The Effects of Cyclic Terminal Groups in 4-Aminoazobenzene and Related Azo Dyes. Part 3.[1] Electronic Absorption Spectra of Some Monoazo Dyes derived from *N*-Phenylmorpholine, *N*-(Phenyl)thiomorpholine, *N*-(Phenyl)-thiomorpholine 1,1-Dioxide, and *N*-Acetyl-*N'*-phenylpiperazine

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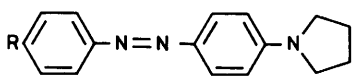
Monoazo dyes containing a terminal morpholino group absorb hypsochromically in comparision with their piperidino counterparts as a result of electron withdrawal by the oxygen atom. Similar shifts are observed with related dyes possessing other γ-heteroatoms in the donor group. In acid solution, protonation takes place at the β-azo nitrogen atom (azonium tautomer) and at the terminal nitrogen atom (ammonium tautomer) to an extent which depends on the inductive effect of the γ-substituent.

In Part 1,[2] a comparison between monoazo dyes derived from *N*-phenylpyrrolidine, (**1**), and their *N*-phenylpiperidine analogues (**2**; X = CH_2) revealed that differences in spectroscopic behaviour could be 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. In this paper the effects of incorporating a heteroatom at the γ-position of the terminal piperidino group are examined.

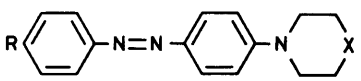
It has previously been pointed out[3] that in donor–acceptor chromogens[4] of the aminoazobenzene type (**3**), the visible electronic transition involves a migration of electron density from the donor group towards the azo moiety. Alkylation of the terminal amino group increases the electron-donating strength of the substituent and hence leads to bathochromic shifts of the long-wavelength band. Conversely, the introduction of electron-withdrawing substituents into the terminal alkyl groups brings about hypsochromic shifts of the first band.[3] For example, 4-diethylaminoazobenzene (**3**; R = H, R^1 = R^2 = Et) absorbs at 415 nm in ethanol[5] whereas compounds (**3**; R = H, R^1 = R^2 = CH_2CH_2OH) and (**3**; R = H, R^1 = R^2 = CH_2CH_2Cl) absorb at 407 (ref. 6) and 397 nm (ref. 7), respectively, in the same solvent. It has been suggested[8] that the effects of such substitution are mainly inductive and can be related quantitatively to appropriate Hammett σ-values. The use of cyclic terminal groups, however, introduces significant steric factors which vary with the size of the ring. Thus, in saturated six-membered ring systems which adopt a chair conformation, such as the piperidino substituent,[9] the equatorial protons of the α-methylene groups are directed towards the *ortho*-protons of the adjacent benzene ring. Relief of this crowding by rotation about the ring–nitrogen bond also reduces the extent of the overlap between the nitrogen lone-pair orbital and the aromatic π-electron cloud, resulting in a hypsochromic shift of $\lambda_{max.}$ together with a reduction in $\varepsilon_{max.}$.[2] The conformational properties of morpholine and piperazine are closely related to those of piperidine,[9] so that terminal substituents based on these rings are likely to have similar steric requirements.

A comparison between the dyes derived from *N*-phenylmorpholine (**2**; X = O) and their piperidino counterparts (**2**; X = CH_2) shows that, in neutral solution, the members of the former series absorb hypsochromically (Table 1). These blue shifts can be attributed to inductive electron withdrawal by the oxygen atom which reduces lone-pair conjugation still further. The values of $\varepsilon_{max.}$ for the two series are very similar, in line with essentially identical steric requirements. These results are somewhat at variance with the limited data reported by Mustroph,[10] who overestimates the angle of rotation of the morpholino group in the parent dye (**2**; R = H, X = O) on the basis of a low value for $\varepsilon_{max.}$. The hypsochromic influence of the morpholino oxygen atom is greater than that exerted by two hydroxy groups in the acyclic analogues (**3**; R^1 = R^2 = CH_2CH_2OH). Thus, for example, the shift of −8 nm observed on passing from 4-diethylaminoazobenzene to dye (**3**; R = H, R^1 = R^2 = CH_2CH_2OH) ($\lambda_{max.}$ 407 nm in ethanol) is increased to −14 nm when the morpholino dye (**2**; R = H, X = O) is compared with the piperidino parent (**2**; R = H, X = CH_2) (Table 1). This difference may be related to the greater electron density at the terminal nitrogen atom in the more sterically hindered heterocyclic dyes as compared with the acyclic analogues.

