



## Dis-azo Dyes Derived from 2-methoxy-5-nitroaniline and 3-chloroaniline and their Application on Polymer Fibres

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### ABSTRACT

Six disazo disperse dyes derived from 2-Methoxy-5-nitroaniline and 3-chloroaniline were synthesized in good yield. The results of the absorption spectra of the dyes show that the dyes exhibited good colour yield. The dyes were characterized by spectral methods. The UV-vis spectral data has also been discussed in terms of structural property relationship. The dyeing assessment of the synthesized dyes was evaluated on polyester and nylon 66 fabrics. The results showed better hue with good colour fastness to washing, rubbing and light. The absorption spectra also show that the dyes have very high tinctoral strength and may act as organic photoconductors.

**Keywords:** Disperse dyes, polyester, nylon, dyeing, light absorption.

### INTRODUCTION

Out of the different classes of dyes, azo dyes constitute the largest group of colourant used in the industry<sup>1-3</sup>. Azo dyes can only be produced through synthetic methods since they do not occur in nature<sup>4</sup>. The emergence of many different classes of synthetic dyes including azo-dyes came as a result of constant efforts to find specific dye class for application on diverse materials of industrial importance such as textile fibres, aluminium, sheet, electro optical devices, ink-jet printers, leather, etc<sup>5-7</sup>. Azo dyes are of particular interest because they can be readily prepared with a wide range of donor and acceptor groups and also because the planarity of the azo bridge against the non-planarity of stilbenes or other systems should contribute to larger  $\pi$  electron transmission effects and lead to

higher optical activity<sup>8</sup>. Our research has previously reported some aspects of the preparation and application of certain dis-azo disperse dyes based on the intermediate, 2-methoxy-5-nitroaniline<sup>9</sup>.

The present study is focused on the synthesis and characterization of 2-methoxy-5-nitroaniline and 3-chloroaniline dis-azo disperse dye derivatives. We also describe the subsequent application of the dyes on polyester and nylon 66 fabrics.

### EXPERIMENTAL

#### Materials

2-methoxy-5-nitroaniline and 3-chloroaniline, obtained from Aldrich Chemical Company were used without further purification. All

other chemicals, such as 4-chloroaniline, N-phenylnaphthylamine, 1-naphthol, 1,3-diaminobenzene and 3-Aminophenol were purchased and also used as received.

## Methods

### Synthesis of Compound 3 (Scheme 1)

2-Methoxy-5-nitroaniline (3.0g, 17.8 mmoles) was dispersed in 50ml of water. To this mixture, was added 6ml of concentrated  $H_2SO_4$ , and the amine was subsequently diazotized by treatment with sodium nitrite (3.0g, 57.9 mmoles) at  $0^\circ C$  with stirring for 20 minutes. The resulting solution of diazonium salt was slowly added with vigorous stirring at  $0 - 5^\circ C$ , over a solution of 3-chloroaniline (3ml, 17.9mmoles) dissolved in acetic acid (5ml). The reaction mixture was further stirred for 1.5h and the brown coloured precipitate was filtered off and recrystallized from dimethylformamide-water (2:1) to give a brown solid (64%) of compound 3.

