

# The Effect of Substitution on the Dyeing and Spectroscopic Properties of Some Monoazo Disperse Dyes

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**Abstract.** A range of monoazo disperse dyes has been synthesized. The colour, dyeing and fastness properties of the dyes on polyester, nylon and secondary acetate fibre at 1/1 standard depth have been examined and rationalized in terms of dye structure. The visible absorption behaviour of the dyes was also investigated. In general, substitutions on the diazo component have a significant effect on the visible absorption maxima of the dyes. Increasing the solvent polarity also had a pronounced effect on the absorption maxima.

**Keywords:** monoazo dyes, diazotization, dyeing, dye migration

## Introduction

The disperse dyes arose out of the endeavour of many workers to find an easy and commercially satisfactory way to dye cellulose acetate. The importance of water insoluble disperse dyes has increased to a very great extent with the appearance of synthetic fibres, some of which, such as polyester and triacetate, are much more hydrophobic than cellulose acetate, and therefore very resistant to the conventional water soluble dyes (Trotman, 1984).

As with other classes, diverse properties are expected of disperse dyes according to the dyeing conditions that will be encountered during use. Disperse dyes for acetate are required to have brightness and fastness of shades, good build-up, and levelling properties. Some dyes, otherwise satisfactory, show a tendency to sublime under domestic ironing conditions. Others are sensitive leading to marked deterioration in their shades (Muller, 1970). Research efforts have been accordingly made to overcome these shortcomings and to determine such structural features that would confer improvements in these properties (Clark and Hildreth, 1973). These have been adapted to meet the requirements of polyester fibres and of different dyeing processes, mainly by varying the substituent types of the dye, which have quickly become important for dyeing acetate fibres (Stead, 1970).

Synthesis of some disperse dyes and their dyeing properties have been reported and discussed in the present paper. The findings of this study have been discussed in term of the structural features of the dye molecules. The focus has remained on dyes derived from conventional diazo component and aniline-based coupler.

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## Materials and Methods

**Synthesis of dyes.** The dyes were synthesized by coupling the appropriate diazonium ions with N,N-diethylaniline. The amines used in the synthesis were 4-nitroaniline, 2-chloro-4-nitroaniline, 2,4-dinitroaniline, 4-nitroanisole, 2-cyano-4-nitroaniline, 2,6-dichloro-4-nitroaniline. All the amines were diazotized in aqueous hydrochloric acid and then gradually added to a well stirred dispersion of N,N-diethylaniline in a weakly basic system. These have been listed as **Ia-Ij**. The parent dye had the general structural formula as given in Fig. 1.

All the dyes were separated from the reaction mixture by filtration and then purified by dimethyl formamide (DMF) and their  $\epsilon_{\max}$  in the visible region were measured on Nicolet evaluation spectrophotometer (Thermo Electron Corporation, Madison, Wisconsin, USA).

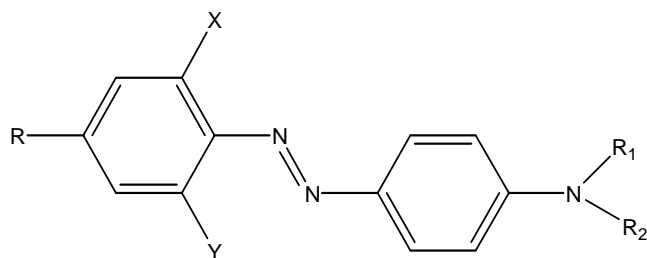
**Dyeing of fabric at different concentrations.** Dyeing of 0.5 %, 1% and 2% was carried on 5 g fabric at 130 °C for 75 min, using high temperature dyeing machine (Ahiba IR Laboratory Dyeing System, model D400ir/I, SDL Atlas Ltd., London, UK) containing 2 g/l dispersing agent, 3 ml/l acetic acid to maintain pH at 4.5-5.5, and the liquid to goods ratio of 1 : 20. After this period (75 min), the study specimens were removed from the dyeing bath and rinsed with cold water and dried. The dyeings were reduction cleared in an aqueous solution of sodium hydro-sulfite (2-3 g/l) and sodium hydroxide (2 g/l), using the liquid to goods ratio of 1 : 20 at 60 °C for 10 min. The samples were then rinsed with water and dried. The prepared dyes exhibited best dyeing properties on polyester and secondary acetate, dyeing on nylon being inferior to those on polyester and secondary acetate.

**Assessment of dyeing properties. Build-up test.** The concept of build-up can be related to the adsorption isotherm under high temperature conditions, since many dyes approach fairly close to the equilibrium adsorption within a practical dyeing time. The dyeing solution of different concentrations, 0.5 %, 1 % and 2 %, were prepared by the amount of dyes required to produce 1 : 1 standard depth at 80 °C (Derbyshire and Lemon, 1964). Dyeing was produced in the normal dyeing times at 100-130 °C. The dyed sample was assessed visually with the standard grey scale. The results are presented in Table 1.

