

Disperse dyes derived from 2-methoxy-5-nitroaniline

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ABSTRACT

A series of disazo disperse dyes containing nitro and methoxy groups were synthesized for dyeing of polyester fibre. The diazo component having the nitro and methoxy groups were prepared and coupled with the corresponding coupling components to give 2-methoxy-5-nitrophenylazo-2-hydroxy-4-aminobenzene dyes. The absorption maxima of the dyes were dependent upon the substituents in the diazo and coupling components and varied from 416 to 767nm in DMF. The dyes showed excellent wash fastness and sublimation fastness on polyester substrate. The light fastness of the dyes on polyester was also good. The structure of each compound was confirmed by infrared, Uv-visible and ¹H NMR analyses.

Key words: Disazo disperse dye, light absorption, polyester, fastness.

INTRODUCTION

Disperse dyes are a group of compounds that have low solubility in water but they can interact with the fibre chains by forming dispersed particles. Their main use is in the dyeing of hydrophobic fibres such as polyesters, cellulose acetates and polyamides. The general structure of disperse dyes is small planar and non-ionic with attached polar groups like NO₂, and CN¹. Their shapes make it easier for the dye molecules to slide between the tightly packed polymer chains. In addition, the polar groups improve the water solubility, dipolar bonding between dye and polymer and also affect the colour of the dye. Their small size indicates that disperse dyes are quite volatile and tend to sublime out of the polymer at sufficiently high temperatures^{2,3}.

2-methoxy-5-nitroaniline is an aromatic base and could therefore be a useful source of diazonium ions for diazo coupling reactions. Previous studies involving the use of this

intermediate have focused on its use in the production of 1-iodo-2-methoxy-5-nitrobenzene and 5-nitroquinoline compounds. In another study, 2-methoxy-5-nitroaniline has been used to produce 4-methoxy-1,3-benzenediamine by catalytic hydrogenation process⁴⁻⁵. Thus from available literature, this intermediate has not been used in the preparation of commercial monoazo and disazo dyes. Hence we report the synthesis of some novel disazo dye derivatives of 2-methoxy-5-nitroaniline. The correlation between the dye structure and spectral properties were discussed. The fastness properties of the dyes on polyester fabric were also investigated.

EXPERIMENTAL

Materials

2-methoxy-5-nitroaniline, 2-hydroxynaphthalene, 1-hydroxynaphthalene, N-phenylnaphthylamine, 1,3-dihydroxybenzene, 2-chloroaniline and 3-aminophenol were purchased

from Aldrich chemical company or sigma chemical company and were used without further purification. All other chemicals used in the synthesis and characterization were laboratory reagents and analytical grade.

Chemical and instrumental analysis

The proton nuclear magnetic resonance (^1H NMR) spectra were obtained with JNM-FX200 (JEOL 200 MH_2) for solutions in an appropriate deuterated solvent. The chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal reference.

Meeting points were determined using a Dsc 7 (Perkin-Elmer, heating rate $5^\circ\text{C}/\text{min}$ -nitrogen gas) the absorption spectra were measured in 1cm quartz cells on a spectrophotometer (Genesys IOS VL, 200 series).

Fourier Transform infrared (FTIR) spectra were recorded on a Nicolet Averser 330 spectrophotometer. The purity of the dyes was assessed by thin layer chromatography (TLC) using whatman 250m silica gel 60 AMK 6F plates as the stationary phase and ether/acetone mixture (1:5 by volume) as developing solvent. Characterizations data are shown in Tables 1 and 2.

