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Disperse and Cationic Dyes from 2-(*o*,*m*,*p*-Aminophenyl)oxazolo[4,5-*b*]pyridine†

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ABSTRACT

*2-(*o,m,p*-Aminophenyl)oxazolo[4,5-*b*]pyridines were diazotized and coupled with N,N-disubstituted anilines, giving monoazo dyes suitable for polyamide fabrics. Some of the dyes were quaternized to give cationic dyes for acrylic fibres. The colour of dyed materials was assessed in terms of tristimulus colorimetry. Electronic spectra of the amines and NMR spectra of the cationic dyes are briefly discussed.*

1. INTRODUCTION

By reacting carboxylic groups or their derivatives with *o*-aminophenols,[1] many benzoxazoles, suitable as intermediates for the synthesis of heterocyclic dyes, have been obtained previously.[2–4]

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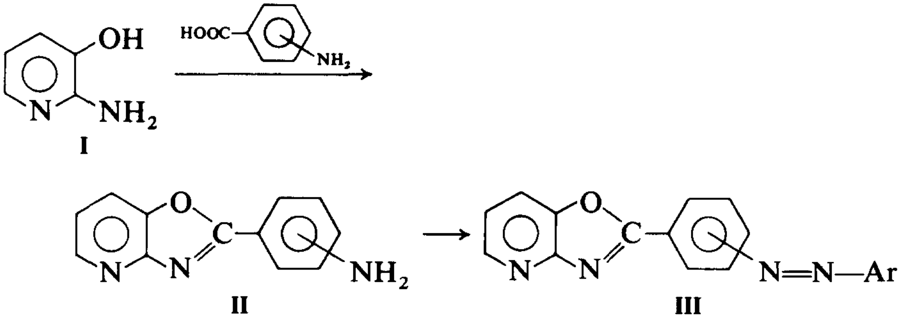
This paper deals with the synthesis of a series of monoazo dyes of the general formula **III**, obtained by diazotization and coupling of amines **II** which, in turn, were derived by the condensation of 2-amino-3-hydroxypyridine (**I**) with *o,m,p*-aminobenzoic acids. In view of the presence of two quaternizable nitrogens in dyes **III** (the azine and the azole nitrogens) some of them were converted into the corresponding cationic dyes. Dyes **III** were found to be suitable for dyeing polyamide fabrics as disperse dyes. The corresponding quaternary salts dyed acrylic fibres.



2. EXPERIMENTAL

2.1. Intermediates and dyes

Commercial 2-amino-3-hydroxypyridine, *o,m,p*-aminobenzoic acids, *N,N*-dimethylaniline, *N,N*-diethylaniline, *N,N*-bis(2-hydroxyethyl)aniline, *N*-ethyl-*N*-(2-hydroxyethyl)aniline, *N*-ethyl-*N*-(2-cyanoethyl)aniline, *N*-(2-hydroxyethyl)-*N*-(2-cyanoethyl)aniline and 2-methoxy-5-methylaniline were employed in the syntheses of **II** and **III**.

2-(*o,m,p*-Aminophenyl)oxazolo[4,5-*b*]pyridines (**IIa, IIb, IIc**) were prepared by condensing *o,m,p*-aminobenzoic acid (1 mol) with 2-amino-3-hydroxypyridine (1 mol) in polyphosphoric acid (85% phosphorus pentoxide). The mixture was stirred at 160 °C for 6 h, and poured into water. The pH was adjusted to 4 with aqueous sodium hydroxide and the yellow solid collected, dried, and crystallized from ethanol/water.

Electronic spectra in ethanol are reported in Fig. 1a. Melting points (°C), elemental analyses (C %, H %, N %, Calc./Found) and R_f values were:

IIa, 236–6, 68·24/68·38, 4·29/4·37, 19·89/19·77, 0·86;

IIb, 182–3, 68·24/68·27, 4·29/4·44, 19·89/19·85, 0·75;

IIc, 262–3, 68·24/68·19, 4·29/4·30, 19·89/19·92, 0·82.