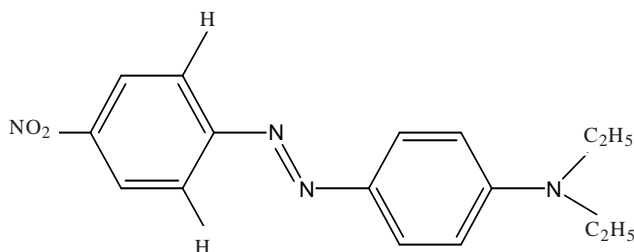
**Migration test.** The 1 : 1 ISO standard depth dyeing was prepared at 80 °C (Derbyshire and Lemon, 1964). Equal weights of this dyeing and similar undyed material were placed in a bath at 80 °C liquid to goods ratio of 50 : 1 and left immersed with agitation for one h. The difference between the two pieces was then assessed with the SDC Grey scale (Grey scale for assessment of the change in colour and staining; BS-1006, ISO-105, G-246-A; Atlas Material Testing Technology, Chicago, Illinois, USA). The results of migration test have been tabulated in Table 2.

**Assessment of fastness properties. Colour fastness to light.** The colour fastness to artificial light of the dyed samples was carried out by ISO-BO2 standard test procedure (SDC, 1999). The test specimen of the dyed fabric was exposed to artificial light (Xenon Arc Fading Lamp, model ci 3000+, Atlas Material Testing Technology, Chicago, Illinois, USA) under standard conditions, using sample of blue wool as the reference. The colour fastness was then assessed by comparing the change in colour with that of the reference blue wool sample. In all such cases, the light fastness exhibited on polyester was high, whereas on nylon it was poor. Light fastness assessment of dyes is given in Table 3.

**Fastness to sublimation.** This method of assessing sublimation fastness of the dye was carried out by ISO PO1 standard test procedure (SDC, 1999). The test sample was sandwiched



**General structural formula of the parent dye**



**Structure of the parent dye (1a)**

dye (1b) X = H, Y = Cl

dye (1c) X = H, Y = NO<sub>2</sub>

dye (1d) X = H, Y = OCH<sub>3</sub>

dye (1e) X = H, Y = CN

dye (1f) X = Cl, Y = Cl

**Dyes synthesized from the parent dye (1a)**

**Fig. 1.** The conventional structure of dyes and the general structural formulae of the dyes synthesized from the parent dye.

between two pieces of undyed material. The composite specimen was heated in an oven for 30 sec at 210 °C. The composite specimen was removed and left for 4 h in air, at room temperature and relative humidity of 65 %. The change in colour of the specimen and the staining of the adjacent fabric was assessed with the SDC Grey scale. The results of the study on fastness to sublimation are presented in Table 4.

**Table 1.** Dyeing properties of monoazo disperse dyes for 2% dyeing

Dye*	Polyester		Secondary acetate		Nylon	
	substantivity	build-up	substantivity	build-up	substantivity	build-up
<b>1a</b>	good	3-4	moderate	3	moderate	2
<b>1b</b>	moderate	3	moderate	2-3	poor	1
<b>1c</b>	good	3-4	good	3	moderate	2
<b>1d</b>	very good	3	good	3-4	moderate	1
<b>1e</b>	good	2-3	good	2	poor	1
<b>1f</b>	very good	3-4	good	3	poor	1

\* = see Fig. 1 for the structure of parent dye and the derivative dyes; build-up has been reported in accordance with the standard Grey scale

## Results and Discussion

Disperse dyes (**1a-1f**) were prepared by the conventional method of diazotization and coupling (Straley, 1970). The dyes were purified and their  $\epsilon_{\text{max}}$  in the visible region were determined. The data presented in Table 5 show  $\epsilon_{\text{max}}$  values of the parent and other dyes. The visible absorption band showed a bathochromic shift with increase in the solvent polarity (hexane to ethanol), confirming a  $\delta - \delta^*$  transition involving the whole conjugated system. Substitution of a chlorine atom in the diazo component produced a bathochromic shift of approximately 5 nm in accordance with the electron donor properties of this substituent. With dyes (**Ic**) and (**Id**) the substituent caused a bathochromic shift in  $\epsilon_{\text{max}}$  with respect to the unsubstituted dye (**Ia**). Variation in Y resulted in a bathochromic shift which increased in the order of H, Cl, NO<sub>2</sub>, OCH<sub>3</sub>, CN. Comparison of the dye (**Ib**) with (**Ic**) showed that the presence of NO<sub>2</sub> group ortho to the azo group in (**Ic**) gave a bathochromic shift of 7 nm in ethanol compared to the dye (**Ib**) containing the chlorine atom reflecting the greater electron withdrawing nature of NO<sub>2</sub> group. The presence of chlorine at 2,6 position

ortho to the azo group resulted in the possible steric effect on the azo benzene system. Steric hindrance prevents a planar alignment of the azobenzene molecule, which leads to a hypsochromic shift with simultaneous loss of clarity. These results are in agreement with similar observations reported in the literature (Peters, 1985; Marion, 1960). These results can be explained in terms of solvent solute interaction. With hexane, this interaction was minimal, since the solvent was non-polar and any stabilizing effect affected the ground and excited states equally. This resulted in a shift towards shorter wavelength. In ethanol, the interaction was much stronger, even to the possibility of formation of H-bonding between the solvent and the solute (Patrik and Svehle, 1977). All dyes exhibited good level of dyeing on polyester and secondary acetate fibre with a good build-up (Table 1), but had poor substantivity for nylon.

