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ORIGINAL ARTICLE

Synthesis and dyeing performance of bisazo disperse dyes based on 3-[4-(4-amino-2-chlorophenoxy)anilino]phenol



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DAP

Abstract The present communication aims to develop bisazo disperse dyes based on 3-[4-(4-amino-2-chlorophenoxy)anilino]phenol (DAP) both as a coupling component as well as a diazonium salt. Coupling reaction of DAP was carried out with a diazonium salt of 4-aminoacetanilide to yield a monoazo disperse dye, and then it was further used as a diazonium salt and coupled with a different aromatic phenol to synthesize bisazo disperse dyes. All the disperse dyes were characterized by elemental analysis, IR, NMR and UV–Visible spectral studies with a view to determine their chemical structure. The dyeing ability of these bisazo disperse dyes has been evaluated in terms of their dyeing behavior and fastness properties on different fabrics.

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1. Introduction

Disperse dyes are the most widely used class of dyes for the dyeing of cellulose acetate as well as of synthetic fabrics. The history and development of these dyes is well documented by Fourness (1956). In recent years the main focus of research and development in the field of dyestuff is to improve fastness properties and to introduce or to modify new characteristics such as fire resistance, crease proofing, shrink proofing, and

dimensional stability, to the fabrics (Binesh, 2005). In this context, one of the approaches is to enhance dye fiber affinity of the dyes. The starting materials 4-amino-2,4'-dichlorodiphenyl ether and *m*-amino phenol have been previously used successfully as coupling components to make disperse azo dyes (Nimmo and Hulms, 1980). The beginning of the synthetic fibers like nylon, polyester, polyacrylonitrile created significant challenge in the dyeing ability of hydrophobic fibers to dyestuff chemists. Consequently in the last three decades, the researchers focused their efforts on the synthesis of dyes for these fibers. Polyester is one of the most hydrophobic of all common fibers and generally dyed with disperse dyes because of their high tinctorial strength with good fastness properties. From the chemical point of view more than 50% of disperse dyes are simple azo compounds because of the ease with which a number of molecular combinations can be achieved by varying diazonium and coupling components, simple manufactur-

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ing process and providing a very wide color range of high color strength (Carr, 1995; Hamprecht and Westerkamp, 2003; Christi et al., 2000). As a result success has been achieved with the discovery of numerous new coupling and diazonium components intended to give disperse azo dyes especially for dyeing polyester and nylon fibers. Literature survey regarding bisazo disperse dyes based on 4-amino-2,4'-dichlorodiphenyl ether as well as DAP have not yet received much attention except for a few reports (Nimmo and Hulms, 1980) even though various 4-amino-2,4'-dichlorodiphenyl ether based dyes and intermediates have extensively been used in textile industries. Therefore, the present communication deals with the synthesis and application of novel bisazo disperse dyes based on DAP.

2. Experimental

2.1. Materials

4-amino-2,4'-dichlorodiphenylether was prepared by the reported method (Wilson and Dougal, 1963). All the other chemicals used were of analytical reagent grade and were crystallized before use.

2.2. Methods and instruments

All the intermediates and dyes were characterized by elemental analysis and spectral study such as UV-Visible, IR, ^1H NMR, ^{13}C NMR. NMR spectra were recorded in DMSO- d_6 solvent

using Bruker 400 MHz NMR Spectrometer. Elemental analyses for C, H, N contents of DAP coupler and the dyes were carried out on Carlo Erba CHN Analyzer (Italy). The infrared absorption spectra were scanned on a Nicolet-400 D FTIR spectrophotometer using potassium bromide pressed pellet technique. The characteristic absorption bands that appeared in IR spectra of all the bisazo disperse dyes are shown in Figs. 1 and 2. The absorption spectra of all of the dyes in DMF-ethanol solution were scanned on a Beckmann UV-Vis spectrophotometer at a concentration of 1.6×10^{-2} mg/ml. The number of azo groups in all the dyes was estimated by redox titration method reported in the literature (Vogel, 1989).

