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Disperse and Cationic Azo Dyes from Heterocyclic Intermediates

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ABSTRACT

A series of aminophenyl-X-azolopyridines were diazotized and coupled to N,N-*diethylaniline. The resulting disperse dyes showed a great versatility towards different fibres such as polyamide, polyester and cellulose acetate. The disperse dyes were transformed into cationic dyes by reaction with methyl iodide. The quaternized dyes dyed polyacrylonitrile fibres with excellent uniformity without using a retarding agent. Physical and spectroscopic parameters, fastness on dyed fabrics and colour data were correlated with the structure of the dyes. Two-dimensional proton-NMR NOESY experiments were useful for the assessment of particular structures.*

1 INTRODUCTION

Substituted azobenzene dyes containing hetaryl moieties such as *m*- and *p*-aminophenyl-X-azolo[4,5-*b*]pyridines have been previously synthesized and their coloration properties on polyamide 6-6, cellulose acetate and

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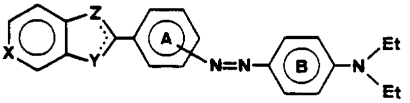
polyester evaluated. Furthermore, their cationic analogues showed similarly good properties on polyacrylic fibres, avoiding the use of retarding and levelling auxiliaries.[1–3] The present paper deals with isomeric dyes, having a different anellation, i.e. [4,5-*c*] or [5,4-*c*], as represented by the general formula **I**.



I

X = N, $^{+}NCH_3$
Y = N, NCH_3
Z = O, S, NH, N, NCH_3

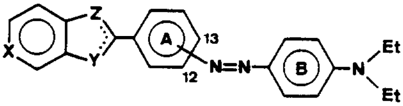
2 EXPERIMENTAL

2.1 Dyes and intermediates

The synthesis of the starting amines has been described elsewhere.[4] Structures and characterization data of the azo dyes are shown in Table 1.

Dyes **1**, **3**, **4** and **5** were obtained by diazotization of the corresponding amines with sodium nitrite/hydrochloric acid and coupling to *N*,*N*-diethylaniline in acetic acid. The pH was then adjusted to 4·5 with a

TABLE 1
Characterization Data of Dyes **I**



Dye no.	*Position in the A-ring*	*X*[a]	*Y*	*Z*[a]	*M.p. (°C)*	λ_{max}	*log ε*	R_f
1	13	N	N	S	205–208	474	4·48	0·88
2	13	N	N	O	184–186	471	4·51	0·82
3	13	N	N	NCH_3	225–227	447	4·44	0·47
4	13	N	NCH_3	N	262–263	452	4·57	0·55
5	12	N	N	S	162–164	433	4·38	0·90
6	12	N	N	O	148–150	431	4·42	0·88
7	13	$^{+}NCH_3$	N	S	240–241	497	4·70	0·35
8	13	$^{+}NCH_3$	N	O	236–238	492	4·58	0·33
9	13	$^{+}NCH_3$	N	NCH_3	244–245	465	4·55	0·26
10	13	$^{+}NCH_3$	NCH_3	N	242–243	477	4·63	0·27
11	12	$^{+}NCH_3$	N	S	203–206	447	4·60	0·36
12	12	$^{+}NCH_3$	N	O	215–216	438	4·50	0·35

[a] The counterion of dyes **7–12** is iodide.

saturated solution of sodium acetate; the crude dyes were collected, washed with water and crystallized from ethanol/water.

Dyes **2** and **6** were similarly prepared, but diazotization was effected with hydrochloric acid/isoamyl nitrite. The crude products were crystallized from ethanol/water. Cationic dyes **7**–**12** were obtained by refluxing the disperse dyes **1**–**6** with an excess of methyl iodide in *tert*-butyl alcohol for 20 h. The crude dyes were collected and crystallized from *tert*-butyl alcohol/ligroin.

2.2 Chromatography

R_f values were determined on silica gel 60 F-254 TLC plates (Merck), using *n*-butanol/acetic acid/water (BAW) (4:1:5, by vol.) as eluent.

