol). It would appear that in the latter compound the overall electron-withdrawing effect of the two substituents is sufficient to



The relative spatial arrangement of *ortho*-phenyl and α-methylene protons in *N*-phenylpyrrolidine (envelope form): (a) ground state, (b) excited state, and in *N*-phenylpiperidine: (c) ground state, and (d) excited state

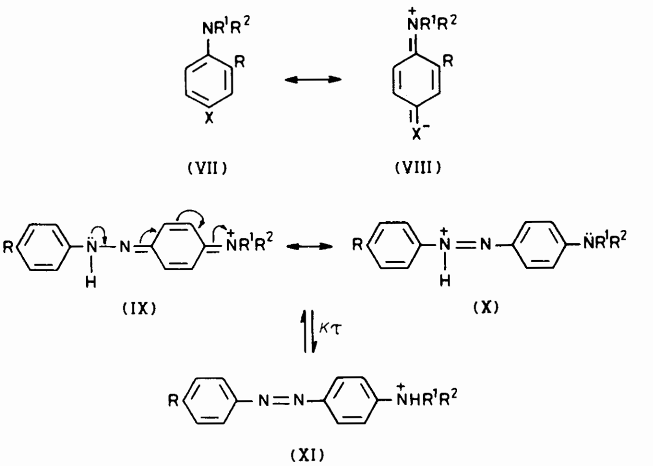


Table 2. Estimated angles of rotation (θ) for some piperidinoazo dyes

Dye	θ [a]/°	Δλ [b]/nm
(II) (R = Me)	25	14
(II) (R = H)	21	13
(II) (R = Br)	28	12
(II) (R = CF_3)	22	11
(II) (R = CN)	25	18
(II) (R = NO_2)	26	18
(IV) (R = NO_2)	22	7

[a] From $\cos^2\theta = \varepsilon/\varepsilon_0$. [b] $\lambda_{max.}$(Pyrrolidinyl) − $\lambda_{max.}$(piperidino).

enforce improved conjugation of the terminal nitrogen lone pair at the expense of increased steric strain, although this is not reflected in the appropriate θ value (Table 2). The shift Δλ (Table 2) tends to increase as the electron-withdrawing strength of the *para*-substituent increases, in accordance with simple perturbation theory; [23] the 2-cyano-4-nitro derivative is clearly anomalous.

It is well known that the visible band in dyes derived from 4-aminoazobenzene generally moves to longer wavelengths in acid solution (halochromism), as a consequence of protonation at the azo linkage which results in the formation of a resonance-stabilised azonium ion, (IX) ⟷ (X); the tautomeric ammonium ion (XI) absorbs in the ultraviolet region.[1] The tautomeric equilibrium constant K_T is usually defined as [azonium]/[ammonium] since increasing acid concentration leads to an increase in [azonium]; [25] Japanese workers have represented K_T by the inverse relationship.[16,26] The tautomeric equilibrium is dependent on steric effects, especially those which lead to deconjugation of the donor group.[1] In acid solution, the 4-pyrrolidinylazobenzene dyes (I) exist almost entirely as the azonium form whereas the 4-piperidinoazobenzene analogues (II) are present very largely as the ammonium form (Table 1). This marked difference in behaviour can be accounted for in terms of the loss of conjugation suffered by the piperidino group arising from the clash between the α-methylene and the *ortho*-protons of the benzene ring. Thus, the electron density is increased at the terminal nitrogen atom and decreased at the azo group; only relatively low concentrations of acid are required to effect full protonation of the neutral dye. These findings are also in accord with earlier work in which it was suggested that an *exo* double bond will destabilise a six-membered ring but favour a five-membered ring.[15,27] In this connection, it is clear that the pyrrolidinylazo dyes show a much greater bias towards the azonium tautomer than do the closely related, but acyclic, diethylamino compounds (V) ($R^1 = R^2 =$ Et).[16] Electron-withdrawing groups in the acceptor ring of the piperidinoazo dyes increase the amount of azonium ion present by increasing the conjugation of the terminal lone pair (Table 1). Thus, $\varepsilon_{max.}$ increases from 1 200 for the *p*-methoxy dye (II) (R = OMe) to 13 300 in the case of the corresponding nitro compound (II) (R = NO_2).