2.3. Synthesis of 3-[4-(4-amino-2-chlorophenoxy)anilino]phenol (DAP)

3-[4-(4-amino-2-chlorophenoxy)anilino]phenol was prepared by the condensation of 4-amino-2,4'-dichlorodiphenyl ether with *m*-aminophenol in the presence of K_2CO_3 . For this purpose, a solution of 4-amino-2,4'-dichlorodiphenyl ether (0.1 mol) in 40 ml methanol was taken in a round bottomed flask equipped with a condenser and was heated at a temperature of 65–70 °C under continuous stirring for 30 min. To this, methanolic solution of *m*-aminophenol (0.1 mole) aqueous K_2CO_3 (0.1 mole) was added. The reaction mixture was then refluxed for an hour and was allowed to stand for half an hour.

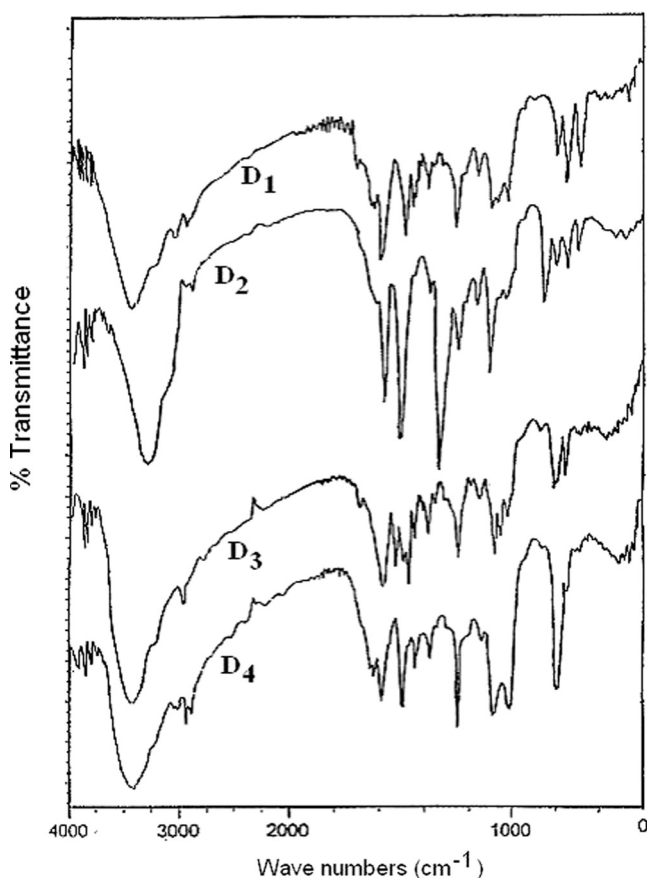


Figure 1 IR spectra of bisazo disperse dyes (D₁–D₄).

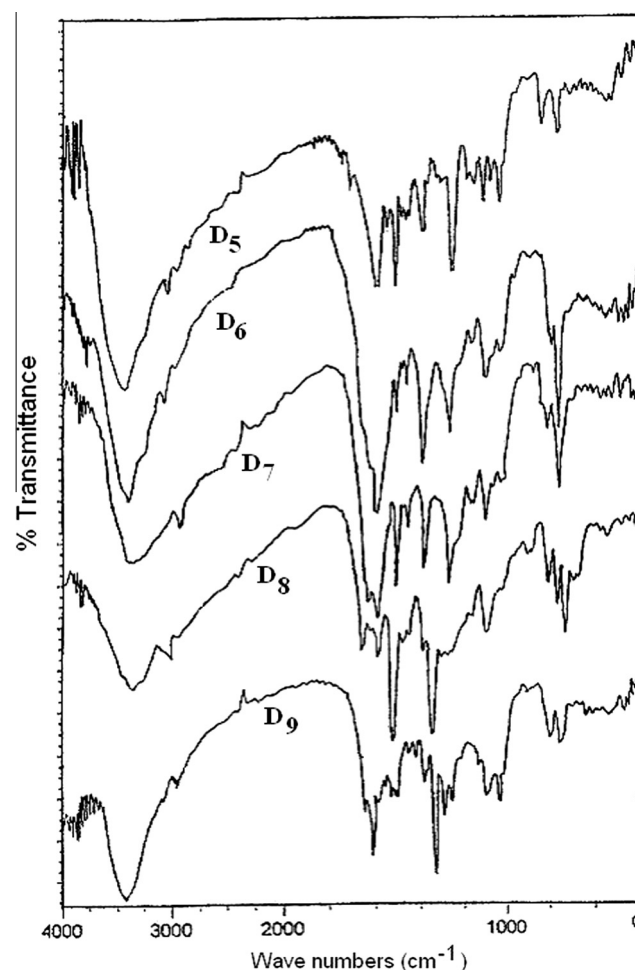
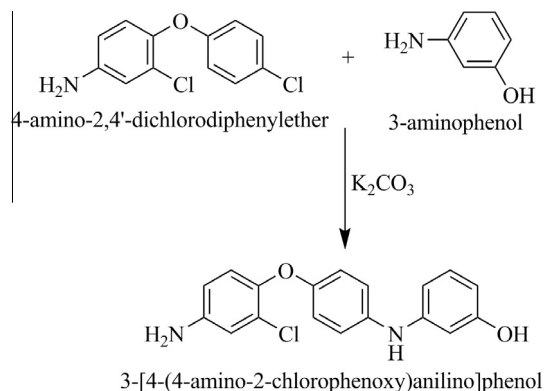


