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Short Communication

Synthesis of Disperse Dyes derived from 1-Cyano-2-substituted-3-azabenzanthrones

SUMMARY

Several disperse dyes have been synthesized by reaction of 6-chloro-1-cyano-2-substituted-3-azabenzanthrones by Ullmann reaction with various amines. The dyes thus obtained have been examined for their absorption characteristics and their dyeing behaviour on polyester.

1 INTRODUCTION

In a recent communication[1] we have described the reaction of 1-aminoanthraquinone derivatives with the Vilsmeier reagent derived from tertiary amides of cyanoacetic acid and phosphorous oxychloride, leading to a new chromophore, namely 1-cyano-2-substituted amino-3-azabenzanthrones. In view of the importance of pyridanthrones and pyrimidanthrones in dyestuffs, we report here the preparation of some 6-amino derivatives of this compound and an evaluation of their colour and dyeing properties on polyester fibre.

2 RESULTS AND DISCUSSION

Reaction of 1-amino-4-chloroanthraquinone (**I**) with cyanoacetic acid morpholide or cyanoacetic acid piperidide in the presence of phosphorous oxychloride afforded the appropriately substituted 6-chloro derivatives of 1-cyano-3-azabenzanthrone (**II** and **III**). These condensed with amines under typical Ullmann reaction conditions to give the 6-aminated derivatives **IVa**–**IVf** and **Va**–**Vf.**

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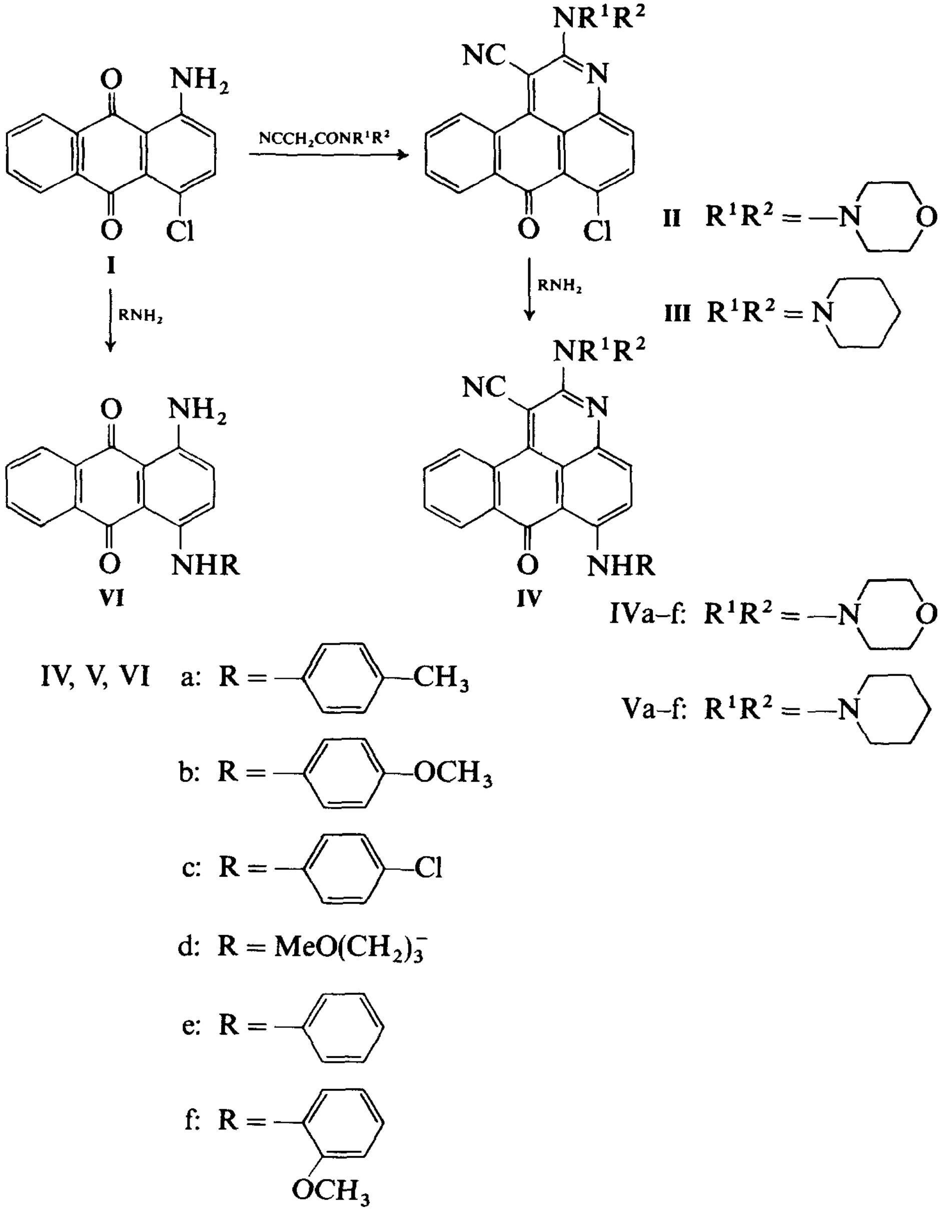