### Synthesis of dyes (5a-f) (Method A)

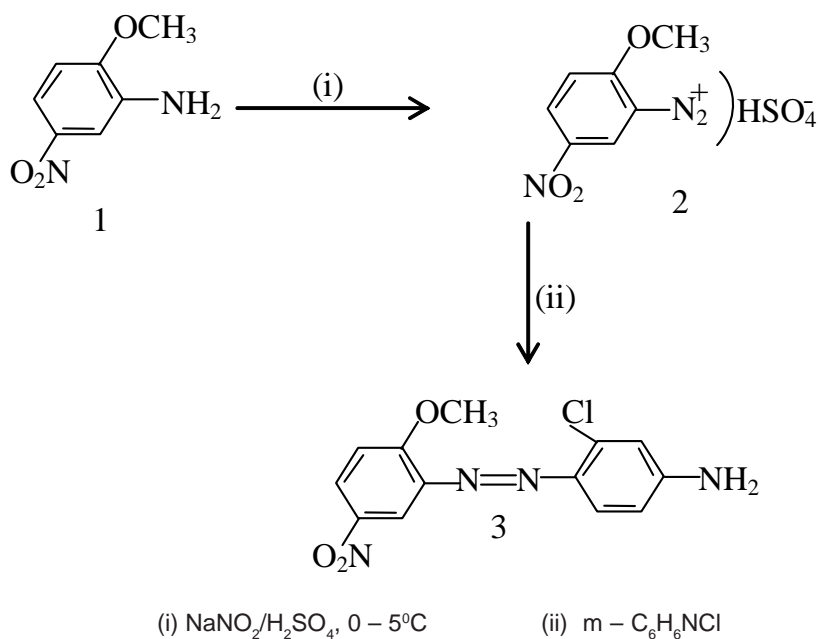
2-Methoxy-5-nitrophenylazo-4-amino-2-chlorobenzene (compound 3) (2.0 g, 6.53 mmoles) was diazotized in, 5 ml conc.  $H_2SO_4$  and 50 ml of water by adding sodium nitrite (3.0 g, 43.8 mmoles) in 10 ml of water at  $0-5^\circ C$  dropwise with stirring until

diazotization was complete. The solution was verified for complete diazotization by using a solution of 4-(N, N-dimethylamino) benzaldehyde which generates colour if undiazotised aromatic amine is still present. The diazonium salt solution prepared was added slowly to a solution (0.83 g, 6.50 mmoles) of p-chloroaniline in acetic acid (5 ml) with stirring for 2 h. The crude product was isolated by filtration, washed with water and recrystallized out of carbontetrachloride to give a brown solid of compound 5a in 58% yield. Compounds 5b, 5c and 5e was similarly obtained by following this procedure.