Synthesis of diazo component 3 (2-methoxy-5-nitrophenylazo-2-hydroxy-4-aminobenzene)

2-methoxy-5-nitroaniline (4.00g, 0.024mol.) was mixed with water (50ml) and concentrated sulphuric acid (6ml). The mixture was cooled to $0-5^\circ\text{C}$. Sodium nitrite (0.01 mol) in water (5ml) was added to this mixture dropwise with vigorous stirring for 20min at $0-5^\circ\text{C}$. The diazonium salt solution was then added slowly to a well-cooled ($0-5^\circ\text{C}$) and stirred solution of 3-aminophenol (0.310g, 0.10mol) in sodium hydroxide (1.0g, 0.025mol) solution for 5min. Stirring was continued for further 1 hour and the precipitated product was filtered off, washed with water several times, dried and recrystallised from hot methylated spirit to give 2-methoxy-5-nitrophenylazo-2-hydroxy-4-aminobenzene, as dark brown crystals (6.32g, 92% yield).

1A Synthesis of 2-methoxy-5-nitrophenylazo-2'-hydroxyphenylazo-4-hydroxynaphthalene

2-methoxy-5-nitrophenylazo-2-hydroxy-4-aminobenzene (4g, 0.091 mol) was diazotised in concentrated sulphuric acid (6ml) and water (50ml) with sodium nitrite (3g, 0.043mol) in 10ml water at $0-5^\circ\text{C}$. Excess nitrous acid was destroyed by adding (0.15g, 0.003mol) urea solution. The diazonium salt solution obtained was added slowly with vigorous stirring for 2 hours and the precipitated product was filtered off, washed with water several times, dried and recrystallised from hot ethanol-methanol mixture to give 2-methoxy-5-nitrophenylazo-2-hydroxyphenylazo-4-hydroxynaphthalene(4) as brown crystals (5g, 82% yield) similar procedure was also used to synthesise dye 5 to 7.

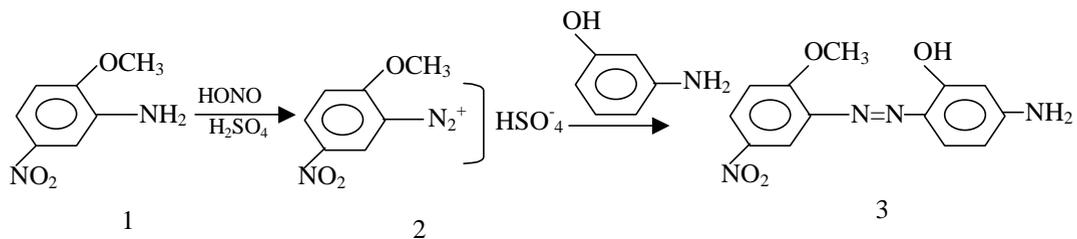
Synthesis of 2-methoxy-5-nitrophenylazo-2-hydroxyphenylazo-N-phenyl-naphthylamine

2-methoxy-5-nitrophenylazo-2-hydroxy-4-aminobenzene (4g, 0.0139 mol) was added to a mixture of water (50ml) and concentrated sulphuric acid (6ml) and the resultant mixture was cooled to $0-5^\circ\text{C}$.

