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Short Communication

1-*N*-Methylamino-4-(arylamino)anthraquinone-2-aryl Ethers: Dyes for Synthetic-Polymer Fibres

SUMMARY

The synthesis of a series of 2-aryl ethers of 1-N-methylamino-4-arylaminoanthraquinone is described. The effect of replacing the bromine atom in the 2-position by aryloxy substituents on the colour, dyeing and fastness properties of these dyes on synthetic fibres is reported.

1 INTRODUCTION

The use of *N*,*N*-substituted-1,4-diaminoanthraquinone as disperse dyes[1] has been long established. However, their fastness properties, especially to sublimation on polyester fibre, tend to be unsatisfactory and research has continued on these dyes with the objective of improving their fastness properties.[2]

The 2-aryl ethers of 1-*N*-methylamino-4-arylaminoanthraquinones (**III**) are brilliant violet dyes for the coloration of synthetic-polymer fibres. Preparative routes to the dyes are described, together with data on the effect of the nature of the substituents R^1 and R^2 on the colour, dyeing and fastness properties of the dyes.

2 EXPERIMENTAL

All melting points are uncorrected. Microanalyses, thin-layer chromatography, mass spectra and visible spectra of the dyes were effected as previously described.[3]

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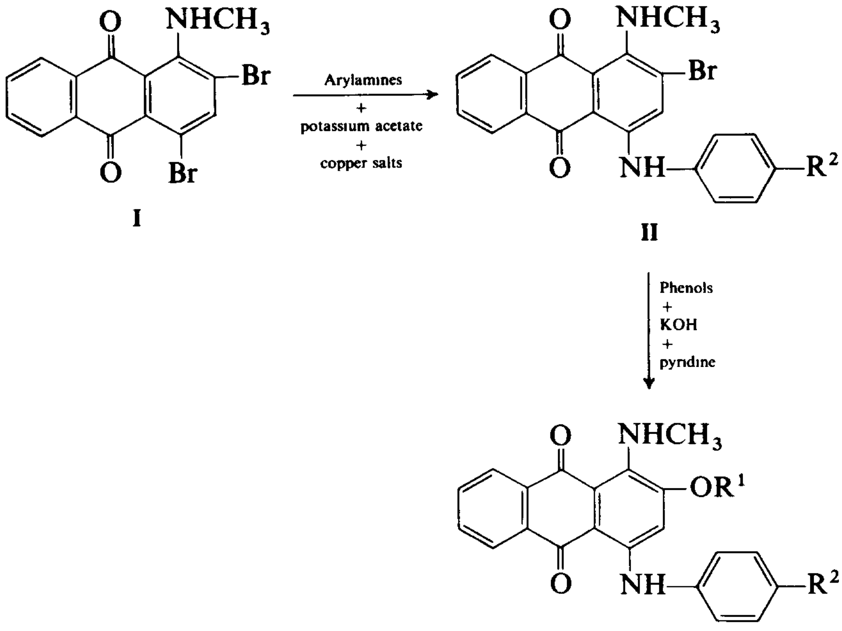

I

II

III

Dyeings of 0·1%, 0·5% and 2·5% depth of shade were carried out at 120°C for 1 h on polyester fibre from a dyebath containing 0·1% Dyapol G (YCL, Leeds, England). All dyeings were reduction cleared in a bath containing 0·1% Dyapol G, 2 g litre^{-1} sodium hydroxide and 2 g litre^{-1} sodium dithionite for 20 min at 70°C.

Dyeings on secondary cellulose acetate and triacetate were also obtained at 0·1%, 0·5%, and 2·5% depths using Dyapol G as dispersing agent; milling and dyeing procedures were as previously described.[4]

Lightfastness ratings were determined on a Xenotest Model 450 (Quarz-Lampen GmbH, Hanau, W. Germany) using standard procedures.[5]

The fastness to sublimation of the dyes were assessed using a multiple bank of the Fixotest machine (Quarz-Lampen GmbH, Hanau); dye samples were treated for 30s over the temperature range of 120–240°C, and the temperature at which the initial visible mark-off on to adjacent white polyester occurred was noted.

