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The Influence of Methyl Groups on the Colour and Dyeing Properties of Acid Dyes Derived from 1-Amino-4-Bromo-Anthraquinone-2-Sulphonic Acid and Arylamines

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ABSTRACT

Four blue acid dyes were synthesized by condensation of bromamine acid with aniline, 2,4-dimethylaniline, 2,6-dimethylaniline and 2,4,6-trimethylaniline. It was found that the number and orientation of the methyl groups on the 4-phenylamino substituent affected both the colour and dyeing properties of the dyes. The more methyl groups present, the higher was the dye uptake and the better the fastness to wet treatments. When a methyl group is present in the ortho position of the phenylamino group, the hue of the dyes is hypsochromically shifted.

1 INTRODUCTION

Anionic anthraquinone dyes are one of the most important class of acid dyes, being principally used for green, blue or violet hues having excellent light and wet fastness. One important group of such dyes are those obtained by condensation of bromamine acid with aromatic or alicyclic amines, by an Ullmann reaction catalyzed by copper or copper salts.[1] This group of blue acid dyes has important usage value and reported commercial structures number around 30;[2-4] the synthesis and properties of several dyes have been studied.[3,5] In this present paper, four dyes were synthesized from bromamine acid and 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,4-dimethylaniline and aniline, following established procedures.[6,7] The influence of the number and orientation of the methyl groups in the 4-phenylamino residue on the colour and dyeing properties of the dyes is discussed.

CI, Acid Blue 129

I   II

CI, Acid Blue 25

III   IV

2 EXPERIMENTAL
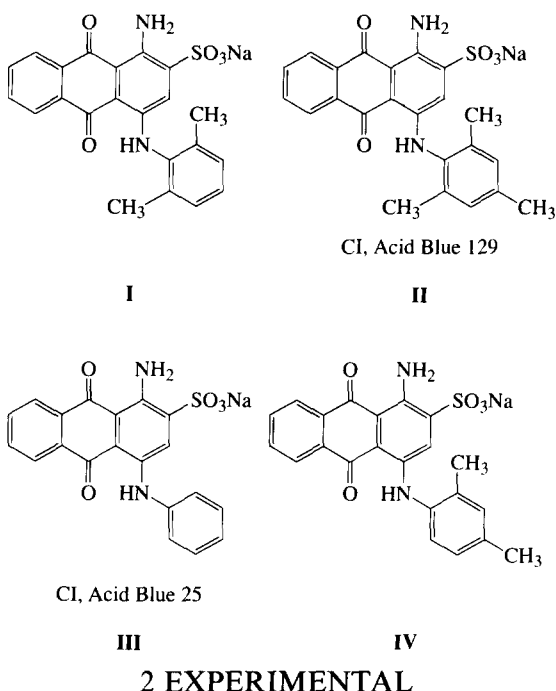
2.1 Synthesis of the dyes

Bromamine acid sodium salt (0·05 mol) was dissolved in 300–400 ml water at 70–80 C, and then a solution of the arylamine (0·10 mol) in 50–200 ml alcohol was added, together with the appropriate copper salt catalysts and acid carbonate.[3,5] After refluxing for 3–4 h, the excess amine was recovered in a yield of about 70%, and the solution was adjusted to acidic and then salted and filtered at room temperature to give the dyes in a yield of 70–80%.

The dyes were washed with aq. acid and aq. alkali alternately until only one spot was apparent on TLC (Silica Gel, using as eluent *n*-butanol:ethyl acetate:acetic acid:water = 3:3:0·5:3). The dyes were then dissolved in water, 36% hydrochloric acid was added to adjust the overall HCE concentration to 3–5%, and the mixture stirred for 1–2 h to ensure that the 2-sodium sulphonate was fully converted to the free acid. The dyes were then filtered and crystallized from an appropriate solvent (e.g. alcohol, DMF).

2.2 Instrumental

Elemental analyses were carried out with a CHNCORDER MF3 TYPE instrument (Yanaco Company, Japan); IR spectra (KBr) were recorded on a Nicolet 5DX FT–IR spectrometer; ^{1}H NMR spectra on a Bruker AM500 and

UV-Vis spectra on a CARL ZEISS JENA Specord UV-Vis meter. Colour properties were measured using a Colour-Eye (Macbeth Company, Hong Kong).