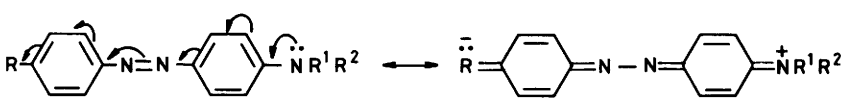
Dyes derived from *N*-(phenyl)thiomorpholine (**2**; X = S) are less hypsochromic than those prepared from *N*-phenylmorpholine (Table 1), in keeping with the lower inductive



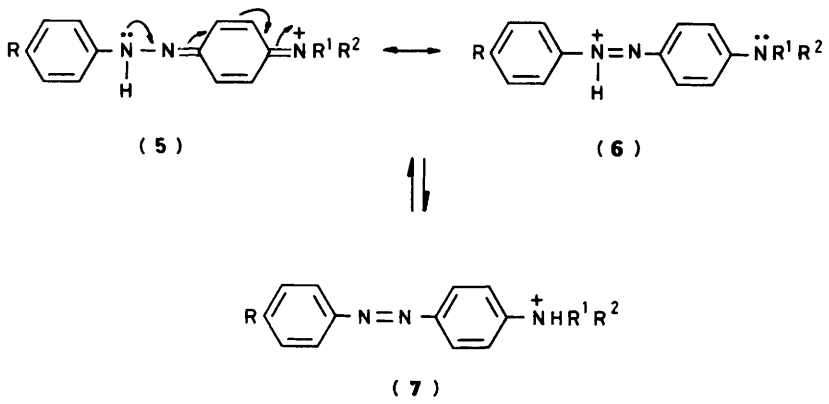
(**1**)



(**2**)



(**3**) (**4**)



(5) (6) (7)

Table 1. Absorption bands of some dyes derived from *N*-phenylpiperidine, *N*-phenylmorpholine, *N*-(phenyl)thiomorpholine, *N*-(phenyl)thiomorpholine 1,1-dioxide, and *N*-acetyl-*N'*-phenylpiperazine in ethanol, and halochromism in ethanol–hydrochloric acid

Dye (2)		$\lambda_{max.}$/nm	$10^{-4}\varepsilon_{max.}$	$\lambda_{max.}$/nm	$10^{-4}\varepsilon_{max.}$	$\Delta\lambda$/nm
R	X	(ethanol)		(EtOH + HCl)		
OMe	CH_2	398	2.80	558	0.12	160
H	CH_2	400	2.49	528	0.35	128
Cl	CH_2	412	2.85	534	0.26	122
CF_3	CH_2	423	2.69	515	0.64	92
CN	CH_2	442	2.89	521	0.99	79
NO_2	CH_2	470	2.76	522	1.33	52
OMe	O	386	2.77	566	1.04	180
H	O	386	2.39	525	2.33	139
Cl	O	396	2.51	530	1.68	134
CF_3	O	404	2.31	514	3.05	110
CN	O	420	2.85	520	3.80	100
NO_2	O	437	2.73	520	4.78	83
OMe	S	393	2.49	569	1.53	176
H	S	395	2.33	531	3.38	136
Cl	S	407	2.52	534	3.40	127
CF_3	S	417	2.54	517	4.56	100
CN	S	434	2.83	522	5.65	88
NO_2	S	456	2.83	526	6.74	70
OMe	SO_2	381	3.01	558	6.08	177
Cl	SO_2	388	2.52	535	6.63	147
CF_3	SO_2	394	2.13	535	6.54	141
CN	SO_2	408	2.67	542	7.79	134
NO_2	SO_2	422	2.55	547	7.28	125
OMe	NAc	387	2.64	565	4.76	178
H	NAc	387	2.47	535	5.92	148
Cl	NAc	396	2.78	532	6.36	136
CF_3	NAc	405	2.45	537	6.38	132
CN	NAc	421	2.80	540	6.97	119
NO_2	NAc	437	2.58	546	7.71	109