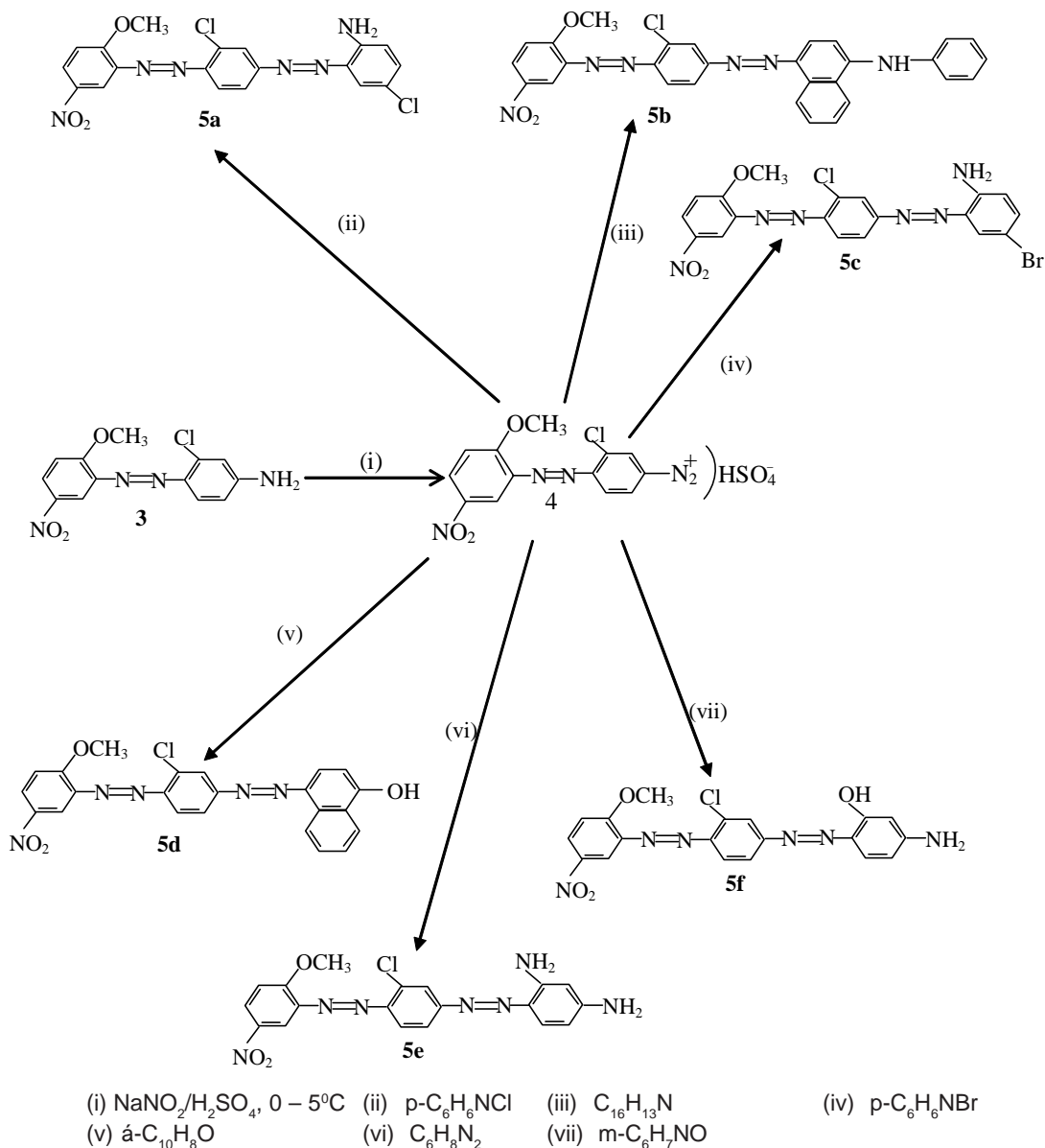
### Method B

To a mixture of compound 3 (2.0 g, 6.53 mmoles), water (50 ml) and conc.  $H_2SO_4$  (5 ml), was added dropwise, a solution of sodium nitrite (3.0 g, 43.8 mmoles) in 10 ml of water at  $0.5^\circ C$  with stirring for 20 minutes. Excess nitrous acid was destroyed by adding urea (0.45 g) into the diazonium salt solution.

Finally, the diazonium salt solution which resulted was slowly added with vigorous stirring at  $0-5^\circ C$ , over a solution of 1-naphthol (0.94 g, 6.5 mmoles) dissolved in sodium hydroxide (1 M, 30 ml). More sodium hydroxide (20 ml, 1 M) was added



**Scheme 1**

**Scheme 2**

to the reaction mixture and allowed to react for 1.5 hours. The precipitate was separated by filtration and washed several times with water, and recrystallized out of hot  $\text{CCl}_4$  to give a dark orange solid of, **5d** in 60 % yield. Compound **5f** was similarly prepared by following this procedure.

#### Chemical and Instrumental Analysis

All the melting points were determined on

a Buchi SMP-20 melting point apparatus, and are uncorrected. Infrared spectra (in KBr pellets) were recorded on a AT1 Wattson genesis series spectrophotometer.  $^1\text{H-NMR}$  spectra were recorded on a Mercury 200BB. MHz spectrometer in  $\text{CDCl}_3$  using TMS as an internal reference. The visible spectra were recorded in 1.0 cm quartz cells on a unicam UV-Vis Spectrophotometer equipped with Hilios Scan Software. The purity of the dyes was

assessed by Thin Layer Chromatography (TLC).

#### Dyeing of Polyester

Polyester fabric (10 x 5 cm) was dipped in a dyebath containing the dye powder (1.0 g) at a liquor ratio 20:1. The dye baths were prepared with the synthesized dyes (5a – f) and using Lignosulfonates (sulphite cellulose liquors) as the dispersing agent. The pH of the dye liquor was adjusted to 5 with acetic acid. Dyeing was carried out and continued for 60 minutes at 130° to 135°C under increased pressures. The dyed fabric was subjected to reduction cleared treatment at 85°C for 10 minutes in a solution of sodium hydroxide (2 g/L, 213.0 mmoles) and 2 g/L, sodium hydrosulphite and then treated in a betaine amphoteric surfactant in water, washed with water and then dried<sup>10, 11</sup>.