An alternative method of synthesis of amine **IIb** has been reported previously.[5]

2-(*o*-Aminophenyl)benzoxazole was prepared as indicated in ref. 6.

The diazotization of the amines was carried out by usual procedures. The coupling was made in moderately acidic medium in the presence of sodium acetate. The dyes, crystallized as indicated in Table 1, gave correct elemental analyses.

The quaternary salts were obtained by refluxing the dyes with an excess of methyl iodide for 12 h. The crude material was washed with diethyl ether and crystallized as indicated in Table 1. The salts gave correct elemental analyses.

2.2. Chromatography

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

2.3. Spectra

The electronic spectra were determined on a Pye–Unicam SP8-100 spectrophotometer in ethanol. Nuclear magnetic resonance spectra were obtained with a Varian T-60 spectrometer in DMSO-d_6 solution (6 %) using TMS as internal standard.

2.4. Dyeings and fastness determinations

Dyeings on polyamide 6.6 were carried out as indicated in refs. 7 and 8.

Dyeings on acrylic fibre (Velicren) were carried out on a Linitest at 2 % depth and 20:1 liquor ratio. The pattern, previously wetted, was entered into the bath containing acetic acid (1 %) and a retardant (Astragal PAN, Bayer) (0·1 %); the temperature was raised to 85 °C and maintained for 15 min. The required amount of the dye was than poured into the bath and the dyeing continued for 1 h at 95 °C. The dyed fibre was removed, rinsed, and aftertreated for 15 min at 95 °C in 1‰ acetic acid.

The fastness of the dyeings were determined by standard procedures.[9] Lightfastness was determined on a Xenotest 150. The fastness to sublimation was assessed after a treatment for 30 s at a temperature of 150 °C.

2.5. Colour measurements

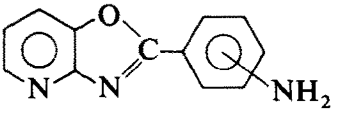
The reflectance data of the dyed fabrics were determined on a Cary 210 spectrophotometer equipped with integrating sphere and connected to an Apple II computer, using the A source and barium sulphate as standard blank.

3. RESULTS AND DISCUSSION

3.1. Chemistry, structure and spectra of amines and dyes

The formulae of dyes **III** and of the cationic dyes, together with their physical and spectroscopic data, are reported in Table 1.

The amines **II** and their [5,4-*b*] isomers are also interesting for their pharmacological properties.[5,10] The electronic spectra of the *meta*- and *para*-isomers closely resemble those of the benzoxazole counterparts **IV**. As was observed for a series of substituted 2-phenylbenz-X-azoles,[11] the broad and intense band in the high wavelength region is ascribed to the benzylidene–imine chromogen **V**. The pyridine derivatives exhibit a bathochromic effect in comparison with the benzo derivatives (*para*-isomers 21 nm, *meta*-isomers 9 nm) and this could be ascribed to the participation of the pyridine nitrogen to the conjugation of the main chromogen. The spectrum of the *ortho*-isomer has a distinctly different pattern. As well as the long-wave band a well structured absorption in the region 290–310 nm appears. It was therefore interesting to prepare 2-(*o*-aminophenyl)benzoxazole, the reference compound in the benzo series.



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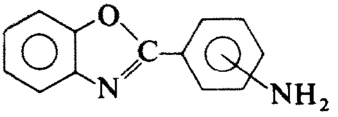

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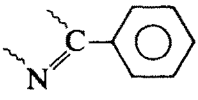