1-*N*-methylamino-2-bromo-4-anilinoanthraquinone (**II**, $R^2 = H$) used in the syntheses was obtained[6] in 51·7% yield, m.p. 224°C (benzene), by refluxing 1-*N*-methylamino-2,4-dibromoanthraquinone (30 g), copper carbonate (0·6 g), potassium acetate (15 g) and aniline (100 ml) for 4–5 h at 130–140°C, cooling the liquor to 80°C and adding methanol (100 ml) to give a dark blue solid. Other intermediates (**II**, $R^2{=}CH_3$ and OCH_3) were similarly prepared.[7]

2.1 Synthesis of 1-*N*-methylamino-4(arylamino)anthraquinone-2-aryl ethers

Method 1: Synthesis of 1-N-methylamino-2-(4′-methylphenoxy)-4-anilino-anthraquinone (IIId)

A mixture of **II** (4 g), *p*-cresol (8 g), potassium hydroxide (2 g) and pyridine (10 ml) was refluxed at 120°C with stirring for 18 h. The reaction mixture was cooled to 80°C, methanol (20 ml) added and the product (4 g, 91%) filtered and washed with water. Thin-layer chromatography indicated that the product was homogeneous. Recrystallisation from toluene gave violet needles, m.p. 158°C.

Reaction with other phenols gave the dyes (**III**) listed in Table 1; a slight variation in the method of preparation described above was necessary in some cases, as described in Method 2 below.

Method 2: Synthesis of 1-N-methylamino-2-(3′-methoxyphenoxy)-4-anilino-anthraquinone (IIIf)

A mixture of **II** (4 g), *m*-methoxyphenol (8 ml), potassium hydroxide (2 g) and pyridine (10 ml) was heated under reflux with stirring for 18 h at 120°C. The reaction mixture was cooled to 80°C, methanol (20 ml) added and the product (4 g, 87%) separated as a thick viscous slurry. This was drowned into aqueous sodium hydroxide (200 ml) and the mixture stirred for 3 h cold and then warmed to 60°C for 1 h to remove excess *m*-methoxyphenol. The resultant liquor was filtered and the solid residue washed with water until free of alkali and then dried. Thin-layer chromatography indicated the major component (approx 85%) to be contaminated with traces of higher R_f (reddish orange) and a lower R_f (blue) by-products. Recrystallisation from acetone gave blue needles of **IIIf**, m.p. 110°C.

3 RESULTS AND DISCUSSION

Replacement of the 2-bromo substituent in 1-*N*-methylamino-2-bromo-4-arylaminoanthraquinone with different phenols in pyridine and in the presence of potassium hydroxide gave 1-*N*-methylamino-4-arylamino-anthraquinone-2-aryl ethers in good yield. The various dyes thus synthesised are shown in Table 1. In general, the dyes were readily isolated by dilution of the reaction liquor with methanol and then filtering. In some cases, however, as in the reaction of **II** with 3-methoxyphenol and with 2,2-bis(4-hydroxyphenyl)propane, a viscous tar was obtained after the dilution with methanol. The products were in these cases isolated by drowning the

TABLE 1
Characterisation Data of 1-*N*-Methylamino-4-(arylamino)anthraquinone-2-aryl Ethers (Dyes **III**)