2.3 Dyeing procedures

Wool pieces were immersed in a dyebath containing the dye solution (at 1% depth), 10% sodium sulfate, 1% acetic acid and 0·5% perpgel at 30–40°C, with a liquor ratio of 50:1. The dyebath was then heated to 90–95°C over 30–40 min, held for 30 min and then heated to boiling over 5 min and then at the boil for 10 min. The bath was then cooled to room temperature and the dyeings washed and dried.

The time–temperature–dyeing curves were also determined using the following procedure. 200 ml dyebath solution was made by using the above system, 1 ml was removed and diluted to 25 ml with water, prior to adding 4·0 g wool piece to the dyebath, together with 1 ml of a solution containing all the above dyebath additives, except for dye, to ensure that the dyebath volume remained constant. The dyebath was heated to 30 C over 20 min, and then the temperature of the dyebath was raised 10°C every 10 min. After every 10-min interval, 1 ml of dye liquor was removed and diluted to 25 ml with water; 1 ml of appropriate dyebath liquor was added to retain constant volume. The dye uptake was calculated by measuring the optical densities of the appropriate dye liquors relative to the original dye solution.

The fastness properties of the dyeings were measured in accordance with GB-8427, GB-3920, GB-3921, GB-3922 (China), which are similar to ISO standards.

3 RESULTS AND DISCUSSION

3.1 Characterization data

Analytical data for the dyes are listed in Table 1 and Fig. 1.

The vibrational band of the carbonyl group in anthraquinone is usually found around 1681 cm, but intramolecular hydrogen bonding between the carbonyl group and groups such as — NH or OH on the α-position of the anthraquinone ring lead to a decrease of the vibrational frequency. The IR spectra of the dyes synthesized show typical bands in the range 1618–1631 cm. In the ^{1}H NMR spectra, it was found that the chemical shifts of the protons on the 3-position were significantly affected by the methyl groups in the 4-phenylamino groups. When there was no or only one methyl group on the *ortho* position of the phenylamino group, the chemical shifts were in the region of 8·00 in ppm, viz; 8·30 for dye **III** and 7·96 ppm for dye **IV**.

TABLE 1

IR Data and Elemental Analysis

| Dye	IR(KBr)/cm	Elemental analysis Found/calc.		
		C	H	N
I	1628 (C=O); 1199·8, 1024, (SO$_3$H);3443, 3368, 1578 1277 (C-NH$_2$, C-NH–), 2959, 2911 (CH$_3$)	– 62·55	– 4·29	– 6·63
II	1631 (C=O); 1213, 1024 (SO$_3$H); 3419, 3272, 1580, 1271 (C-NH$_2$, C-NH–); 2926, 2894 (CH$_3$)	63·12 63·29	5·24 4·62	6·50 6·42
III	1618 (C=O); 1200, 1024 (SO$_3$H); 3435, 3384, 1572, 1279 (C-NH$_2$, C-NH–);	60·74 60·91	3·70 3·58	6·34 7·10
IV	1622 (C=O); 1200, 1026 (SO$_3$H); 3435, 3352, 1574, 1275 (C-NH$_2$, C-NH–); 2920, 2872 (CH$_3$)	62·41 62·55	4·83 4·29	6·33 6·63
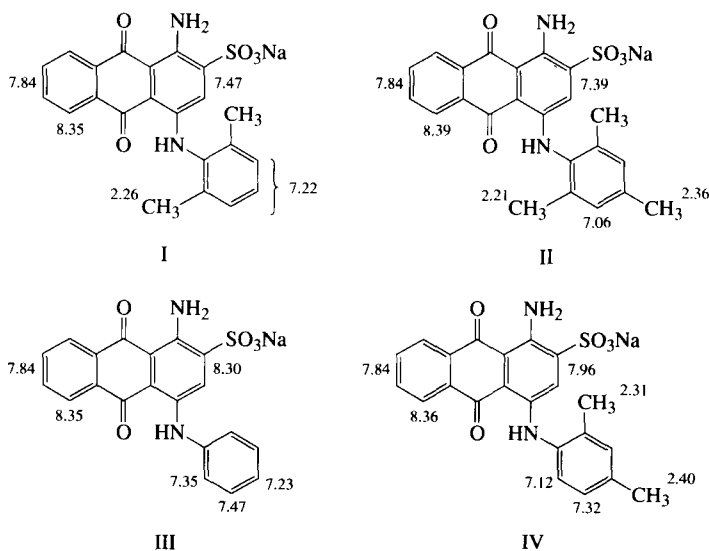
Fig. 1.   The chemical shifts of the dyes.