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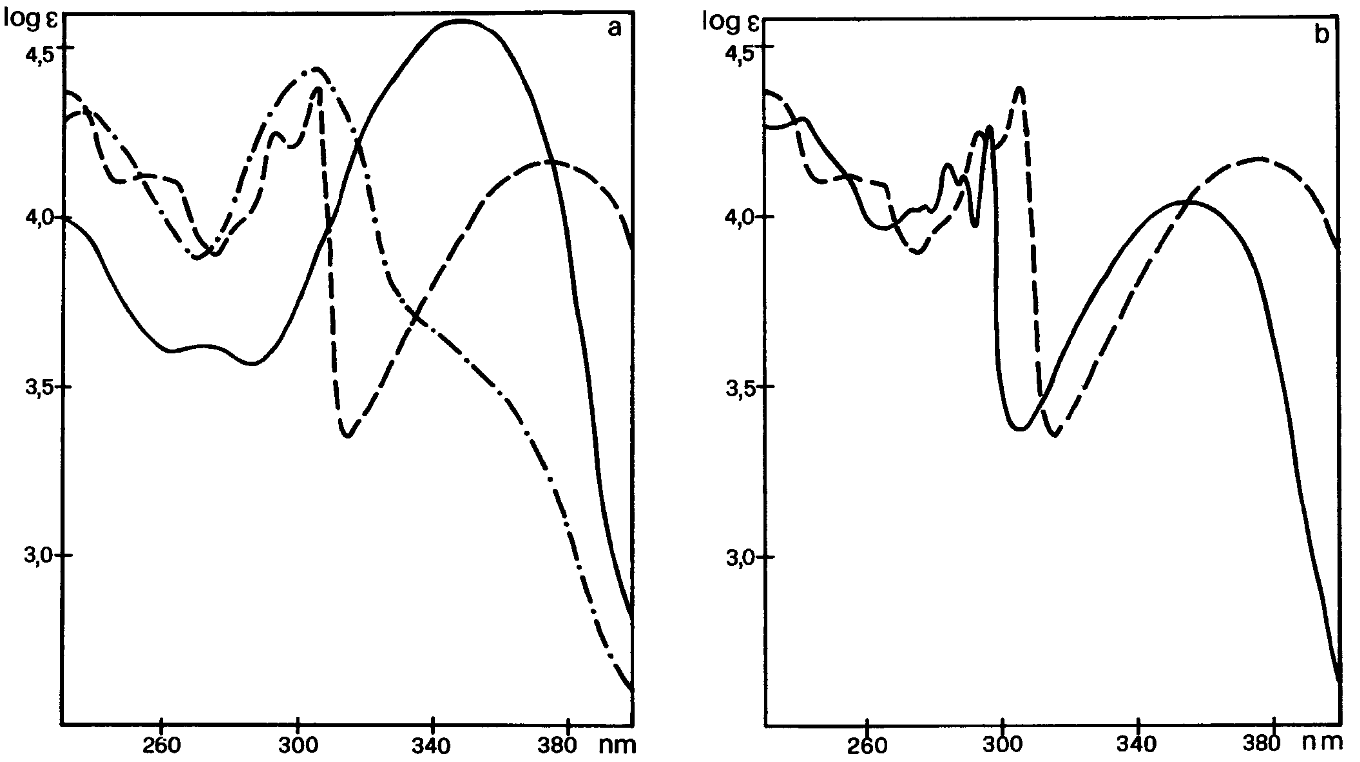
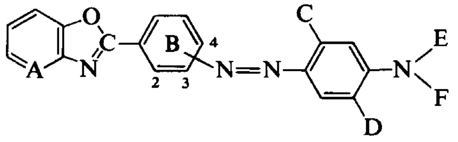


Fig. 1. Absorption spectra of amines **II** and **IV**. (a) ---- **IIa** (*ortho*); -·-·-·-·- **IIb** (*meta*); —— **IIc** (*para*). (b) ---- **IIa**; —— **IV**.