Figure 2 IR spectra of bisazo disperse dyes (D₅–D₉).

Table 1 Characterization of DAP.

Physical parameters	
Color	Light Brown
Molecular formula	C ₁₈ H ₁₅ N ₂ OCl
Molecular weight	310.5 gm/mole
Elemental composition	%C %H %N
Calculated	69.5 4.83 9.03
Found	69.4 4.82 9.00
IR spectral characteristic absorption bands	
Phenolic O–H	3333 cm ⁻¹
–C=C– stretching	1480 cm ⁻¹
In plane vibration	1576 cm ⁻¹
Out of plane vibration	815 cm ⁻¹
C–Cl stretching	3345 cm ⁻¹
C–H stretching	2921 cm ⁻¹
Secondary amine:	3390 cm ⁻¹
N–H stretching	
¹ H NMR data	
Peak observed δ ppm	Assignment
5.20 (s)	1H, –NH group
4.46 (s)	2H, –NH ₂ group
10.16 (s)	1H, –OH group
6.58–7.26 (m)	11H, Three aromatic rings
¹³ C NMR data peak observed δ ppm	
77.0 (due to CDCl ₃), 99.58, 107.80, 109.5, 111.34, 116.71, 117.49, 120.67, 125.12, 125.72, 131.18, 137.10, 144.48, 147.45, 149.45, 154.80, 158.97.	

**Scheme 1** Synthetic protocol of DAP.

The obtained reaction mixture was poured into ice cold water and it was filtered and washed with hot water. The yield was 74% having a melting point of 151 °C (uncorrected). Characterization of DAP is shown in Table 1. The details of reaction steps involved are shown in Scheme 1.

2.4. Synthesis of *N*-[4-(2-{4-[4-(4-amino-2-chlorophenoxy)anilino]-2-hydroxyphenyl}diazenyl)phenyl]acetamide

3-[4-(4-Amino-2-chlorophenoxy)anilino]phenol was used as a coupling component to synthesize disperse monoazo dye with 4-amino acetanilide. For this purpose, 4-amino acetanilide was diazotized by using HCl and sodium nitrite as per the procedure reported in the literature (David and Blangy, 1949).

The resulting diazonium salt was carefully added to a solution of 3-[4-(4-amino-2-chlorophenoxy)anilino]phenol (DAP) in alkali medium at a temperature of 0–5 °C by adjusting the pH at 6–6.5 to yield *N*-[4-(2-{4-[4-(4-amino-2-chlorophenoxy)anilino]-2-hydroxy phenyl}diazenyl)phenyl]acetamide. The precipitated dye was then filtered, washed with hot water and dried in air. The yield was 78% having a decomposition temperature of 122–126 °C (uncorrected). ¹H NMR data are shown in Table 2. The details of reaction steps involved are shown in Scheme 2 (see Scheme 3).