When both ortho positions were substituted by methyl groups the shifts were displaced to 7·42 and 7·39 ppm for dyes **I** and **II** respectively. These results differ from the previously reported data of 8·0–8·2.[8]

UV-Vis spectral data are shown in Table 2.

TABLE 2

UV-Vis Data of the Dyes (in Water)

Dye	I	II	III	IV
λ_{max} (nm)	265·630	262·644	279·625	275·650
ϵ (L' mol^{-1} cm^{-1})	9460	10600	8960	9090

3.2 Influence of methyl groups on the colour properties of the dyes

Comparing the colour measurement results of the dyeings (Table 3), it is apparent that relative to dye III as standard, the ΔH values are 9·51, 4·97 and –8·35 for dyes I, II and IV, respectively, i.e. there is a bathochromic effect in the following sequence:

Dye I (reddish blue) < dye II (less reddish blue) < dye III (blue) < dye IV (greenish blue).

As is well established, the colour properties of the dyes will be determined by the donor properties of 4-arylamino group and by the relative coplanarity of the 4-arylamino group with the anthraquinone ring system. The greater the donor ability of the 4-arylamino group and the more coplanar it is with the anthraquinone ring, the greater the bathochromic effect.

Dyes I and II both have two methyl groups on the ortho positions, and this substitution pattern will severely inhibit coplanarity of the substituent with the anthraquinone ring, leading to a hypschromic shift. Dye II contains a methyl group on the 4 position, the donor native of which results in the λ_{max} being at longer wavelength than that of Dye I. Dye IV has two donor methyl groups in the 4-phenylamino residue, one of which is on an *ortho* position; only slight interference with coplanarity occurs and these effects together result in the λ_{max} of this dye being at the longest wavelength of the four dyes. With regard to dye III, there is no donor methyl group and its colour is deeper than that of dyes I and II, but lighter than dye IV; its coplanar properties are the optimum of the four dyes studied.

TABLE 3

Colour Parameters of the Dyes

Dye	L*	A*	B*	h*	ΔE	ΔH
I	256·578	12·795	–44·222	286·137	13·16	9·51
II	32·951	7·924	–46·109	279·751	12·68	4·97
III	26·701	1·867	–36·885	272·897	bases	
IV	28·782	–6·111	–31·026	258·858	10·11	–8·35

TABLE 4
Dyeing Fastness Properties of the Studied Dyes

Dye	I	II	III	IV
Light (1/1 depth).	5–6	5–6	5–6	5–6
Washing (soap)	3–4	3–4	3	3–4
wool staining	3–4	3–4	2–3	3–4
cotton staining	4	4	4	3
Perspiration	3–4	3–4	3	3–4
wool staining	2–3	2–3	2	2–3
cotton staining	3–4	3–4	3	3–4
Rubbing dry	4	4	4	3–4
wet	3	3	3	2
Dye uptake (%)	84·7	89·8	78·1	84·2

Table 2 shows that the λ_{max} of dye **III** is 625 nm, which implies that the dye exhibits a hypsochromic shift. However, the absorption curve of this dye is not symmetrical, showing greater inclination on the long wave side. As a result, the dye produces a bathochromic effect on dyeing. In general, it is concluded that coplanarity factors are the key factors, relative to the donor properties of the methyl groups, influencing the colour of the dyes.

3.3 Influence of methyl groups on dyeing properties

The dyeing results (Table 4) show that all four dyes have good fastness to light, but that the wet fastness is influenced by the number of methyl groups. It is also apparent that the dye uptake of dye **II**, in which three methyl groups are present, is the highest; those dyes **I** and **IV**, which contain two methyl groups, are comparable; and that the dye uptake of dye **III**, which has no methyl groups, is the lowest. Increase in dye uptake can thus be correlated with the number of methyl groups in the 4-phenylamino substituent. Increase in the number of methyl groups also results in an improvement in wet fastness properties.

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