TABLE 1
Characterization Data for Dyes III



Dye no.	*Position in the B ring*	*A*	*C*	*D*	*E*	*F*	*Crystallization[a] solvent*	*M.p. (°C)*	λ_{max} *(nm)*	*log ε*	R_f
1	4	N	H	H	CH_3	CH_3	A	295–6	465	4·53	0·85
2	4	N	H	H	C_2H_5	C_2H_5	A	251–3	478	4·56	0·90
3	4	N	H	H	C_2H_5	CH_2CH_2CN	A	221–2	445	4·55	0·85
4	4	N	H	H	C_2H_5	CH_2CH_2OH	A	233–5	474	4·61	0·91
5	4	N	H	H	CH_2CH_2OH	CH_2CH_2CN	A	257–8	445	4·51	0·81
6	4	N	H	H	CH_2CH_2OH	CH_2CH_2OH	A	245–6	468	4·61	0·78
7	4	N	CH_3	OCH_3	H	H	A	193–4	466	4·46	0·84
8	3	N	H	H	CH_3	CH_3	A	217–8	424	4·38	0·87

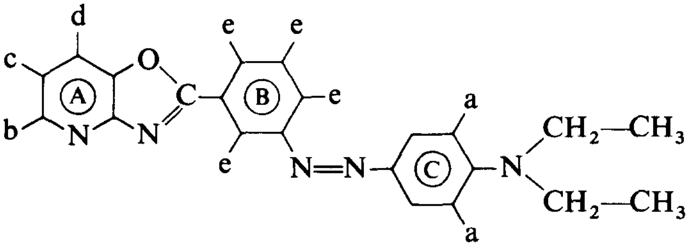
9	3	N	H	H	C_2H_5	C_2H_5	A	201–2	437	4·49	0·91
10	3	N	H	H	C_2H_5	CH_2CH_2CN	A	151–3	416	4·46	0·86
11	3	N	H	H	C_2H_5	CH_2CH_2OH	A	187–8	431	4·42	0·87
12	3	N	H	H	CH_2CH_2OH	CH_2CH_2CN	A	193–4	414	4·46	0·78
13	3	N	H	H	CH_2CH_2OH	CH_2CH_2OH	A	218–9	426	4·35	0·79
14	3	N	CH_3	OCH_3	H	H	A	193–5	425	4·29	0·85
15	2	N	H	H	CH_3	CH_3	A	151–2	436	4·40	0·76
16	2	N	H	H	C_2H_5	C_2H_5	B	146–7	438	4·03	0·85
17	2	N	H	H	C_2H_5	CH_2CH_2CN	A	110–12	420	4·08	0·85
18	2	N	H	H	C_2H_5	CH_2CH_2OH	B	134–6	431	4·17	0·81
19	2	N	H	H	CH_2CH_2OH	CH_2CH_2CN	A	126–8	424	4·36	0·78
20	2	N	H	H	CH_2CH_2OH	CH_2CH_2OH	A	151–3	441	4·34	0·74
21	2	N	CH_3	OCH_3	H	H	A	174–6	436	4·14	0·76
22	4	$\overset{+}{N}—CH_3$	H	H	C_2H_5	CH_2CH_2CN	A	206–7	446	4·55	0·27
23	3	$\overset{+}{N}—CH_3$	H	H	C_2H_5	C_2H_5	A	197–8	441	4·42	0·30
24	2	$\overset{+}{N}—CH_3$	H	H	CH_3	CH_3	A	181–2	473	4·32	0·29

[a] A = ethanol, B = dioxane.

The spectra are directly compared in Fig. 1b, which shows the close resemblance of the two patterns, apart from the general shift to longer wavelengths of the pyridine derivative. The structured absorption could be due to the appearance of benzenoid bands connected to the formation of $\mathrm{N_{azole}}\cdots\mathrm{H}$—N hydrogen bonds (a similar phenomenon has also been observed for *o*-hydroxy derivatives.[12,13]

The absorption maxima of the dyes in solution for a given coupling follow the order $p > o > m$ as predicted by simple resonance interaction.