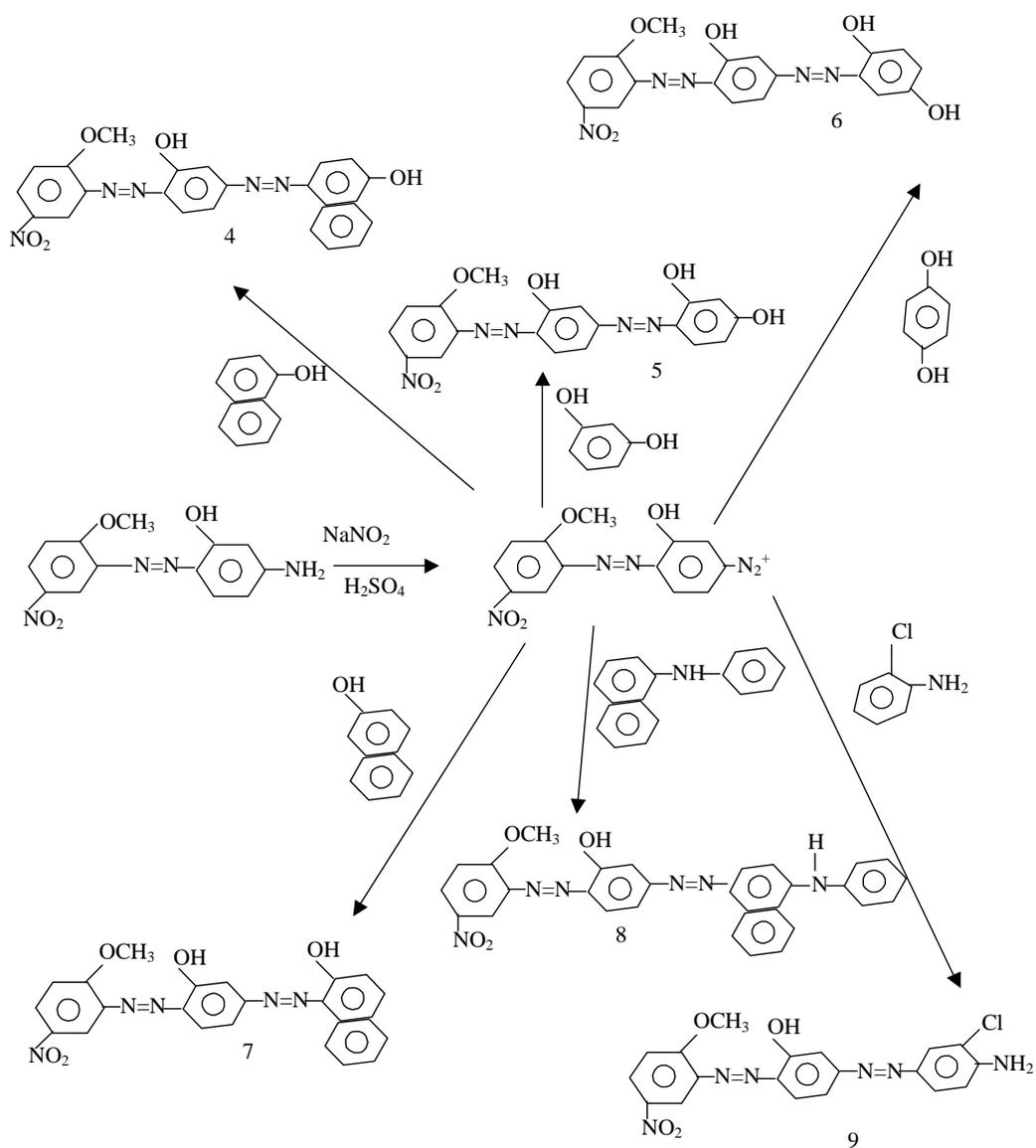
Sodium nitrite (3g, 0.043 mol) in 10ml water at $0-5^\circ\text{C}$ was added dropwise with vigorous stirring for 20min. The amino-compound was certified to be completely diazotised by adding a solution of 4-(N, N-dimethylamine) benzaldehyde which generates colour if undiazotised aromatic amine is still present. The resulting diazonium salt solution was then added in small portions for 10min with vigorous stirring to a solution of N-phenyl-naphthylamine (3g, 0.137mol) in acetic acid (15ml). The reaction mixture was further stirred for 2 hours and the dye precipitate was filtered, washed with water and dried. Recrystallisation from hot ethanol gave brown crystals of the product dye 8 (4.48g, 64,% yield). This procedure was also used to synthesise dye 9

Dyeing of polyester

Polyester fabric was dyed in an ahiba dyeing machine at a liquor ratio of 20:1. The dyebaths were prepared with the synthesized dyes 4-9 and using lignosulfonates (sulfite cellulose liquors) as the dispersing agent. The pH of the dye liquor was adjusted to 5 with acetic acid. Dyeing was carried out at 70°C , the dyebath temperature being raised at a rate of $1^\circ\text{C}/\text{min}$ to 130°C . The dyeings were rinsed and then reduction



Scheme 1



Scheme 2

cleared in an aqueous solution of 2g/l solution of sodium hydroxide and 2g/l sodium hydrosulphite at 80°C for 30min. Dye bath preparation and dyeing procedure were as previously described [6].