2.5. Synthesis of bisazo disperse Dyes (**D₁**–**D₉**)

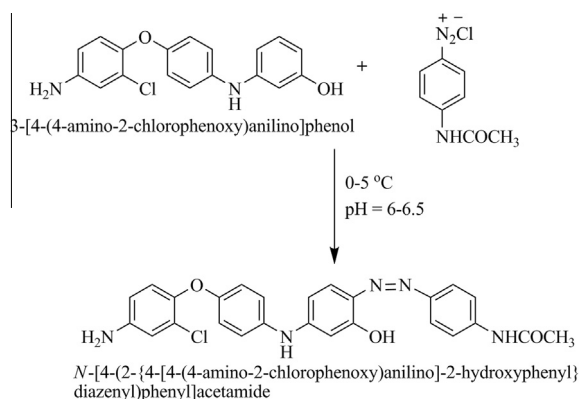
N-[4-(2-{4-[4-(4-amino-2-chlorophenoxy)anilino]-2-hydroxyphenyl}diazenyl)phenyl]acetamide was diazotized using HCl and sodium nitrite by the procedure reported in the literature (David and Blangy, 1949). The resulting diazonium salt solution was carefully added to the solution of different phenolic derivatives in alkali medium at 0–5 °C while adjusting the pH at 6–6.5 to yield bisazo disperse dyes. The precipitated dye was filtered, washed with hot water and air dried. These dyes are abbreviated as **D₁**–**D₉**. They are soluble in polar solvents like DMF, THF, methanol, ether, etc. and recrystallized with methanol. General properties of all of the dyes are reported in Table 3.

2.6. Dyeing process

Dyeing on polyester and nylon was carried out by the reported dyeing procedure (Szymczyk et al., 2007; Hallas and Choi, 1999; Bello, 1995). The polyester and nylon fabrics were treated at pH 5–6 (adjusted with acetic acid) for 15 min at 60 °C. A laboratory model glycerine bath of metallic beaker-dyeing machine was used. A paste of dye (4×10^{-5} kg) was prepared with the dispersing agent Dodamol (80×10^{-3} kg), wetting agent Tween-80 (5×10^{-6} kg) (in case of polyester) and water (1×10^{-3} dm³) in a beaker. To this paste, 160×10^{-3} dm³ water was added under stirring and the pH was adjusted to 4 using acetic acid to give the dyeing solution. This solution was then transferred to a metallic beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a pretreated patch of polyester or nylon fabric (2×10^{-6} kg) was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerine bath. The temperature of the bath was raised to 110 and 95 °C, for polyester and nylon fabrics respectively at the rate of 2 °C/min. The dyeing was continued for 90 min. under pressure. After cooling for an hour, the beaker was removed from the bath and washed thoroughly with water. The mother liquor after dyeing was collected and used further for exhaustion study. The dyed pattern was washed several times with cold water followed by detergent (0.2×10^{-6} kg) and sodium carbonate (0.1×10^{-6} kg) in 100×10^{-3} dm³ water at 80 °C for 30 min. Finally, it was washed thoroughly with water and dried at room temperature. The dyeing behavior of these dyes was examined by studying the percentage of dye bath exhaustion and fixation of the dye on the fabric according to a standard method (Kochergin, 1956). The dyed polyester and nylon fabrics were tested for wash-fastness according to ISO 105 test (Hamprecht and

Table 2 ^1H NMR data of monoazo and bisazo disperse dyes.

Dyes	-OH on R δ ppm	-OH δ ppm	-NH δ ppm	-NHCO δ ppm	-CH ₃ δ ppm	Aromatic protons δ ppm
D₀	–	9.39 (1H, s)	4.92 (1H, s) 5.96 (2H, s)	7.40 (1H, s)	2.04 (3H, s)	6.76–8.22 (14H, m)
D₁	10.28 (1H, s)	9.42 (1H, s)	4.96 (1H, s)	7.44 (1H, s)	2.02 (3H, s)	6.78–8.34 (18H, m)
D₂	10.29 (1H, s)	9.38 (1H, s)	4.94 (1H, s)	7.45 (1H, s)	2.06 (3H, s)	6.80–8.63 (17H, m)
D₃	10.12 (1H, s)	9.40 (1H, s)	4.98 (1H, s)	7.46 (1H, s)	2.04 (3H, s)	6.78–8.34 (20H, m)
D₄	10.18 (1H, s)	9.41 (1H, s)	4.92 (1H, s)	7.40 (1H, s)	2.04 (3H, s)	6.76–8.37 (17H, m)
D₅	10.26 (1H, s)	9.42 (1H, s)	4.95 (1H, s)	7.43 (1H, s)	2.05 (3H, s) 2.52 (3H, s)	6.69–8.28 (17H, m)
D₆	10.58 (1H, s)	9.40 (1H, s)	4.96 (1H, s)	7.47 (1H, s)	2.01 (3H, s) 2.43 (3H, s)	6.72 – 8.33 (17H, m)
D₇	11.32 (2H, s)	9.42 (1H, s)	4.95 (1H, s)	7.44 (1H, s)	2.03 (3H, s)	6.74–8.35 (17H, m)
D₈	9.72 (1H, s)	9.41 (1H, s)	4.92 (1H, s)	7.40 (1H, s)	2.04 (3H, s)	6.76–8.37 (17H, m)
D₉	10.36 (1H, s)	9.42 (1H, s)	4.96 (1H, s) 5.27 (2H, s)	7.45 (1H, s)	2.03 (3H, s)	6.69–8.38 (17H, m)