For comparison purposes, analogous 1-amino-4-substituted aminoanthraquinones were prepared by Ullmann condensation from 1-amino-4-chloroanthraquinone. In the case of the condensation with 4-chloroaniline, a pure product could not readily be obtained and the 4-(4-chloroanilino) derivative was more readily obtained by reaction of 1-amino-4-bromoanthraquinone-2-sulphonic acid, followed by desulfonation.

TABLE 1
Visible Spectra

Dye	λ_{max} *(nm)*[a]	*log e*	*Pick-up*	*Lightfastness*	*Sublimation fastness*
I	480	3·89			
II	454	3·62			
III	470	3·61			
IVa	539	3·87	2	5–6	4
Va	546	4·07	2	5	4+
VIa	616	3·75	4	4–5	2–3
	574 (sh)	3·75			
IVb	538	4·08	2	4–5	4+
Vb	538	3·83	1	3+	4+
VIb	575	3·85			
	610 (sh)	3·83			
	530	3·84	4	4+	4
IVc	538	4·14	2	5–6	4
Vc	540	3·93	2	5	4
VIc	610	3·93			
	580	3·92	4	5–6	4
IVd	539	4·16	1	1–2	4
Vd	530	3·94	2	3+	4−
	508 (sh)	3·92			
VId	594	4·24	2	3–4	2–3
	555	4·11			
IVe	535	3·79	<4	3–4	4
VIe	574	3·98			
	496	3·98	<2	4	3
	615	3·90			
IVf	540	4·10	<4	6	3–4
VIf	612	4·16	<4	4	4

[a] λ_{max} = Wavelength of maximum absorption in *N*,*N*-dimethylformamide.

The dyes thus obtained were applied to polyester at 1% depth of shade, dyeing at 130°C for 1 h. Relevant pick-up values, fastness properties and visible absorption maxima are given in Table 1. The 3-azabenzanthrone derivatives are significantly hypsochromic, in the order of 60–70 nm, with respect to the 1-amino-4-substituted amino analogues. For example, whilst 1-amino-4-*p*-toluidinoanthraquinone (**VIa**) absorbs at 574 nm and 616 nm, the 6-*p*-toluidino-3-azabenzanthrones **IVa** and **Va** absorb at 539 nm and 546 nm respectively. The magenta to violet coloured azabenzanthrone derivatives are however more bathochromic in respect of their absorption maxima than other ring-closed derivatives such as the pyrimidanthrones and the pyridanthrones. Ring closure affects the pick-up of the dyes detrimentally with respect to analogous 1,4-disubstituted anthraquinones **VI**, with the exception of dyes **IVe** and **IVf**, which showed good tinctorial properties. Lightfastness of the dyeings of the ring-closed derivatives **IV** varied from moderate, for the 6-alkylamino derivatives, to good, for the 6-arylamino derivatives. The results indicate the potential applicability of the ring-closed azabenzanthrone derivatives as useful disperse dyes.

3 EXPERIMENTAL PROCEDURE

All melting points are uncorrected.

The visible spectra were recorded on a Bausch and Lomb Spectronic 505 spectrophotometer.

1-Amino-4-chloroanthraquinone was prepared by chlorination of 1-benzamidoanthraquinone followed by acid hydrolysis, yield 85%, m.p. 180°C (HOAc). Cyanoacetic acid morpholide, m.p. 83°C, and cyanoacetic acid piperidide, m.p. 84°C, were prepared by known methods.