Fastness Test

The dyed fabrics were subjected to wash (ISO 105-CO2 in which 5g/l soap solution was used at a temperature of 50°C for 45min (liquor ratio 50:1/ C2S:1994), [7] light (AATCC Test Method 16-1998)⁸ and rub (ISO 105-X12:2001) [9] fastness tests after heat setting at 180°C for 60s. The shade change, together with staining of adjacent fabrics, was assessed according to appropriate society of Dyers and colourists (SDC) grey scale.

The sublimation test was carried out according to ISO 105-POI, 1993 Method (ISO 105-POI, 1993)¹⁰. The dyed samples were treated in a sublimation testing machine at 177°C for 30s and related against the grey scales for assessing staining.

RESULTS AND DISCUSSION

Synthesis of intermediates and dyes

The diazo components 3 was synthesised as illustrated in reaction scheme 1. 2-Methoxy-5-nitroaniline (1) was used as a starting material and was diazotised using sulphuric acid and, sodium nitrite to give diazo component 3-in accordance with a standard method¹¹⁻¹³.

The six dyes⁴⁻⁹ were prepared by coupling of the diazotised diazo component with various couplers as shown in reaction scheme 2. The structures of the synthesized dyes 4-9 were characterized by IR, UV-visible and ¹H NMR analyses as shown in Tables 1 and 2. The meeting points of the dyes showed variations depending on the coupling components and ranged between 178 and >360°C.

Light absorption characteristics

Important information concerning the structure of azo dyes could be obtained from an ultraviolet-visible spectrum. The principal features that may be detected are multiple bonded systems, conjugated systems, and aromatic transitions in these systems which give rise to absorptions in the

200-700nm regions are n→π and n→π* and these are of diagnostic importance [14,]

The term chromophore is used to describe any structural feature which leads to absorption in the ultraviolet-visible region of the spectrum and this includes groups in which n→π* and n→π* transitions are possible.

An auxochrome is a substituent that does not itself absorb in the ultra-violet region but has the effect of shifting chromophore peaks to longer wavelengths as well as increasing their intensities. For example, -OH and -NH₂ have an auxochromic effect on the benzene chromophore. Auxochromic substituents have at least one pair of n (non-bonding) electrons on oxygen and nitrogen which are capable of interacting with the π electrons of the ring^{15,16}. This interaction apparently has the effect of stabilizing the π* state, thereby lowering its energy; a bathochromic shift then results. A group having the opposite, hypsochromic effect is called hypochrome (ie having electron-attracting substituents such as CHO, COR, NO₂, Cl).

The wavelength of maximum absorption (λ_{\max}) and the intensity of absorption (ϵ , the molar absorptivity or extinction coefficient) are useful in elucidating structural features. Thus, a high λ value indicates a high probability of the occurrence of the relevant electronic transition and is observable in systems in which the relative symmetry of the ground and excited states lead to a change in the transition moment¹⁷. Changes in the molecular environment adjacent to a chromophore may either increase or decrease the intensity of the absorption and such correlations were of help in the interpretation of our spectra. Thus, the visible absorption spectra of dyes 4-9 are shown in Table 2. The difference in absorbance between dye 4 and 7 could be explained as being due to the relative position of the hydroxyl (-OH) groups in each of the two coupling components. Thus, dye 7 has the -OH group in the ortho position to the azo group which resulted in a bathochromic (red) shift in contrast to dye 4 which has the -OH group in the para position.