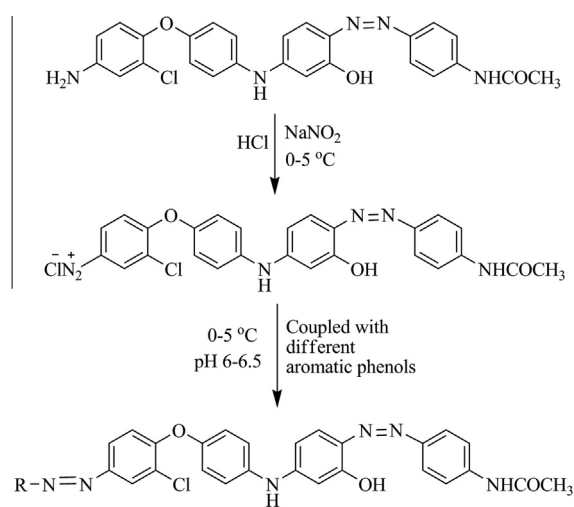
**Scheme 2** Synthetic protocol of monoazo disperse dyes.

Westerkamp, 1984) using a detergent and 2% sodium carbonate. The change in shade and staining of adjacent fabrics were assessed using grey scales. A light-fastness test was carried out in accordance with the ISO 105 test (Hamprecht and Westerkamp, 1984).

3. Results and discussion

3.1. Characterization of DAP

DAP was a light green colored solid compound and was soluble in polar solvents like THF, Dioxane, DMF etc. The data of



Where R = Phenol, 4-Nitrophenol, 2-Naphthol, 2-Cresol, 3-Cresol, 4-Cresol, Resorcinol, 2-Chlorophenol, 3-Aminophenol.

Scheme 3 Synthetic protocol of bisazo disperse dyes.

C, H and N content of DAP are shown in Table 1. These are found to be in good accordance with the calculated value based on the synthetic and proposed structure.

Inspection of IR spectrum of DAP revealed that IR spectrum of DAP was associated to the aromatic ring system. The absorption band at 3333 cm^{-1} was due to phenolic

(-OH) group and the band at 1480 and 2921 cm^{-1} of -C=C- and -CH stretching of aromatic ring system respectively. Another absorption band was also in good agreement with the proposed structure.

^1H NMR spectrum data of DAP revealed the following features. The singlet observed at 5.20 δ ppm is assigned to the proton of the secondary amine (-NH) group of DAP. This

indicates the presence of the secondary amine group of the heterocyclic substrate is present. The singlet observed at 4.46 δ ppm value is assigned to the protons of aromatic primary amine (-NH₂) group of DAP. This indicates that only one primary amine group had been involved in the synthetic substrate. The singlet observed at 10.16 δ ppm value in the DAP indicates the presence of the phenolic -OH group of

Table 3 General properties of bisazo disperse dyes.