Comparison with the neutral dye system, (V) ⟷ (VI), shows that for the azonium species, (IX) ⟷ (X), the ground and excited states are much closer together in energy terms so that a bathochromic shift is observed on protonation (positive halochromism). Although the azonium ion can be regarded as a charge-resonance system, it is best represented in the ground state by the quinonoid structure (IX), so that the first

Table 3. Preparative and microanalytical data for some azo dyes

Dye	M.p.(°C)	Crude yield (%)	Appearance	Molecular formula	Required (%) [Found (%)]			
					C	H	N	Hal
(I) (R = OMe)	168—170	89	Orange crystals	$C_{17}H_{19}N_3O$	72.6	6.8	15.0	
					(73.0	6.9	15.0)	
(I) (R = Me)	198—200 [a]	86	Orange crystals	$C_{17}H_{19}N_3$	77.0	7.2	15.9	
					(77.2	7.2	16.0)	
(I) (R = H)	163—164 [b]	74	Orange leaflets	$C_{16}H_{17}N_3$	76.5	6.8	16.7	
					(76.4	6.8	16.9)	
(I) (R = Cl)	199—200 [c]	61	Orange crystals	$C_{16}H_{16}ClN_3$	67.3	5.6	14.7	12.5
					(67.4	5.8	14.8	12.3)
(I) (R = Br)	202—203	74	Orange crystals	$C_{16}H_{16}BrN_3$	58.2	4.9	12.7	24.3
					(58.4	4.9	12.5	24.7)
(I) (R = CF₃)	206—208	90	Orange crystals	$C_{17}H_{16}F_3N_3$	64.0	5.0	13.2	17.9
					(64.2	5.0	13.4	18.1)
(I) (R = COMe)	213—215	78	Maroon leaflets	$C_{18}H_{19}N_3O$	73.7	6.5	14.3	
					(73.8	6.4	14.5)	
(I) (R = CN)	222—224	78	Red plates	$C_{17}H_{16}N_4$	73.9	5.8	20.3	
					(74.1	5.8	20.5)	
(I) (R = NO₂)	226—227	74	Purple needles	$C_{16}H_{16}N_4O_2$	64.8	5.4	18.9	
					(64.5	5.5	18.8)	
(III) (R = H)	151—152	58	Dark red leaflets	$C_{17}H_{16}N_4$	73.9	5.8	20.3	
					(73.7	5.9	20.3)	
(III) (R = NO₂)	210—211	72	Blue-black crystals	$C_{17}H_{15}N_5O_2$	63.6	4.7	21.8	
					(63.5	4.7	21.7)	
(II) (R = OMe)	149—150	47	Yellow leaflets	$C_{18}H_{21}N_3O$	73.2	7.1	14.3	
					(73.5	7.2	14.5)	
(II) (R = Me)	166—167	57	Yellow leaflets	$C_{18}H_{21}N_3$	77.4	7.5	15.1	
					(77.4	7.4	15.1)	
(II) (R = H)	151—152	64	Orange leaflets	$C_{17}H_{19}N_3$	77.0	7.2	15.9	
					(76.8	7.3	16.0)	
(II) (R = Cl)	133—135	73	Orange leaflets	$C_{17}H_{18}ClN_3$	68.1	6.0	14.0	11.9
					(68.2	5.9	14.1	11.9)
(II) (R = Br)	147—149	90	Orange leaflets	$C_{17}H_{18}BrN_3$	59.3	5.3	12.2	23.2
					(59.2	5.2	12.1	23.5)
(II) (R = CF₃)	151—153	83	Orange crystals	$C_{18}H_{18}F_3N_3$	64.9	5.4	12.6	17.1
					(65.0	5.2	12.7	17.0)
(II) (R = COMe)	191—192	90	Red leaflets	$C_{19}H_{21}N_3O$	74.3	6.9	13.7	
					(74.3	7.0	13.7)	
(II) (R = CN)	188—190	79	Red leaflets	$C_{18}H_{18}N_4$	74.5	6.2	19.3	
					(74.4	6.3	19.4)	
(II) (R = NO₂)	202—203	84	Maroon leaflets	$C_{17}H_{18}N_4O_2$	65.8	5.8	18.1	
					(65.7	5.8	18.0)	
(IV) (R = H)	108—110	43	Dark red plates	$C_{18}H_{18}N_4$	74.5	6.2	19.3	
					(74.3	6.5	19.4)	
(IV) (R = NO₂)	128—130	77	Blue-black crystals	$C_{18}H_{17}N_5O_2$	64.5	5.1	20.9	
					(64.8	5.1	20.8)	