2.3 Spectra and colour measurements

The electronic spectra were determined on a Pye–Unicam SP 8-100 spectrophotometer using methanol as solvent (molarity of the dyes 1×10^{-5}). In view of the phototropic *trans–cis* isomerization of 4-aminoazobenzene and its derivatives,[5] dye solutions were retained in the cells in the spectrophotometer until the maximum ε value was reached.

The colour parameters of the dyed fabrics were determined on a Cary 210 spectrophotometer equipped with an integrating sphere and connected to an Apple II computer, using the D_{65} source and barium sulphate as standard blank.

^{1}H-NMR spectra were obtained with a JEOL EX 400 spectrometer in DMSO-d_6 solution (2%). The two-dimensional NOESY experiment was performed with a spectral width of 3700 Hz over 2 K. The mixing time was set at 500 ms. The spectrum (32 scans) was obtained after multiplying the data with a squared sine bell function in both dimensions.

2.4 Dyeing and fastness determinations

The dyeing procedures have been previously detailed.[3] The fastness properties were assessed by standard procedures.[6] Lightfastness was determined on a Xenotest 150.

3 RESULTS AND DISCUSSION

3.1 Melting points and chromatographic data

The R_f and melting point values show regular patterns when compared with previously described analogous compounds.[2,3] Thus, *meta* isomers are lower-melting than *para* ones, and the trend is reversed with respect to R_f values. The presence of the positive charge (with the exception of **4** and **10**) in cationic dyes raises the melting points and markedly lowers the R_f values, the charged molecules being more retained on the polar substrate.

N-Methylimidazoles **3** and **4** show surprisingly low R_f values (0·47 and 0·55), as observed for the parent amines.[4] This could be due to the stronger basicity of heterocyclic functionalities which allows a more intense interaction with the acidic sites of the substrate.

3.2 ^{1}H-NMR spectra

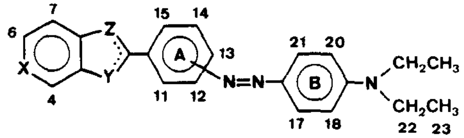
In Table 2 ^{1}H-NMR data are reported for the series of dyes. In ambiguous cases the assignments of the aromatic protons were made using selective decoupling techniques and by comparison with simpler systems, i.e. dyes containing substituents other than heteroaryls.

To obtain more conclusive data, two-dimensional proton NMR NOESY[7] spectra were also recorded for compound **8**, which was selected as a typical representative for structural elucidation in the whole series of dyes, i.e. determination of the reaction site of the heterocycles with methyl iodide. This experiment offers a means of determining spatial relationships between nuclei in a molecule by allowing the observation of nuclear Overhauser effect (nOe)[8] cross peaks between neighbouring nuclei. In the spectrum reported in Fig. 1, the bond of the methyl group with the pyridine nitrogen is straightforward since the methyl shows a cross peak with H_4 and a weaker correlation with the H_6 proton. Furthermore, the spectrum shows (i) the connectivities between contiguous pairs of protons shown by the corresponding cross peaks (pairs **6–7**, **11–12**, **17–18**) and (ii) the correctness of the assignments reported in Table 2 (for example, the attribution of signals to protons 6 and 7 without NOESY experiments could have been ambiguous).

From the data in Table 2 some generalizations can be drawn. Protons in the benzene B ring and *ethyl* protons are practically unaffected by the nature of the Z and Y heteroatoms and by the quaternization. These observations preclude the reaction of methyl iodide with the nitrogen atoms near the above-mentioned protons. Changes of heteroatoms in the pentatomic ring influence the chemical shifts of the protons of the benzene A ring contiguous to the linking position. The deshielding effects follow the order $O > S > NCH_3$. After quaternization, the same protons are deshielded in the range 0·06–0·14 ppm.