Dyes	Fusing Temp. °C	Mol. Wt.	% Yield	No. of azo group	% Elemental Composition					
					%C		%H		%N	
					Calc.	Found	Calc.	Found	Calc.	Found
D₁	128-138	592.5	80	2.16	64.8	64.5	4.21	4.20	14.1	14.0
D₂	126-136	685.5	82	2.15	63.0	63.1	3.90	3.91	12.3	12.2
D₃	125-135	685.5	89	2.03	63.0	62.9	3.90	3.89	12.3	12.1
D₄	131-144	622.5	78	2.10	63.6	63.4	4.33	4.32	13.4	13.2
D₅	135-146	622.5	76	2.12	63.6	63.5	4.33	4.31	13.4	13.3
D₆	140-149	622.5	80	2.11	63.6	63.5	4.33	4.34	13.4	13.5
D₇	136-149	608.5	81	2.17	52.5	52.4	4.10	4.11	13.8	13.7
D₈	140-148	627.0	72	2.10	61.2	61.0	3.98	3.99	13.3	13.2
D₉	141-148	607.5	73	2.12	63.2	63.1	4.27	4.25	16.1	16.0

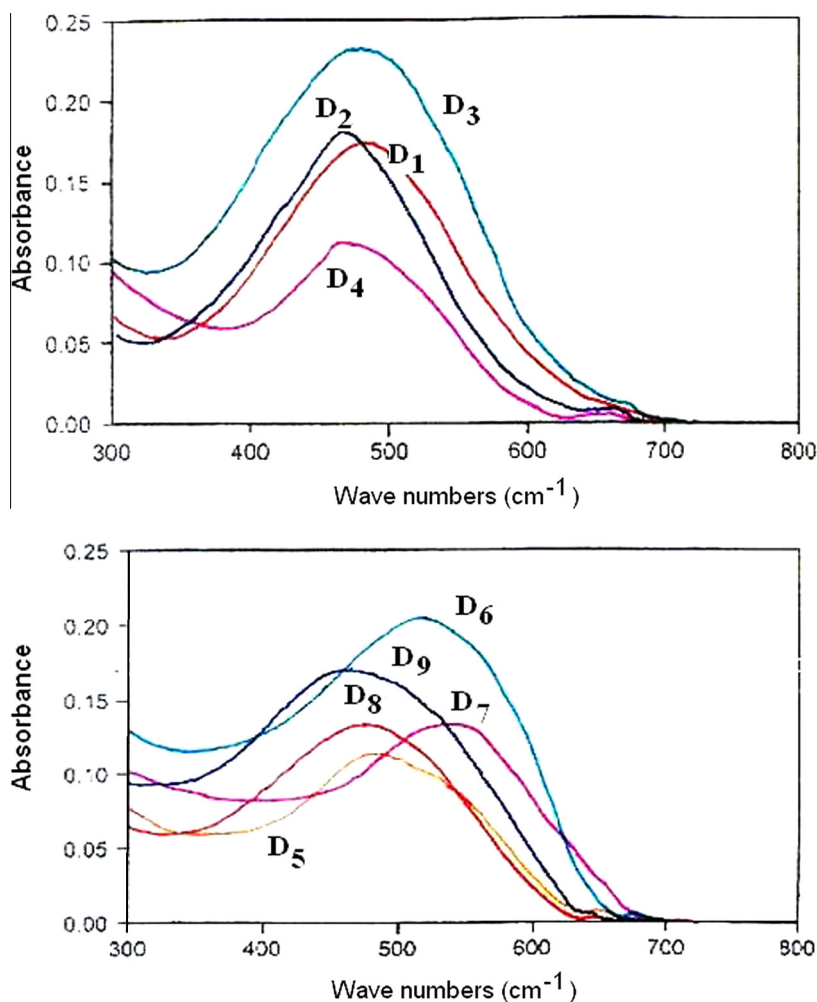


Figure 3 Visible Spectra of bisazo disperse dyes (D₁-D₉).

Table 4 Absorption spectral data of monoazo and bisazo disperse dyes.

Coupling compound	Dye designation	λ_{\max} (nm)	Absorbance ^a	log ϵ
DAP	D₀	455	0.308	4.189
Phenol	D₁	476	0.336	4.448
<i>p</i> -Nitrophenol	D₂	476	0.458	4.596
β -Naphthol	D₃	471	0.354	4.580
<i>o</i> -Cresol	D₄	466	0.20	4.268
<i>m</i> -Cresol	D₅	486	0.232	4.297
<i>p</i> -Cresol	D₆	521	0.410	4.567
Resorcinol	D₇	536	0.270	4.358
<i>o</i> -Chlorophenol	D₈	460	0.260	4.351
<i>m</i> -Aminophenol	D₉	476	0.268	4.369

^a Concentration of dye solution 1.6×10^{-2} mg/ml.