strength of sulphur. The values of $\varepsilon_{max.}$ for all the series are close, thereby confirming that the steric requirements of the various six-membered terminal rings are effectively constant. Inductive electron withdrawal by the γ-heteroatom is greatly increased in dyes obtained from *N*-(phenyl)thiomorpholine 1,1-dioxide (**2**; X = SO_2) (Table 1). The $\lambda_{max.}$ values of the various dyes originating from *N*-acetyl-*N'*-phenylpiperazine (**2**; X = NAc) are almost identical with those of the corresponding morpholine derivatives (Table 1). This finding can be related to the very similar Hammett σ_m values for methylthio and acetylamino groups.[11] The acetyl derivative of *N*-phenylpiperazine was chosen as a coupler in an attempt to obviate any complications arising from protonation of the γ-heteroatom of the derived dyes in acid solution. The data given in Table 1 show that the electron-donor power of the terminal substituent decreases in the order piperidino > thiomorpholino > morpholino ~ *N*-acetylpiperazinyl > dioxothiomorpholino. This sequence is supported, in part, by ^{1}H n.m.r. chemical shifts of protons *ortho* to NR_2 groups in benzene derivatives[12] and by dipole moment measurements of some of the parent *N*-phenyl amines.[13]

For each series of dyes, the effects of *para*-substituents on $\lambda_{max.}$ can be accounted for qualitatively in terms of the valence-bond resonance approach.[2] Thus, for the system (**3**) ⟷ (**4**), the high-energy dipolar structure (**4**), which can be regarded as a fairly close approximation to the excited state of the molecule, is stabilised when R is an electron-withdrawing group, so that such substituents exert a bathochromic effect, since ΔE becomes smaller. The first band is shifted by an amount that is approximately proportional to the appropriate Hammett σ-constant.

In acid solution, there are clear differences amongst the various series. As pointed out previously,[2] 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, leads to an increase in electron density at the terminal nitrogen atom and a decrease at the azo group. Consequently, this dye system (**2**; X = CH_2) is readily protonated at the piperidino nitrogen atom (ammonium tautomer). Electron-withdrawing groups in the acceptor ring of the piperidinoazo dyes, however, increase the amount of azonium ion present by increasing the conjugation of the terminal line pair (Table 1). The tautomeric equilibrium, represented in general terms by [(**5**) ⟷ (**6**)] ⇌ (**7**), is dependent on the γ-substituent in the terminal six-membered ring. Thus, inductive electron withdrawal reduces the electron density at the two protonation sites and consequently increases the amount of acid needed to generate a cation; for example, the parent piperidinoazo dye (**2**; R = H, X = CH_2) requires 1 000 equiv. of hydrochloric acid to give an optimum concentration of azonium ion, whereas the corresponding morpholino compound (**2**; R = H, X = O) needs 40 000 equiv. At the same time, the β-azo nitrogen atom becomes a relatively more favoured site for protonation, especially when the dye contains an electron-withdrawing *para*-substituent, and this situation is reflected in the $\varepsilon_{max.}$ values (Table 1). In the case of the morpholinoazo dyes, the methoxy compound (**2**; R = OMe, X = O) exists largely as the ammonium tautomer in acid solution, in contrast to the nitro derivative (**2**; R = NO_2, X = O) where the azonium form is dominant. This situation is accentuated with the corresponding sulphur analogues whereas the opposite effect might be expected on the basis of the lower electronegativity of sulphur. The dyes derived from *N*-acetyl-*N'*-phenylpiperazine and from *N*-(phenyl)thiomorpholino 1,1-dioxide, in particular, exist in acid solution almost entirely as the azonium tautomers. Since

the amount of acid present in these cases is high, it is possible that a positive charge is developed at the γ-heteroatom by protonation at the acetyl group and at the sulphone group, respectively, so that the electron density at the terminal nitrogen atom is greatly reduced. In this connection, it is clear that the close similarity shown by the morpholinazo dyes and the *N*-acetyl-*N'*-phenylpiperazinylazo dyes in neutral solution is lost in ethanolic hydrogen chloride (Table 1).