#### Dyeing of Nylon 66

The dye bath was prepared by mixing the dye (1.0 g), solution in DMF with Lenacid NL (1.2 ml of 10 %) as an acid buffer (pH 5 to 5.5) and water (18 ml). The Nylon fabric (2g) was wetted and immersed in the dyebath at 45°C. The bath temperature was then raised to 102°C over 15 minutes and maintained for 30 minutes. At this temperature formic acid (1.5 ml of 10 %), was added to the dyebath to achieve good exhaustion<sup>12</sup>. After cooling of the dyebath, the dyed fabric was rinsed and reduction-cleared twice with Iodet T (2 g/l) in a bath containing water (material to liquor 1:2) at 46°C for 15 minutes followed by washing thoroughly with cold water and drying in air.

#### Fastness Test

The dyed fabrics were subjected to wash (International standard Organisation, ISO 105-C-

6/C2S: 1994)<sup>13</sup> Light. AATCC Test Method (16 - 1998)<sup>14</sup> and Crocking (rubbing) fastness at 180°C for 60 s (ISO 105 – X12:2001)<sup>15</sup> fastness lest after heat setting sublimation fastness of the dyed fabrics were tested according to ISO 105-PO1, 1993 protocol<sup>16</sup>. The shade change; together with staining of adjacent fabrics, was assessed according to appropriate Society of Dyers and Colourists (SDC) grey scale.

### RESULTS AND DISCUSSION

The intermediate (1) was the starting material for this study, and compound 3 was prepared. The 2-Methoxy-4-nitroaniline was diazotized, using the Standard Methods<sup>17-18</sup> and the diazonium salt solution obtained was coupled with 3-Chloroaniline to give compound 3 which was recrystallized from carbontetrachloride to give 64 % yield. The coupling reaction was carried out under acidic conditions for some and others under alkaline conditions. In the second stage of the reaction scheme, compound 3 was diazotized using nitrosylsulphuric acid and sodium nitrite because the electron-withdrawing group in the diazo components made them weaker basic amines.

The six dyes (5a-f) were prepared by the coupling of the diazonium salts of compound 3 with various coupling compounds as illustrated in scheme 2. The structures of the synthesized dyes 5a – 5f were characterised by IR and <sup>1</sup>H-NMR analysis as shown in Table 1. The melting points of the dyes differ considerably from each other with dye 5a having the highest melting point. This may be attributed to the presence of NO<sub>2</sub> and two chlorine atoms in the molecule. Dye 5b has the

Table 1: Yield, melting point and spectral data of dyes 5a – 5f

Dye	Yield (%)	Mp (°C)	Absorption	R <sub>f</sub>	λ <sub>max</sub> (nm)	ε <sub>max</sub> (Mol <sup>-1</sup> cm <sup>-1</sup> )	Log ε (Intensity)
5a	59	>360	0.447	0.50	54.5	66.716	4.8236
5b	52	138-140	0.448	0.45	494	80000	4.9031
5c	57	158-160	0.445	0.43	467	73114	4.8640
5d	60	238-240	0.165	0.52	494	24626	4.3913
5e	58	1.48-150	0.346	0.46	512	48873	4.6890
5f	70	248-250	0.138	0.47	620	19714	4.2947

lowest melting point of 138 – 140°C. This may be due to the presence of N-phenyl-naphthylamine component in the dye structure.

### Spectral Properties of Dyes

Table 1 shows the spectral data of synthesized dyes **5a** – **5f**. The absorption maxima of the dyes varied greatly from 467 to 620 and all the dyes showed absorption in the near-infrared region at about 785 nm.

The value of the logarithm of the molar extinction coefficient ( $\log \epsilon$ ) of dyes **5a-f** corresponds with their high absorption intensities. Moreover, the presence of electron donating or electron attracting groups did actually bring about marked increase or decrease in  $\lambda_{\max}$  in the visible region. Dye **5b** gave the highest molar absorptivity value of 80,000. This is probably attributed to the increased conjugation brought about by the  $\pi$  electron system in the coupler component.