Dye 6 has a lower wavelength of 482nm with a λ_{\max} of 533nm and absorbance of 0.277. The

Table 1: IR and ¹HNMR data of the dyes 4-9

Dye	IR	¹ HNMR, δ (ppm)	Solvent
4	3441(OH) 1631-1630cm ⁻¹ 1518 & 1341(NO ₂) 743(Ar-ring)	4.90(s, 3H, OCH ₃)	CDCl ₃
		6.60 (d, 1H naphthalene proton)	
		7.00 (d, 1H phenyl proton)	
		7.20 (d, 1H naphthalene proton)	
		7.45 (m, 1H phenyl proton)	
		7.55 (m, 1H naphthalene proton)	
		7.60 (m, 1H naphthalene proton)	
		7.85 (d, 1H naphthalene proton)	
		8.05 (t, 1H naphthalene proton)	
		8.25 (d, 1H phenyl proton)	
		8.55 (d, 1H, naphthalene proton)	
		8.70 (t, 1H, phenyl proton)	
		9.02 (s, 1H phenyl bonded OH)	
9.20 (d, 1H phenyl bonded OH)			
5	3423 (b)(OH) 1664(C-O-C) 1518 & 1341 (NO ₂) 1277 (C-O)745 (Ar-ring)	4.02 (s, 3H, OCH ₃)	CDCl ₃
		6.45 (d, 1H phenyl proton)	
		6.60 (d, 1H phenyl proton)	
		7.02 (d, 1H phenyl proton)	
		7.35 (m, 1H phenyl proton)	
		7.55 (m, 1H phenyl proton)	
		7.22 (d, 1H, phenyl proton)	
		7.98 (t, 1H phenyl proton)	
		8.02 (s, 1H bonded OH)	
		8.60 (d, 1H bonded OH)	
6	3452 (OH) 2845 (aromatic C-H) 1604(C-O-C) 1518 & 134 (NO ₂) (Symmetric and asymmetric stretch) 1201 (C-O)719 (Ar-ring)	4.05(s, 3H CH ₃)	d ₈ -Acetone
		6.72 (t, 1H, phenyl proton)	
		7.02 (d, 1H, phenyl proton)	
		7.20(d, 1H, phenyl proton)	
		7.42 (t, 1H, phenyl proton)	
		7.50 (m, 1H, phenyl proton)	
		7.60 (d, 1H, phenyl proton)	
		7.68 (m, 1H, phenyl proton)	
		8.20 (d, 1H, phenyl proton)	
		8.52(d, 1H, bonded OH)	
8.80 (d, 1H, bonded OH)			
7	3439(OH, NH) 1618 (C-O-C) 1518 & 1341 (NO ₂ symmetric and asymmetric stretch)745 (Ar-ring)	1.52 (s, 2H, NH ₂)	CDCl ₃
		4.02 (s, 3H, OCH ₃)	
		6.56 (d, 1H, phenyl proton)	
		7.02 (d, 1H, phenyl proton)	
		7.32 (m, 1H, phenyl proton)	
		7.52 (d, 1H, phenyl proton)	
		7.65(m, 1H, phenyl proton)	
		7.72 (m, 1H, phenyl proton)	

Table 1. Cont.

		7.82 (m, 1H, phenyl proton)
		8.45 (d, 1H, phenyl proton)
		8.79 (d, 1H, bonded OH)
8	3442 (OH very broad)	4.00 (s, 3H, OCH ₃)
	1630 (C-O-C)	6.60 (s, 1H, naphthalene proton)
	1518 & 1341 (NO ₂ symmetric and asymmetric stretch)	6.85 (d, 1H, phenyl proton)
	1203 (C-O_)	7.02 (t, 1H, phenyl proton)
	745 (Ar-ring)	7.30 (m, 1H, phenyl proton)
		7.50 (b & (m) 1H, phenyl proton)
		7.61 (m, 1H, naphthalene proton)
		7.70 (m, 1H, naphthalene proton)
		7.51 (m, 1H, naphthalene proton)
		7.65 (m, 1H, naphthalene proton)
		8.05 (d, 1H, naphthalene proton)
		8.60 (d, 1H, bonded OH)
		8.80 (d, 1H, phenyl proton)
9	3452 (OH, NH very broad)	1.60 (d, 1H, NH)
	1637 (C-O-C)	4.02 (s, 3H OCH ₃)
	1521 & 1341 (NO ₂ symmetric and asymmetric stretch)	6.40 (d, 1H, phenyl proton)
	744 (Ar-ring)	6.60 (d, 1H, naphthalene proton)
		7.00 (d, 1H, phenyl proton)
		7.02 (t, 1H, phenyl proton)
		7.20 (m, 1H, phenyl proton)
		7.22 (d, 1H, naphthalene proton)
		7.50 (m, 1H, naphthalene proton)
		7.65 (m, 1H, phenyl proton)
		7.80 (m, 1H, phenyl proton)
		8.05 (d, 1H, naphthalene proton)
		8.70 (d, 1H, phenyl proton)
		8.90 (t, 1H, bonded OH)