Migration test also showed a similar behaviour (Table 2), while the light-fastness test by Xenon Arc Lamp showed a very good stability for polyester and secondary acetate fibre (Table 3). The sublimation fastness (Table 4) clearly indicated that

**Table 2.** Migration test rating of disperse dyes on different fibres for 2 % dyeing (reported in standard Grey scale)

Dye*	Polyester	Secondary acetate	Nylon
<b>Ia</b>	4-5	4-5	3-4
<b>Ib</b>	3-4	4	2
<b>Ic</b>	4	4-5	3
<b>Id</b>	4-5	4	2-3
<b>Ie</b>	4-5	4	2-3
<b>If</b>	4-5	4	3

\* = see Fig. 1 for the structure of parent dye and the derivative dyes

**Table 3.** Light fastness rating for 2% dyeing on different fibres (reported in standard Grey scale)

Dye*	Polyester	Secondary acetate	Nylon
<b>Ia</b>	4-5	4	2
<b>Ib</b>	4	4	2
<b>Ic</b>	5	5-6	3
<b>Id</b>	6	5-6	2-3
<b>Ie</b>	6	5	2-3
<b>If</b>	6-7	6	3

\* = see Fig. 1 for the structure of parent dye and the derivative dyes

**Table 4.** Fastness to dry heat of disperse dyes for 2% dyeing (reported in standard Grey scale)

Dye*	For polyester			For secondary acetate			For nylon		
	change in shade	staining cotton	staining polyester	change in shade	staining cotton	staining polyester	change in shade	staining cotton	staining polyester
<b>Ia</b>	4-5	4	4-5	5	4-5	4-5	2-3	2-3	2-3
<b>Ib</b>	4	4	4	4-5	4	3-4	2-3	2-3	2
<b>Ic</b>	4-5	4	4	4	4	3-4	3	2-3	3
<b>Id</b>	5	4-5	4	4-5	4	4	2-3	2-3	2-3
<b>Ie</b>	4-5	4	4	4	4	3-4	3	3	3
<b>If</b>	3-4	4	4	4-5	4	4	2	3	2-3

\* = see Fig. 1 for the structure of parent dye and the derivative dyes

**Table 5.** Effect of substitution on visible absorption values of disperse dyes ( $R_1 = R_2 = C_2H_5$ )

Dye*	R	X	Y	$\epsilon_{\max}$ (in ethanol)	Log $\xi$	$\epsilon_{\max}$ (in hexane)	Log $\xi$
<b>Ia</b>	NO <sub>2</sub>	H	H	514	4.410	482	4.381
<b>Ib</b>	NO <sub>2</sub>	H	Cl	519	4.410	490	4.380
<b>Ic</b>	NO <sub>2</sub>	H	NO <sub>2</sub>	526	4.416	495	4.389
<b>Id</b>	NO <sub>2</sub>	H	OCH <sub>3</sub>	534	4.417	495	4.388
<b>Ie</b>	NO <sub>2</sub>	H	CN	539	4.417	497	4.388
<b>If</b>	NO <sub>2</sub>	Cl	Cl	480	4.380	462	4.380

\* = see Fig. 1 for the structure of parent dye and the derivative dyes

the dyes were quite stable at high temperature. The shades were generally reddish-violet to dull reddish-brown, depending on the nature of the substituent groups present in the diazo components as shown in Table 5.

### Conclusion

The important conclusion that may be drawn from this work is that the synthesized disperse dyes showed good dyeing and fastness properties of an acceptable range. The strong electron donating influence of the substituted groups tended to stabilize monoazo disperse dyes. By increasing the solvent polarity there was a remarkable effect on the absorption maxima. The dyes are especially useful on polyester and secondary acetate, but more selective structural modifications are required for the colouration of nylons. A fair to good light fastness rating may be attributed in part to the non-polar nature of the dye molecule, which does not readily attract water molecules and other polar agents that may have a degrading effect. Further, the aromatic or benzene structure of the dyes gave them a relatively stable structure. The substitution variations in the diazo component demonstrated the facility with which different colours may be developed. Thus, the present data not only provide a base for assessing various disperse dyes but could also be extended to develop new disperse dyes with better exhaustion, built-up, colour, and fastness properties.

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