The protons in the pyridine ring are obviously more affected (i) by the nature of Z and Y heteroatoms (0·09–0·60 ppm) and (ii) by the presence of the positive charge in cationic dyes (0·29–0·73 ppm). Among these protons, H_4

TABLE 2
^{1}H-NMR Spectra of Dyes **I**



Dye no.	Position in the A-ring	X^a	Y	Z^a	4	6	7	10	11	12	14	15	17	18	22	23	NCH_3	$^+NCH_3$
1	13	N	N	S	9·37	8·57	8·28	—	8·30	7·96	7·96	8·30	7·85	6·86	3·51	1·19	—	—
2	13	N	N	O	9·18	8·66	7·96	—	8·38	7·98	7·98	8·38	7·85	6·86	3·52	1·21	—	—
3	13	N	N	NCH_3	9·02	8·42	7·74	—	8·08	7·96	7·96	8·08	7·85	6·85	3·51	1·20	3.99	—
4	13	N	NCH_3	N	9·02	8·41	7·68	—	8·07	7·96	7·96	8·07	7·85	6·87	3·52	1·22	4·06	—
5	12	N	N	S	9·40	8·58	8·29	8·18	—	8·47	8·02	7·78	7·87	6·86	3·52	1·19	—	—
6	12	N	N	O	9·20	8·69	7·98	8·28	—	8·55	8·08	7·82	7·87	6·85	3·51	1·19	—	—
7	13	$^+NCH_3$	N	S	9·95	8·94	8·87	—	8·38	7·99	7·99	8·38	7·85	6·87	3·52	1·19	—	4·50
8	13	$^+NCH_3$	N	O	9·80	9·05	8·64	—	8·44	8·04	8·04	8·44	7·86	6·88	3·52	1·19	—	4·49
9	13	$^+NCH_3$	N	NCH_3	9·63	8·78	8·42	—	8·16	8·00	8·00	8·16	7·86	6·87	3·52	1·19	4·17	4·46
10	13	$^+NCH_3$	NCH_3	N	9·75	8·70	8·32	—	8·21	8·01	8·01	8·21	7·86	6·87	3·52	1·19	4·14	4·44
11	12	$^+NCH_3$	N	S	10·01	8·96	8·90	8·27	—	8·52	8·10	7·93	7·87	6·86	3·51	1·19	—	4·51
12	12	$^+NCH_3$	N	O	9·84	9·07	8·68	8·34	—	8·59	8·18	7·88	7·88	6·87	3·52	1·20	—	4·51

[a] The counterion of dyes **7**–**12** is iodide.

TABLE 3
Fastness Properties of Dyes **I**
An asterisk indicates a rating of 5

Dye no.[a]	*Washing*[b]															*Perspiration*[b]						*Acid*	*Alkali*	*Tetra-chloro-ethylene*[b]			*Rubbing*		*Light*
	CO1 40°C			*CO2 50°C*			*CO3 60°C*			*CO4 95°C*			*CO5 95°C+ steel balls*			*pH 5*			*pH 8*								*Dry*	*Wet*	
1	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$	3	$\frac{4}{5}$	$\frac{2}{3}$	3	$\frac{4}{5}$	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{2}{3}$
2	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$	3	$\frac{4}{5}$	3	3	$\frac{4}{5}$	*	*	*	*	*	*	*	*	*	*	*	*	*	4
3	*	*	*	*	*	*	4	*	*	$\frac{2}{3}$	*	*	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$
4	*	*	*	*	*	*	4	*	*	1	*	*	1	4	*	*	*	*	*	*	*	*	*	*	$\frac{4}{5}$	*	*	*	4
5	*	*	*	*	*	*	$\frac{4}{5}$	*	$\frac{4}{5}$	3	$\frac{2}{3}$	*	2	3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$
6	*	*	*	*	*	*	*	*	*	3	3	*	$\frac{2}{3}$	3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$
1	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{4}{5}$	$\frac{4}{5}$	*	*	*	*	*	*	*	*	*	*	*	*	*	3
2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{2}{3}$
3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{2}{3}$
4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
5	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$

1	*	*	*	*	*	*	*	*	*	2	4	$\frac{4}{5}$	1	$\frac{3}{4}$	$\frac{4}{5}$	*	*	*	*	*	*	*	*	*	*	*	*	*	2
2	*	*	*	*	*	*	*	*	*	$\frac{1}{2}$	4	$\frac{4}{5}$	1	$\frac{3}{4}$	4	*	*	*	*	*	*	*	*	*	*	*	*	2	$\frac{4}{5}$
3	*	*	*	*	*	*	*	*	*	$\frac{2}{3}$	*	*	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
4	*	*	*	*	*	*	*	*	*	3	*	*	1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$
5	*	*	*	*	*	*	*	*	*	2	$\frac{4}{5}$	*	1	$\frac{3}{4}$	*	*	*	*	*	*	*	*	*	*	*	*	4	3	4
6	*	*	*	*	*	*	*	*	*	$\frac{2}{3}$	4	*	1	4	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{4}{5}$	4	$\frac{5}{6}$
7	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{3}{4}$
8	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{4}{5}$	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
9	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
10	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
11	*	*	*	*	*	*	*	*	*	*	*	*	$\frac{4}{5}$	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
12	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2