Table 2: Yield, meeting points and spectral data of dyes 4-9

Dye	Synthesis method and recrystallisation solvent	Yield (%)	m.p(° C)	absorption	R _f	λ _{max} ^a (nm)	ε _{max} ^a (1mol ⁻¹ cm ⁻¹)
4	1A	82	>360	0.303	0.56	533	67,000
5	1A	76	238-240	0.277	0.32	533	57,000
6	1A	60	258-260	0.940	0.45	482	96,000
7	1A	84	>360	0.322	0.60	416	71,000
8	2A	64	178-180	0.113	0.71	512	59,000
9	2A	58	>360	0163	0.62	767	63,000

^aMeasured in DMF

Table 3: Fastness properties of dyes 4-9 (1% owf) on polyester fabric

Dye	Change/staining			Rubbing		Colour on fabric
	Light	Wash	Sublimation	Rubbing		
				Dry	Wet	
4	6	5	5	4/5	4/5	Orange
5	5	5	5	4/5	4/5	Orange
6	5	5	5	4/5	4	Orange
7	6	5	5	4	4/5	Orange
8	5	5	5	4/4	3/5	Brown
9	5	5	5	4/5	3/4	Brown

difference in absorbance could be attributed to the relative positions of the two –OH groups in dye 6 for instance, the two –OH groups are capable of forming intramolecular hydrogen bond with the azo linkage. This ensures a maximum degree of π -orbital overlap and hence a higher absorbance [18]. In dye 5, however, only the –OH group ortho to the azo linkage can interact.

The absorbance of dye 8 is less than that of dye 9 due to the low availability of non bonding electron pairs to interact with the benzene ring.

All the dyes showed very broad absorption curves in the range of 380-800nm leading to a large tinctorial strength. This could be due to the presence of –OH group in all the dyes that could probably form intramolecular hydrogen bond between the hydroxyl group and the azo linkage¹⁹.

The effect of the substituents in the diazo component ring and the coupling components on the λ_{\max} and ϵ_{\max} values was also outstanding. A large bathochromic (66-151nm) and hypsochromic effect were observed when comparing the λ_{\max} values and molar extinction coefficients of dyes 8 and 9, and dye 5 and 6 respectively. The bathochromic effect is due to the introduction of the electron-withdrawing chloride group into the coupling component of dye 9.

Fastness properties

All the dyeings for the fastness tests were carried out at pH5, which had been demonstrated to be the optimum. The results of the wash fastness tests for the dyes on polyester fabrics are

summarized in Table 3 and they showed excellent wash fastness. This could be due to the high molecular weight of the dyes and their state in the fibre. Table 3 also gives the results of light and rubbing fastness tests. The rubbing results were moderate to good and light fastness was good. The general high light fastness of the dyes on polyester is probably attributed to the relative positions of the 3-nitro group and the 2'-methoxy group relative to the azo group in the diazo component²⁰ and also the crystalline nature of polyester fibre. The sublimation test results showed excellent performance on polyester substrate. The reason for this is due to the high molecular size and the polar substituent groups such as –OH, –NH and NH₂ groups present in the benzene rings.