Comparison with the neutral dye system, (**3**) ⟷ (**4**), shows that for the azonium species, (**5**) ⟷ (**6**), the ground and excited states are much closer in energy terms so that a bathochromic shift is observed on protonation (positive halochromism). For this system, the visible electronic transition involves a migration of electron density from the β-nitrogen atom to the terminal nitrogen atom.[2] Consequently, the positive halochromism tends to increase as the electron-donating capacity of substituent R increases, due to preferential stabilisation of structure (**6**). For the various series of dyes shown in Table 1, only small changes are observed in the $\lambda_{max.}$ values for the azonium ions. As a consequence of the opposite directions of charge migration associated with electronic excitation in the neutral dyes and their azonium cations, however, the visible absorption bands of the two species converge with increasing electron-withdrawing capacity of R [(**3**) and (**5**)]. As with other series of azo dyes,[2,3] excellent linear correlations are found between the wavelength shift on protonation (Δλ) and the appropriate Hammett σ-constant. A comparison amongst the different cyclic terminal groups can be made from a consideration of the Δλ values for the various *p*-nitro derivatives. Thus, the electron-donor power of the heterocyclic group decreases in the order piperidino > thiomorpholino > morpholino > *N*-acetylpiperazinyl > dioxothiomorpholino. This sequence is

Table 2. Preparative and microanalytical data for some azo dyes

Dye (**2**)						Required (%) [Found (%)]				
R	X	M.p. (°C)	Crude yield (%)	Appearance	Molecular formula	C	H	N	Hal	S
OMe	O	215—217	50	Orange leaflets[a]	$C_{17}H_{19}N_3O_2$	68.7 [68.8	6.4 6.5	14.15 14.25]		
H	O	194—196	66	Yellow leaflets[a]	$C_{16}H_{17}N_3O$	71.9 [71.9	6.35 6.35	15.75 15.95]		
Cl	O	202—204	69	Orange plates[a]	$C_{16}H_{16}ClN_3O$	63.7 [63.35	5.3 5.4	13.95 13.8	11.75 11.9]	
CF_3	O	219.221	90	Orange leaflets[a]	$C_{17}H_{16}F_3N_3O$	60.9 [61.3	4.8 4.8	12.55 12.6	17.0 16.85]	
CN	O	209	209—211	Red leaflets[a]	$C_{17}H_{16}N_4O$	69.85 [69.9	5.5 5.6	19.2 19.35]		
NO_2	O	229—230	82	Purple needles[a]	$C_{16}H_{16}N_4O_3$	61.55 [61.5	5.15 5.2	17.95 18.15]		
OMe	S	147—159	73	Orange crystals[b]	$C_{17}H_{19}N_3OS$	62.5 [65.2	6.05 5.95	13.4 13.6		10.2 10.25]
H	S	152—153	87	Yellow flakes[b]	$C_{16}H_{17}N_3S$	67.85 [67.8	6.0 6.0	14.85 14.6		11.3 11.55]
Cl	S	179—181	63	Orange needles[b]	$C_{16}H_{16}ClNS$	60.45 [60.5	5.05 5.0	13.25 13.1	11.2 11.05	10.1 10.15]
CF_3	S	178—180	96	Red leaflets[b]	$C_{17}H_{16}F_3N_3S$	58.1 [57.9	4.55 4.25	12.0 11.95	16.25 16.35	9.1 9.05]
CN	S	182—184	91	Red crystals[a]	$C_{17}H_{16}N_4S$	66.25 [66.2	5.2 5.1	18.2 18.1		10.4 10.05]
NO_2	S	220—222	76	Red plates[b]	$C_{16}H_{16}N_4O_2S$	58.55 [58.65	4.9 4.6	17.05 17.05		9.75 9.4]
OMe	SO_2	227—229	*e*	Yellow leaflets[a]	$C_{17}H_{19}N_3O_3S$	59.15 [59.3	5.5 5.3	12.2 12.45		9.3 9.35]
Cl	SO_2	238—240	49	Yellow leaflets[a]	$C_{16}H_{16}ClN_3O_2S$	54.95 [55.25	4.6 4.45	12.0 11.75	10.15 10.45	9.15 9.25]
CF_3	SO_2	221—223	55	Orange crystals[a]	$C_{17}H_{16}F_3N_3O_2S$	53.25 [53.25	4.2 4.2	11.0 11.15	14.9 14.7	8.35 8.65]
CN	SO_2	273—275	69	Orange crystals[c]	$C_{17}H_{16}N_4O_2S$	60.0 [60.2	4.7 4.7	16.5 16.3		9.4 9.05]
NO_2	SO_2	279—281	79	Dark red crystals[a]	$C_{16}H_{16}N_4O_4S$	53.35 [53.7	4.45 4.45	15.55 15.3		8.9 8.9]
OMe	NAc	213—214	30	Yellow flakes[a]	$C_{19}H_{22}N_4O_2$	67.45 [67.1	6.5 6.65	16.55 16.8]		
H	NAc	209—210	49	Orange needles[a]	$C_{18}H_{20}N_4O$	79.15 [70.45	6.5 6.45	18.2 18.25]		
Cl	NAc	226—227	81	Orange leaflets[a]	$C_{18}H_{19}ClN_4O$	63.05 [63.0	5.55 5.65	16.35 16.3	10.35 10.15]	
CF_3	NAc	208—209	85	Orange powder[a]	$C_{19}H_{19}F_3N_4O$	60.65 [60.9	5.05 5.2	14.9 15.05	15.15 15.3]	
CN	NAc	207—209	80	Orange leaflets[a]	$C_{19}H_{19}N_5O$	68.45 [68.8	5.7 5.6	21.0 21.2]		
NO_2	NAc	238—240	43	Dark red powder[a]	$C_{18}H_{19}N_5O$	61.2 [60.85	5.4 5.05	19.85 19.9]		