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[a] Structures in Table 1. The first set of data refers to polyamide, the second to polyester, the third to cellulose acetate, and the fourth to polyacrylonitrile.

[b] Values in the first column of each test refer to the change of colour, in the second column to the staining of the proper fibre (indicated in Ref. 6) and in the third column to the staining of the same kind of fibre as the specimen.

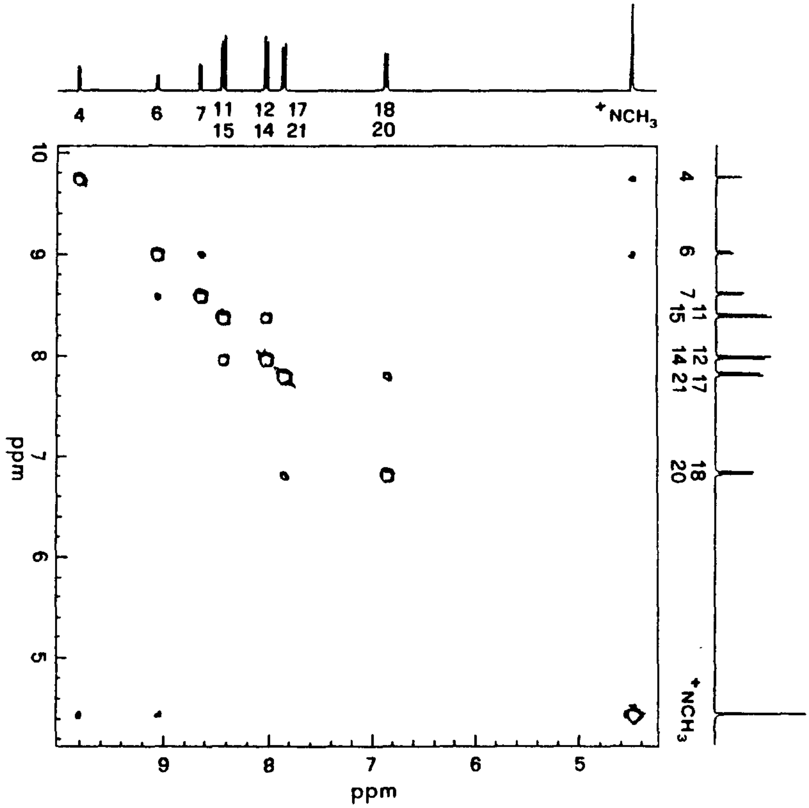

Fig. 1. Part of the two-dimensional NOESY proton spectrum of compound **8** (400 MHz) showing the aromatic protons and their relationship to the *N*-methyl resonance via the cross peaks shown.

shows the highest chemical shift values, whereas H_7 (followed by H_4) is the most susceptible to the introduction of the positive charge.

3.3 Electronic absorption spectra

In view of the well-established electron-withdrawing character of heteroaryls[9] and the electron-releasing character of the *N*,*N*-diethylamino substituent, the dyes may be considered as donor–acceptor-substituted azobenzenes.[3] If *para* isomers are compared with their *meta* analogues, marked bathochromic ($\Delta\lambda_{max} = 40$–54 nm) and hyperchromic ($\Delta \log \varepsilon =$ 0·08–0·10) effects are observed for both uncharged (pairs **1**–**5**, **2**–**6**) and charged dyes (pairs **7**–**11**, **8**–**12**). Similar effects are apparent on comparison of the cationic dyes with their precursors ($\Delta\lambda_{max} = 7$–25 nm, $\Delta \log \varepsilon =$ 0·21–0·54, pairs **1**–**7**, **2**–**8**, **3**–**9**, **4**–**10**, **5**–**11**, **6**–**12**). Furthermore, the above effects, due to the heteroaryl → heteroarylium change are, as expected, more marked for *para* isomers. With respect to the effect of the structure of the heteroaryl moiety, the higher basicity of *N*-methylimidazoles (**3**, **4**, **9** and **10**; i.e. both neutral and charged dyes) causes a lowering of the electron-attracting ability and, therefore, the λ_{max} of the dyes are blue-shifted compared with their oxazole and thiazole analogues. The above data agree with those obtained from chromatographic tests.