CONCLUSIONS

Disazo disperse dyes of 2-methoxy-5-nitroaniline derivatives were synthesized and their light absorbance and fastness properties were evaluated. Introduction of benzene rings containing –OH groups and arylamino groups in the coupling component ring resulted in the bathochromic and hypsochromic effects and increase of extinction coefficient of the dye. The absorbance of the dyes depends on the nature of the substituent groups present as well as their relative positions in the couplers. The dyes gave orange to brown hues in polyester fabrics and showed good leveling properties. The dyes exhibited excellent wash and sublimation fastness while rubbing was moderate to good. The light fastness results, were outstandingly good.

These dyes could, therefore, achieve commercial importance especially in the textile industry and other areas of human endeavor that

require excellent wash, sublimation and good light fastness properties.

REFERENCES

1. L. Shuttleworth and M.A. Weaver in the chemistry and application of dyes (Eds. R.W. David and H. Geoffrey). New York and London Plenum press (1994).
2. I.L. Finar Organic Chemistry. Essex. Vol. 1 6th edn. Longman group Ltd (1973).
3. E.P.G. Gohl and L.D. Vilensky. Textile Science. An explanation of fibre properties. London. Longman pub. Ltd (1983).
4. S.P. Bawane and S.R. Sawant catalytic hydrogenation of p-nitroaniline and 2-methoxy-5-nitroaniline. *Indian Journal of Chem. Tech.* **10**(6): 632-637 (2003).
5. D. Roberts, J.A. Joule, M.A. Bros and M. Alvarez. Synthesis of pyrazole (4,3,2-) diquinolines. *J. American Chem. Soc. Org. Chem.* **62**: 568-577 (1999).
6. C.H. Hiles. A Laboratory course in dyeing. Bradford. Soc. Dyers and Colourists (SDC), (1974).
7. ISO 105-CO6. Textile test for colour fastness to wash part CO6. Geneva, ISO (1994).
8. Technical manual. American Association of Textile chemists and colourists (AATCC). North Carolina (1998).
9. ISO 105-X12. Textile-Test for colour fastness to rubbing part X12. (Geneva, ISO, 2001).
10. ISO 105-POI. Textile Test for colour fastness to dry heating excluding pressing (Geneva ISO (1993).
11. J.O. Otutu, D. Okoro and E.K. Ossai. Preparation of disazo dyes derived from p-aminophenol and their fastness properties for synthetic polymer-fibres. *Jour. Appl. Sci. Pak* **8**(2): 334-339 (2008).
12. Y.B. Paula Organic chemistry. New York, Prentice-Hall Inc (1995).
13. J.J. Lee, W.J. Lee, J.H. Choi and J.P. Kim. Synthesis and application of temporarily solubilised azo disperse dyes containing. β -sulphatoethylsulphonyl group. *Dyes and pigments* **65**(2): 75-81 (2005).
14. D.A. Skoog, F.J. Holler and T.A. Nieman. Principles of instrumental analysis 5th edn. U.S.A. Thomson learning, Inc., (1998).
15. D.O. Ukponmwan, A. Osaze-Amayaevbo and A.P. Oviawe. Mono-azo disperse dyes derived from 4-Amino-3-nitrotoluene and 4-aminophenol *Jour. Chem. Soc. Pak.* **21**(20): 179-183 (1999).
16. Y.M. El-kholy, S.A. Abdel-Hatiz and S.H. Ahmed. Synthesis and dyeing properties of novel disperse dyes. Part 2: Pyrazole disperse dye derivatives. *Jour. Soc. Dyers Colourists* **114**(5): 45-48 (1998).
17. D.H. Williams and I. Fleming. Spectroscopic Methods in organic chemistry. 4th edn, New York., (1989).
18. C.N. Banwell. Fundamentals of molecular spectroscopy, 3rd edn. New York, McGraw-Hill Co., (1983).
19. F.A. Carey, Organic chemistry. 5th edn. New York. McGraw-Hill Co., (2003).
20. K. Ventakaraman. The Chemistry of synthetic dyes 5th edn. Vol III. New York. Wiley Interscience Pub. Co., (1977).