Dye no.	R^1	R^2	*Method of synthesis*	*Crude product yield (%)*	*Recryst. solvent*	*M.p. (°C)*
IIIa	H	H	—	82·5	Toluene	194·5
IIIb	Br	H	—	51·7	Benzene	224
IIIc	C_6H_5	H	1	81·4	Acetone	185
IIId	$C_6H_4CH_3$—*p*	H	1	91·0	Toluene	158
IIIe	$C_6H_4OCH_3$—*p*	H	1	87·0	Toluene	180
IIIf	$C_6H_4CH_3$—*m*	H	2	87·0	Acetone	108–110
IIIg	C_6H_4OH—*p*	H	1	91·0	Acetone	228
IIIh	$C_6H_4NH_2$—*p*	H	1	77·3	Toluene	194
IIIi	$C_6H_4[C(CH_3)_2$—C_6H_4OH—*p*—]*p*	H	1	94·6	Ethanol	108
IIIj	C_6H_5	CH_3	1	87·8	Acetone	160
IIIk	$C_6H_4CH_3$—*p*	CH_3	1	100·0	Toluene	186
IIIl	$C_6H_4OCH_3$—*p*	CH_3	1	81·8	Toluene	196
IIIm	$C_6H_4CH_3$—*m*	CH_3	2	79·5	Ethanol	116
IIIn	C_6H_4OH—*p*	CH_3	1	102·0	Ethanol	238
IIIo	$C_6H_4NH_2$—*p*	CH_3	1	93·0	Toluene	214
IIIp	$C_6H_4[C(CH_3)_2$—C_6H_4OH—*p*—]*p*	CH_3	1	96·2	Ethanol	90
IIIq	C_6H_5	OCH_3	1	78·0	Acetone	108
IIIr	$C_6H_4CH_3$—*p*	OCH_3	1	66·6	Acetone	176
IIIs	$C_6H_4OCH_3$—*p*	OCH_3	1	68·2	Toluene	195
IIIt	$C_6H_4CH_3$—*m*	OCH_3	2	79·5	Ethanol	136
IIIu	C_6H_4OH—*p*	OCH_3	1	76·3	Ethanol	218
IIIv	$C_6H_4NH_2$—*p*	OCH_3	1	132·5	Toluene	208
IIIw	$C_6H_4[C(CH_3)_2$—C_6H_4OH—*p*—]*p*	OCH_3	1	70·0	Ethanol	176

TABLE 2
Electronic Spectra, Light and Sublimation Fastness of Dyes III

Dye no.	R^1	R^2	$\lambda_{max}(\log e)$ in $C_6H_5Cl^a$	Lightfastness (0·1%, 0·5%, 2·5%)			Sublimation fastness (2·5% dyeing on polyester) (°C)
				Secondary acetate	Tricel	Polyester	
IIIa	H	H	545_s (3·93), 573 (4·11), 610 (4·12)	5, 6, 6	6, 6, 6	5, 5, 4	140
IIIb	Br	H	581 (4·16), 618 (4.15)	– – –	– – –	6, 6, 6	150
IIIc	C_6H_5	H	534_s (3·97), 561 (4·16), 598 (4·16)	– – –	– – –	5–6, 5, 5	160
IIId	$C_6H_4CH_3$—*p*	H	534_s (4·00), 560 (4·18), 598 (4·19)	– – –	– – –	5–6, 5, 5	160
IIIe	$C_6H_4OCH_3$—*p*	H	534_s (3·99), 560 (4·18), 598 (4·18)	– – –	– – –	5, 5, 5	170
IIIf	$C_6H_4CH_3$—*m*	H	536_s (4·02), 561 (4·18), 598 (4·19)	5, 5, 5	– – –	5, 5, 5	150
IIIg	C_6H_4OH—*p*	H	536_s (3·98), 560 (4·15), 598 (4·15)	5, 5, 5	– – –	5, 5, 5	160
IIIh	$C_6H_4NH_2$—*p*	H	534_s (4·90), 510 (4·19), 598 (4·20)	– – –	– – –	5, 4–5, 4	160
IIIi	$C_6H_4[C(CH_3)_2$—C_6H_4OH—*p*—]*p*	H	536_s (4·04), 510 (4·20), 597 (4·21)	– – –	– – –	5, 5, 5	160
IIIj	C_6H_5	CH_3	538_s (3·98), 566 (4·15), 601 (4·16)	– – –	6, 6, 6	5, 5, 4–5	150
IIIk	$C_6H_4CH_3$—*p*	CH_3	536_s (3·97), 565 (4·16), 601 (4·17)	– – –	– – –	5, 4–5, 5	170
IIIl	$C_6H_4OCH_3$—*p*	CH_3	534_s (3·95), 564 (4·13), 600 (4·14)	– – –	– – –	5, 5, 4–5	170
IIIm	$C_6H_4CH_3$—*m*	CH_3	536_s (3·99), 566 (4·18), 601 (4·19)	– – –	5, 6, 6	5, 5, 5	150
IIIn	C_6H_4OH—*p*	CH_3	536_s (3·95), 564 (4·13), 600 (4·15)	– – –	– – –	4, 4, 4	180
IIIo	$C_6H_4NH_2$—*p*	CH_3	536_s (3·97), 564 (4·14), 599 (4·16)	– – –	– – –	4, 4–5, 4	170
IIIp	$C_6H_4[C(CH_3)_2$—C_6H_4OH—*p*—]*p*	CH_3	536_s (3·97), 564 (4·14), 599 (4·16)	– – –	– – –	5, 5, 5	160
IIIq	C_6H_5	OCH_3	540_s (4·00), 568 (4·13), 599 (4·15)	5, 6, 6	– – –	5, 5, 5	160
IIIr	$C_6H_4CH_3$—*p*	OCH_3	534_s (3·91), 568 (4·10), 599 (4·12)	– – –	– – –	5, 5, 5	160
IIIs	$C_6H_4OCH_3$—*p*	OCH_3	536_s (3·96), 567 (4·14), 598 (4·15)	– – –	– – –	5, 5, 5	150
IIIt	$C_6H_4OCH_3$—*m*	OCH_3	536_s (3·96), 570 (4·12), 600 (4·14)	5, 4, 5	– – –	6, 5, 5	140
IIIu	C_6H_4OH—*p*	OCH_3	536_s (3·85), 566 (4·03), 599 (4·03)	– – –	– – –	5, 5, 5	180
IIIv	$C_6H_4NH_2$—*p*	OCH_3	532_s (3·93), 566 (4·15), 599 (4·17)	4, 4, 4	– – –	5, 5, 5	180
IIIw	$C_6H_4[C(CH_3)_2$—C_6H_4OH—*p*—]*p*	OCH_3	536_s (3·95), 567 (4·14), 599 (4·15)	– – –	– – –	5, 5, 4	150