**Table 2: Fastness Properties of the dyes on polyester and nylon 66 fabrics**

Dye	Type of Fabrics	Change/Staining			Rubbing		Colour on Fabrics
		Light	Wash	Sublimation	Dry	Weight	
5a	Polyester	6	5	5	4/5	4/5	Brown
	Nylon 66	5	5	5	4/5	4/5	
5b	Polyester	6	5	5	4	4/5	Yellowish brown
	Nylon 66	5	5	5	4	4/5	
5c	Polyester	6	5	5	4	4/5	Brown
	Nylon 66	5	5	4	4/5	4/5	
5d	Polyester	5	5	5	4	4	Orange
	Nylon 66	5	4/5	5	4/5	4/5	
5e	Polyester	5	5	5	4	4	Yellowish brown
	Nylon 66	5	5	5	4	4/5	
5f	Polyester	4	5	5	4	4	Brown
	Nylon 66	4	4/5	5	4	4	

Grey scale ratings ranged from 1 (poor) to 5 (excellent)

For light fastness, Grey scale ratings ranged from 1-2 (poor) to 8 (excellent)

The  $\lambda_{\max}$  values range from 19000 to 80000 with broad absorption curves. Hence the area under the absorption curve, which is the true measure of tinctorial strength is large. The hues range from yellow to brown in view of their broad absorption curves. The IR spectrum of each dye exhibited the important features of aromatic-azo, aromatic-OH, methyloxyde, aromatic amine, C-Cl and nitro groups. The  $^1\text{H-NMR}$  spectra also showed the important signals at their expected positions with slight variations for some groups. The structures of the azo dyes shown were thus confirmed. The IR and  $^1\text{H-NMR}$  value were in agreement with those found in literature<sup>19-20</sup>.

### Fastness Properties

The results of the light fastness (Table 2) showed that all the dyes gave good light fastness on polyester and nylon 66 fabrics except dye **5e** with ratings of 5 to 6. The good light fastness is due to the nature of the polyester fibre and also the presence of the 3-nitro group and 2-methoxy group present in the dye molecule<sup>21</sup>. The position of the two substituents tend to increase the light fastness. The lower photostability of dye **5e** on the two fibre substrates could also be due to the amino substituent in the 2 position of the dye molecule to the azo group. The amino group tend to bring about high electron density around the azo group and this lowers light fastness.