[a] Toluene. [b] Dichloromethane–light petroleum (b.p. 40—60 °C). [c] Acetic acid, then butanol. [d] Acetic acid. [e] Mainly coupler.

effectively the same as that deduced from an examination of the dyes in neutral solution.

Experimental

Electronic absorption spectra were recorded with a Unicam SP 800 spectrophotometer for solutions of the dyes in ethanol and ethanol containing dissolved hydrogen chloride. The quantity of hydrogen chloride required to obtain optimal protonation of the azo group, between 1 000 and 3×10^6 equiv., varied according to the nature of the cyclic terminal group.

The dyes were obtained by coupling the appropriate diazonium ion with *N*-phenylmorpholine, *N*-(phenyl)thiomorpholine, *N*-(phenyl)thiomorpholine 1,1-dioxide, and *N*-acetyl-*N'*-phenylpiperazine. The first of these compounds, m.p. 53 °C,[14] was commerically available. The preferred route to *N*-(phenyl)thiomorpholine, m.p. 31—32 °C,[15] involved conversion of *N*,*N*-bis-(2-hydroxyethyl)aniline into *N*,*N*-bis-(2-chloroethyl)aniline, m.p. 42—44 °C,[15] with phosphorus pentachloride in chloroform and subsequent reaction with sodium sulphide in ethanol. *N*-(Phenyl)thiomorpholine 1,1-dioxide, m.p. 118—121 °C,[16] was prepared in 30% yield from aniline and divinyl sulphone. *N*-Acetyl-*N'*-phenylpiperazine, m.p. 96 °C,[17] was obtained in 87% yield from the parent amine.

Conventional methods[18] were used to diazotise the various amines, each of which was then gradually added to a well stirred dispersion of the coupling component in aqueous acetic acid containing sodium acetate. The mixture was kept at 0 °C for 3 h and the coupling reaction was then completed by stirring the mixture overnight before basification. In the case of the deactivated *N*-(phenyl)thiomorpholine 1,1-dioxide, however, reaction with the more weakly electrophilic diazonium ions proved to be very difficult and incomplete; some improvement resulted from using a phase-transfer procedure.[19] It was not possible to isolate a pure sample of the parent dye (**2**; R = H, X = SO_2).

The crude dyes were generally purified by column chromatography on alumina, using dichloromethane as solvent and eluant, followed by recrystallisation from toluene. The thiomorpholine dyes, with the exception of (**2**; R = CN, X = S), were dissolved in toluene for chromatographic purification. Two column treatments were required in the case of (**2**; R = OMe, X = SO_2), followed by preparative layer chromatography on silica, before recrystallisation, using toluene throughout. The dye (**2**; R = CN, X = NAc) was chromatographed on silica. Yields, m.p.s, and microanalytical data are summarised in Table 2.

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