In the quaternized dyes, it would be expected that the pyridine nitrogen atom is the preferred site of reaction with alkyl halides. NMR spectroscopy confirms this. As an example, dyes **9** and **23** are briefly discussed (analogous deductions can be drawn for the couplings **3**–**22** and **15**–**24**). First, the chemical shift of methylene (3·50 ppm), methyl (1·17 ppm) and protons a (6·83 ppm) is the same in both dyes **9** and **23**. This clearly indicates that the nitrogen atom of the *N*-diethylamino group remains unchanged. Also unchanged is the position of protons e in the B ring (a complex multiplet in the range 7·77–8·33 ppm), since, if the azole nitrogen was charged, a downfield shift of these protons would be expected. Finally, the proton b is shifted from 8·68 ppm in dye **9** to 9·12 ppm in dye **23**, similarly protons c and d are shifted downfield by 0·60 and 0·84 ppm respectively. Further, in the spectrum of dye **23** the signal of the methyl group linked to the pyridine nitrogen is clearly detected



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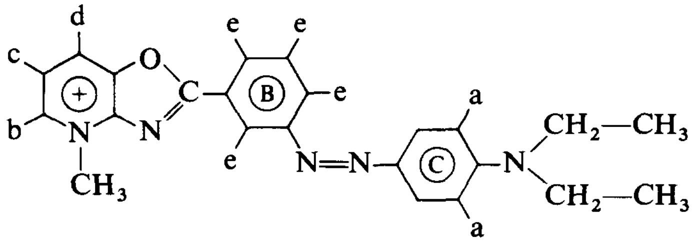

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TABLE 2
Fastness Properties of Dyes **III**

Dye[a] no.	Washing at 60°C[b]			Perspiration[b]			Acid	Alkali	Rubbing		Subli- mation	Light
									Dry	Wet		
1	5	5	5	5	5	5	4–5	4–5	3–4	3	4–5	4–5
2	5	5	5	5	5	5	4–5	4–5	3–4	3	4–5	4–5
3	5	5	5	5	5	5	4–5	4–5	4	3	4–5	1–2
4	4–5	4	5	4–5	4	4	4	4–5	4–5	2–3	4–5	3–4
5	4–5	5	5	5	5	5	4–5	4–5	5	4–5	4–5	2–3
6	5	5	5	5	4	4–5	4	4–5	4–5	2	4–5	3–4
7	4	2–3	3	4	2–3	2–3	3–4	4	2–3	2–3	4–5	4–5
8	5	5	5	5	4–5	5	4–5	4–5	4–5	2–3	4–5	3–4
9	5	5	5	5	5	5	4–5	4–5	4	4	4–5	1–2
10	5	5	5	5	4–5	5	4–5	4–5	4–5	2–3	4–5	3–4
11	5	5	5	4–5	4–5	4–5	4–5	4–5	4–5	2–3	4	3–4
12	5	5	5	5	4–5	5	4–5	4–5	4–5	3	4–5	2–3
13	5	5	5	5	5	5	4–5	4–5	5	2–3	4	1–2
14	4–5	4	4–5	4–5	4–5	4–5	4–5	4–5	3–4	4–5	4–5	3–4
15	3–4	5	5	4–5	4–5	5	4–5	4–5	4–5	3	4–5	1–2
16	4–5	4–5	4–5	4–5	3–4	4–5	4–5	4–5	3–4	2–3	4–5	1–2
17	5	5	5	5	5	5	4–5	4–5	4–5	3	4–5	1–2
18	5	5	5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	1–2
19	5	5	5	4	2–3	2–3	4–5	4–5	5	3	4–5	1–2
20	4	4–5	5	4–5	3	2–3	4–5	4–5	5	4–5	4–5	1–2
21	5	4–5	5	4–5	4–5	4–5	4–5	4–5	4–5	2–3	4	3–4
22	3	4–5	4–5	2–3	4	4	4–5	4–5	3	2	4	2
23	3–4	5	4	3	2	2	4–5	4–5	3	2	4	2
24	3–4	4–5	5	4	4–5	4	4–5	4–5	3	2	4	2

[a] Structures given in Table 1.