**Table 3: Spectral data of Synthesized dyes with assignments**

Dye	Frequency (cm <sup>-1</sup> )	Characteristics	<sup>1</sup> H NMR, d (ppm)	Solvent
5a	3449	Ar – NH <sub>2</sub>	8.800 (1H, s, Ar-H)	CDCl <sub>3</sub>
	1596	Ar-rings	8.40(1H, m, Ar-H)	
	1523	Ar-NO <sub>2</sub> (Assymmetric stretch)	8.18 (1H, m, Ar-H)	
	1421	Ar-N = N	7.00 – 6.65(3H, m, Ar-H)	
	1340	Ar-NO <sub>2</sub> (Symmetric stretch)	7.40 – 7.65(3H, m, Ar-H)	
	861	Ar - NO <sub>2</sub> (Disubstituted)	4.80 – 4.15(2H, s, Amine)	
	828	C – Cl	3.25 (3H, s, O-CH <sub>3</sub> )	
	1232	O-CH <sub>3</sub>		
746	Ar-ring (monosubstituted)			
5b	3450	Ar – NH	9.80 – 8.60(3H, m, Ar-H)	CDCl <sub>3</sub>
	1619	naphthalene-ring	8.20-7.97(6H, m, Ar-H)	
	1594	Ar-rings	7.74(2H, m, Ar-H)	
	1525	Ar-NO <sub>2</sub> (Assymmetric stretch)	7.60-6.92(6H, m, naphthalene-H)	
	1498	Ar-N = N	4.00 (1H, m, NH)	
	1340	Ar-NO <sub>2</sub> (Symmetric stretch)	3.85 (3H, s, O-CH <sub>3</sub> )	
	1275	O-CH <sub>3</sub>		
	811	C – Cl		
744	Ar-ring (monosubstituted)			
5c	3438	Ar – NH <sub>2</sub>	8.63 – 8.00 (5H, m, Ar-H)	CDCl <sub>3</sub>
	2942	Ar-C-H	7.40-7.00(3H, m, Ar-H)	
	1589	Ar-rings	6.95(1H, m, Ar-H)	
	1518	Ar-NO <sub>2</sub> (Assymmetric stretch)	3.95(3H, s, O-CH <sub>3</sub> )	
	1462	Ar-N = N	1.15 (2H, s, NH <sub>2</sub> )	
	1340	Ar-NO <sub>2</sub> (Symmetric stretch)		
	1234	O-CH <sub>3</sub>		
	821	C – Cl		
678	C-Br			
5d	3448	Ar – OH	12.25 (1H, s, Bonded OH)	CDCl <sub>3</sub>
	2944	Ar-CH	9.00-8.20 (5H, m, Ar-H)	
	1628	Naphthalene-ring	7.85-6.65(6H, m, naphthalene)	
	1580	Ar-rings	4.00(3H, s, O-CH <sub>3</sub> )	
	1521	Ar-NO <sub>2</sub> (Assymmetric stretch)		
	1490	Ar-N = N		
	1342	Ar-NO <sub>2</sub> (Symmetric stretch)		
	1276	O-CH <sub>3</sub>		
820	C – Cl			
5e	3439	Ar – NH <sub>3</sub>	8.52 – 8.15(5H, m, Ar-H)	CDCl <sub>3</sub>
	1624	Ar-rings	7.50 – 7.02(3H, m, Ar-H)	
	1518	Ar-NO <sub>2</sub> (Assymmetric stretch)	6.50 (1H, d, Ar-H)	
	1482	Ar-N = N	3.96(3H, s, O-CH <sub>3</sub> )	
	1342	Ar-NO <sub>2</sub> (Symmetric stretch)	2.09 (4H, s, NH <sub>2</sub> )	
	1276	O-CH <sub>3</sub>		
830	C – Cl			
5f	3450	Ar – OH, NH <sub>2</sub>	9.25 (1H, s, Bonded OH)	CDCl <sub>3</sub>
	2945	Ar-C-H	8.26 – 8.16(3H, m, Ar-H)	
	1589	Ar-rings	7.26-7.25 (4H, m, Ar-H)	
	1521	Ar-NO <sub>2</sub> (Assymmetric stretch)	7.17(1H, m, Ar-H)	
	1460	Ar-N = N	6.98(1H, m, Ar-H)	
	1342	Ar-NO <sub>2</sub> (Symmetric stretch)	3.89(3H, s, O-CH <sub>3</sub> )	
	1273	O-CH <sub>3</sub>	2.25 (2H, s, NH <sub>2</sub> )	
	823	C – Cl		

The wash fastness test results showed good to excellent performance on the polyester and nylon 66 fabrics. The high molecular size of the dyes is believed to account for the high wash fastness. This showed that the dyes have high affinity for the two fibre substrates <sup>22</sup>.

The sublimation fastness results (Table 2) also showed good to excellent ratings on both polyester and nylon 66. This is attributed to the fact that the dyes are all having chlorine atoms in the molecule which usually enhances increased sublimation of disperse dyes <sup>23</sup>. The rubbing fastness results were good with ratings of 4/5.

### CONCLUSIONS

Disazo disperse dyes of 2-Methoxy-4-

nitroaniline and 3-chloroaniline derivatives were synthesized and their application on polyester and nylon66 fabrics were examined. The nature and position of the substituent in the diazonium and coupling components influenced the absorption maxima of the dyes and the shade of the dyeing. The coupling component that showed the highest absorption maxima is the N-phenyl-naphthylamine. The dyes gave yellow to brown hues on polyester and nylon 66 fabrics and showed good levelling properties. The dyes exhibited good to excellent wash and sublimation fastness while rubbing and light fastness results were good and moderate to good. The high wash fastness of the dyes indicates excellent affinity for polyester and nylon 66 fibres. Dyes 5a, 5b and 5f showed absorption into the near-infrared region indicating that they may act as organic photoconductors.

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