TABLE 4
Colour of Dyed Fibres

Dye no.[a]	*Luminance factor Y (%)*	*CIELAB coordinates*			*Helmholtz coordinates*		λ_{max} (*nm*)
		L^*	a^*	b^*	*Dominant wavelength, λ_D (nm)*	*Purity, P (%)*	
1	35·24	65·93	45·08	50·07	595	69·13	474
2	37·42	67·59	45·30	61·24	593	77·44	471
3	50·29	76·25	31·97	72·58	587	79·47	452
4	63·37	83·64	17·00	49·05	583	54·89	447
5	68·24	86·13	6·96	86·77	578	81·55	433
6	63·70	83·81	5·23	84·43	578	81·24	431
1	37·80	67·88	42·56	57·97	592	74·45	474
2	38·92	68·69	36·38	60·41	590	75·32	471
3	59·02	81·30	20·27	72·70	583	75·92	452
4	55·99	79·61	23·07	66·87	584	72·83	447
5	66·44	85·22	2·38	80·11	577	77·57	433
6	59·04	81·31	6·81	83·68	578	82·17	431
1	42·02	70·89	34·62	42·05	592	57·07	474
2	41·37	70·43	37·30	55·31	590	70·14	471
3	53·61	78·23	27·62	80·57	585	83·14	452
4	66·31	85·15	13·84	49·42	582	54·09	447
5	65·87	84·93	3·82	77·51	577	76·07	433
6	63·29	83·60	13·74	101·66	580	90·23	431
7	15·70	46·58	55·66	10·42	495[b]	45·62	497
8	22·43	54·48	53·98	20·96	626	45·34	492
9	17·92	49·40	63·86	3·42	498[b]	51·52	477
10	19·83	51·65	63·11	−1·90	496[b]	50·09	465
11	36·27	66·73	47·56	42·55	598	61·82	447
12	34·44	65·31	42·76	44·28	595	63·72	438

[a] Structures in Table 1. The first set of data refers to polyamide, the second to polyester, the third to cellulose acetate, and the fourth to polyacrylonitrile.

[b] Complementary wavelength λ_C (nm).

3.4 Dyeing properties

Table 3 reports the fastness properties of the dyes on four substrates: polyester, polyamide 6-6, cellulose acetate and polyacrylonitrile. An asterisk indicates the maximum rating (5) and makes the overall data self-evident, showing the main deviations.

Excellent exhaustion of dye liquors, levelling and colour yields were obtained at 0·25–1% depths, Disperse dyes showed a great versatility, giving good results on three different substrates. Cationic dyes, as previously observed for [4,5-*b*] isomers, gave excellent uniformity of coloration of acrylic fabrics without the use of a retarding agent. Besides the behaviour of individual dyes, some falling-off was observed in the most drastic washing tests at 95°C, although these conditions are in practice quite unusual. Lightfastness ratings generally showed medium-to-low values, with the exception of dyeings on cellulose acetate, which showed, in some cases, very good ratings.

3.5 Colour assessment

Table 4 reports the colour parameters of dyed fabrics assessed by tristimulus colorimetry. From this point of view, the main structural features which influence the colour are (i) the position in the A-ring, i.e. *para* or *meta* isomerism in thiazole and oxazole derivatives and (ii) the presence of the *N*-methylimidazole moiety. Thus, as a general trend, values of λ_{max} in solution, of λ_D and of redness (a^*) decrease in the order *para* $>$ N—CH$_3$ $>$ *meta*, whereas luminance factor ($Y\%$), luminosity (L^*), yellowness (b^*) and purity ($P\%$) increase. The colour shifts of acrylic fibres (dyed with cationic dyes) towards red and purplish-red hues were larger than the values estimated from λ_{max} data of the dyes in solution.

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