[a] Lit.,[16] m.p. 187—188 °C. [b] Lit.,[16] m.p. 166—167 °C. [c] Lit.,[16] m.p. 197—198 °C.

band is associated with a migration of electron density from the β-nitrogen atom to the terminal nitrogen atom. The direction of charge migration accompanying electron excitation is therefore the opposite to that associated with the neutral dyes. Consequently, the positive halochromism tends to increase as the electron-donating capacity of substituent R increases (Table 1), owing to preferential stabilisation of structure (X). It is interesting that the azonium species for both the pyrrolidinyl- and the piperidino-azo dyes absorb at essentially the same wavelengths (Table 1). Thus, Δ*E* for the transition is apparently not influenced by the size of the terminal ring. However, it seems likely that both ground and excited states are stabilised by the presence of a five-membered ring, relative to those of the acyclic analogue, whereas both states are destabilised when a six-membered terminal group is present.

As a consequence of the opposite directions of charge migration associated with electronic excitation in the neutral dyes and their azonium cations, the visible absorption bands of the two species converge with increasing electron-withdrawing capacity of R [(V) and (IX)]. An excellent linear correlation is observed between the wavelength shift ($\lambda_{\text{azonium}} - \lambda_{\text{neutral}}$), or more precisely the frequency difference, and the appropriate Hammett σ-constant [9] in agreement with theory [28] and with earlier findings.[1] For both the pyrrolidinyl- and the piperidino-azo dyes, the value of $\lambda_{\text{azonium}} - \lambda_{\text{neutral}}$ decreases steadily as the electron-accepting strength of R increases (Table 1), the absolute values being smaller in the case of the pyrrolidinyl series. The presence of more than one electron-withdrawing group in the acceptor ring of the dye can lead to negative halochromism where the azonium ion absorbs at a shorter wavelength than the neutral dye. Thus, for example, the 2-cyano-4-nitro dye (III) (R = NO_2) shows a significant negative halochromism (38 nm).

Experimental

Electronic absorption spectra were recorded with a Unicam SP 800 spectrophotometer.

The dyes were obtained by coupling the appropriate diazonium ion with *N*-phenylpyrrolidine and *N*-phenylpiperidine, respectively. The former compound, b.p. 91—92 °C at 0.6 mmHg, was prepared in 78% yield from aniline and 1,4-dichlorobutane.[13] A similar condensation involving 1,5-dichloropentane afforded *N*-phenylpiperidine, b.p. 100 °C at 0.7 mmHg, in 70% yield.

Conventional methods[4] were used to diazotise the various amines, which were then gradually added to a well stirred dispersion of the coupling component in aqueous acetic acid containing sodium acetate and kept at 0 °C for 3 h; the coupling reaction was completed by stirring the mixture overnight before basification.

The crude dyes were purified by column chromatography on alumina, using dichloromethane as solvent and eluant, followed by recrystallisation from toluene. Yields, melting points, and microanalytical data are summarised in Table 3.

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