[a] s = shoulder.

slurry into dilute aqueous sodium hydroxide to remove phenolic residues, filtering and washing with water.[8]

Visible absorption maxima of the dyes **III** are given in Table 2. The dyes all absorb at lower wavelength than the bromo-substituted reference dyes **II**. Thus, replacement of the 2-bromo group in **II** by aryloxy substituents gives a hypsochromic shift in the region of 20 nm in the principal long-wavelength absorption band (cf. dyes **IIIc–IIIi**, Table 2). Variations in the nature of the 2-aryloxy substituent produced only negligible colour shifts. The 2-aryloxy derivatives **III** were also hypsochromic, in the order of 10 nm, with respect to the 2-unsubstituted analogues, i.e. 1-methylamino-4-arylaminoanthraquinones, indicating the influence of the electron-donor 2-aryloxy substituent in inhibiting the resonance interactions responsible for the colour of the 2-unsubstituted derivatives. Similar hypsochromic shifts resultant from the presence of electron-donor substituents in the 2-position are also apparent in acid dyes based on 1,4-diaminated anthraquinones.

All the dyes **III** had excellent coloration properties on polyester giving intense reddish-violet to bluish-violet hues. Dyes containing the 2-phenoxy, 2-(4′-methylphenoxy), 2-(3′-methoxyphenoxy) and 2-(4′-hydroxyphenoxy) substituents gave brilliant deep violet coloration. The 2-bromo derivatives (**II**), in contrast, gave brilliant blue hues on polyester.

Build-up of the dyes **III** on cellulose acetate and triacetate fibres was generally poor and only the 2-(3′-methoxyphenoxy) derivative gave an acceptable degree of coloration on these fibres.

Lightfastness of the dyes on polyester was moderate to good and replacement of the bromine atom in **II** by aryloxy groups did not result in any improvement in the fastness properties. Dyes **IIIa**, **IIIj** and **IIIm** had fairly good fastness properties on cellulose triacetate, but dye **IIIv** gave a somewhat lower rating on secondary cellulose acetate.

Sublimation fastness of the dyes on polyester fibres was generally moderate (see Table 2). Only dyes **IIIe**, **IIIk**, **IIIl**, **IIIn**, **IIIo**, **IIIu** and **IIIv** showed a slight improvement (20–30°C) in the initial mark-off temperature compared with the reference dyes (**II**).

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