3.1 General procedure for the preparation of 6-chloro-1-cyano-2-substituted amino-3-azabenzanthrone derivatives

To a well cooled solution of the tertiary amide of cyanoacetic acid (0·023 mol) in 1,4-dioxan (35 ml), $POCl_3$ (0·023 mol) was added slowly maintaining the temperature below 5°C. After stirring for 30 min, 1-amino-4-chloroanthraquinone (0·019 mol) was added and the mixture stirred for a further 30 min and then heated at 80°C for 3 h. The reaction mixture was poured into ice water, neutralized with 20% aqueous Na_2CO_3 solution to pH 8 and the resultant precipitate filtered, washed with water and dried. 6-Chloro-1-cyano-2-morpholino-3-azabenzanthrone(**II**) was thus obtained in 96% yield, m.p. 258°C (HOAc). (Found: N, 10·8; $C_{21}H_{16}ClN_3O_3$ requires N, 10·7%) and 6-chloro-1-cyano-2-piperidino-3-azabenzanthrone (**III**) in 96% yield, m.p. 225°C (HOAc) (Found: N, 10·8; $C_{22}H_{19}ClN_3O_3$ requires N, 10·7%).

3.2 General procedure for Ullmann reaction on 6-chloro-3-azabenzanthrone

The 6-chloro-3-azabenzanthrone derivative (0·0076 mol), the amine (0·0093 mol) and a pinch of Cu powder were added to a solution of sodium acetate (0·0076 mol) in ethanediol (100 ml) at 60°C, and the reaction mixture was refluxed for 10 h, during which time its colour changed from red to

TABLE 2

Yield and Physical Data of the Various Substituted 3-Azabenzanthrones

Compound	*Yield* (%)	*m.p.* (°*C*)	*Crystallization solvent*	*Molecular formula*	*Analysis: N*	
					Found (%)	*Calc.* (%)
IVa	94	232	Benzene	$C_{28}H_{24}N_4O_3$	11·6	12·0
Va	95	242	Benzene	$C_{29}H_{26}N_4O_2$	12·4	12·1
IVb	95	248	Benzene	$C_{28}H_{24}N_4O_4$	11·2	11·5
Vb	96	242	Benzene	$C_{29}H_{26}N_4O_3$	12·2	11·9
IVc	95	255	Benzene	$C_{27}H_{21}ClN_4O_3$	11·5	11·6
Vc	95	218	Benzene			
IVd	94	168	Benzene	$C_{25}H_{26}N_4O_4$	12·8	12·5
Vd	94	135	Benzene			
IVe	94	145	Benzene	$C_{27}H_{22}N_4O_3$	13·0	12·6
Ve	84	185				
IVf	96	185	Benzene	$C_{28}H_{24}N_4O_4$	11·3	11·5
VIf	86	192				

violet. The cooled reaction mixture was poured into ice water, filtered and the residue was stirred with HCl (30 ml, 10%) at 70°C for 30 min. The precipitate was filtered, washed free of acid and dried. The yield, m.p., crystallization solvent and molecular formula of the various products (**IV**) thus prepared are given in Table 2.

Using the above procedure the 1-amino-4-substituted aminoanthraquinones **VI** were prepared from 1-amino-4-chloroanthraquinone and the appropriate amines. Relevant data are shown in Table 2.

3.3 Preparation of 1-amino-4-(4-chloroanilino)anthraquinone

(*a*) *Condensation*

To a slurry of Bromaminic Acid (0·0026 mol) in water (100 ml), Na_2CO_3 (0·052 mol) was added and the mixture stirred at 50°C for 1 h. 4-Chloroaniline (0·028 mol) and freshly prepared copper oxide (from 1 g copper chloride, 2·5 ml conc. HCl and 1 g Na_2CO_3) were added, the temperature raised to 70°C and maintained for 3 h. The reaction mixture was cooled, filtered and the residue washed with NaCl solution.

(*b*) *Desulfonation*

The above condensation product (0·01 mol) in water (100 ml) at pH 8 was heated slowly to 95–98°C and sodium dithionite (0·012 mol) was added over

15 min. Reaction was continued at 95–98°C for 3 h, maintaining pH 8–8·5 throughout. The product was filtered and dried to yield **VIc**, yield 82%, m.p. 300°C.

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