[b] Values in the first column refer to the change of colour, in the second column to the staining of the same kind of fibre as the specimen, and in the third column to the staining of wool (of cotton for dyes **22–24**).

(4·55 ppm). All the above signals are consistent with those usually observed in pyridinium salts. NMR data, combined with other analytical data, confirm the structure assigned to the cationic dyes.

The R_f values of the cationic dyes are, as expected, consistently lower than those of the corresponding bases due to the stronger interaction of the cations with the polar substrate.

TABLE 3
Colour of Dyed Fibres

Dye[a] *no.*	*Colour on fibre*[b]	*Chromaticity coordinates*		*Luminance factor*	*Helmholtz coordinates*		
		x	*y*	*Y (%)*	*Dominant wavelength* λ_D *(nm)*	*Complementary dominant wavelength* λ_c *(nm)*	*Purity P (%)*
1	O.	0·56	0·40	47·18	595	496	72·90
2	O.	0·56	0·39	48·86	598	497	66·00
3	O.	0·56	0·41	46·67	592	494	79·79
4	R.O.	0·62	0·36	24·81	605	499	86·54
5	O.	0·56	0·41	49·69	592	494	79·79
6	R.O.	0·60	0·38	37·11	599	498	86·81
7	R.O.	0·64	0·33	15·54	619	502	79·56
8	O.	0·55	0·43	58·74	588	491	86·70
9	O.	0·55	0·43	58·07	588	491	86·70
10	O.	0·54	0·43	61·83	588	491	79·83
11	O.	0·56	0·42	54·07	590	493	86·66
12	Y.O.	0·53	0·44	60·32	586	488	79·87
13	O.	0·55	0·43	55·86	588	491	86·70
14	O.	0·57	0·41	40·89	592	494	86·67
15	O.	0·58	0·40	38·25	595	496	86·66
16	O.	0·56	0·41	35·67	592	494	79·79
17	O.	0·55	0·42	48·62	590	493	79·78
18	O.	0·54	0·41	31·55	592	494	66·03
19	O.	0·57	0·41	33·17	592	494	86·64
20	R.O.	0·61	0·37	25·45	599	498	86·58
21	R.O.	0·59	0·38	31·68	599	498	79·73
22	R.O.	0·62	0·35	13·57	608	500	79·57
23	O.	0·58	0·40	36·33	595	496	86·66
24	R.O.	0·59	0·37	13·52	605	499	72·82

[a] Structures given in Table 1.

[b] Abbreviations: O., orange; R.O., red–orange; Y.O., yellow–orange.

3.2. Dyeing properties and colour assessment

Table 2 reports the fastness properties of the dyes. Dyes **1–21** gave satisfactory results as disperse dyes for polyamide 6.6. The exhaustion of dye liquors, levelling and colour yield compared favourably with commercial dyes under similar conditions.

Whilst properties were generally good, lightfastness was variable, being highest (4–5) from dyes **1**, **2** and **7**. As a general trend, the *ortho*-isomers show less satisfactory behaviour.

The cationic dyes **22–24** were suitable for dyeing acrylic fibres in solution. Their technical properties, as a whole, were not essentially different from those of the original disperse dyes.

Reflectance and related data are given in Table 3.

In previous studies[7,8] a correlation between the position of the absorption maxima in solution and the complementary dominant wavelength of dyed fabrics was observed. In this present work, λ_c values, for a given coupling, have an order $p > o > m$ in agreement with the observed sequence of λ_{max} values.

4. CONCLUSIONS

2-(*o*,*m*,*p*-Aminophenyl)oxazolo[4,5-*b*]pyridines, besides their pharmacological interest are also suitable for the preparation of monoazo disperse dyes characterized by good fastness. Some of these dyes were quaternized and the structures of these elucidated by NMR spectroscopy. The cationic dyes gave good dyeings on polyacrylic fibres although lightfastness was not good. The behaviour of *para*- and *meta*-isomers was generally better than that of *ortho*-isomers.

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