Table 5 Dye ability of monoazo and bisazo disperse dyes.

Dyes	Nylon		Polyester		Fastness Properties			
					Nylon		Polyester	
	% E	% F	% E	% F	Light ^a	Wash ^b	Light ^a	Wash ^b
D₀	76	80	75	81	5.5	3.5	4	4
D₁	81	81	79	83	4.5	4	5	4
D₂	74	83	78	84	4	4	5.5	5
D₃	80	84	82	89	5	5	4.5	4.5
D₄	85	86	83	85	5	4.5	4	4
D₅	83	81	81	82	5.5	5	3.5	4
D₆	84	82	84	85	5	5	5	5
D₇	81	88	85	90	3.5	4	4	5
D₈	82	89	80	88	4	5	5	4.5
D₉	80	85	77	87	4	4	4	4

^a Grading: 8, maximum; 7, excellent; 6, very good; 5, good; 4, fairly good; 3, moderate; 2, poor; 1, very poor.

^b Grading: 5, excellent; 4, very good; 3, good; 2, fair; 1, poor.

DAP. Further, the signals appeared in the region of 6.58–7.26 δ ppm in the spectrum corresponding to the 11 proton of three aromatic rings. The ¹H NMR data of all newly synthesized dyes are given in Table 2. The ¹³C NMR signals were in good accordance with the proposed synthetic structure of DAP.

3.2. Characterization of bisazo disperse dyes

The estimation of the number of azo groups in all the dyes indicated the presence of two azo groups in each of the dye (Table 3). The data of C, H and N contents of all the dyes were found to be comparable to those of the calculated results. Inspection of IR spectra of these dyes revealed that all the IR spectra resembled each other and have shown the characteristic IR absorption bands at 1595 cm^{-1} due to the azo group bridged to the two 2-naphthol end groups of bisazo disperse dyes. In addition to this, the medium band at 760 cm^{-1} was assigned to the substituted naphthalene ring moiety of 2-naphthol. Eventually, the substituents present at the para position to the azo group of the dye have shown two vibrational frequencies, one at 1110 cm^{-1} due to the presence of 1,4-substituted benzene ring and the other at 1375 cm^{-1} and 3382 cm^{-1} due to particular substituents such as $-\text{CH}_3$ and $-\text{OH}$ group respectively.

3.3. Color and absorption spectra of bisazo disperse dyes

Scrutinization of the absorption spectra of these dyes has supported the information regarding λ_{\max} of the dye **D₁** at 476 nm in visible spectrum and gave a light-orange shade on both the dyed patterns. The change in λ_{\max} and absorbance values of bisazo dyes can be correlated in terms of substituent effect of the groups present in the diazo component of the dye (shown in Fig. 3). Inspection of data reported is in Table 4 and envisaged that the presence of *p*-NO₂ group in the dye **D₂** has shown a marked hyperchromic effect resulting into a deep bright-orange red tinctorial shade on both the fabrics and this can be explained on the basis of resonating *p*-quinonoid structure of the dye **D₂**. Bathochromic shift was observed in the absorption spectra of the dyes **D₃**, **D₆**, **D₇** giving light to dark brown color shade because of the presence of auxochromes such as naphthalene ring, *p*-CH₃ and *p*-OH respectively. Lastly, *o*-Cl and *m*-NH₂ groups of the dyes (**D₈**, **D₉**) have shown the hypsochromic effect due to antiauxochromic effect with a light brown shade on both the fabrics.

3.4. Dyeing ability of bisazo disperse dyes

Exhaustion and fixation studies of all of the bisazo disperse dyes on nylon and polyester fabrics were carried out in accor-

dance with the method mentioned in the literature (Kochergin, 1956; Dixit et al., 2010). The percentage of exhaustion of all the bisazo dyes on nylon and polyester fabric was estimated in the range of 75–85% whereas that of percentage fixation of these dyes on both the fabrics was in the range of 80–90% and is shown in Table 5. The color fastness of these dyes to washing is excellent, and to light is of moderate class (Table 5). The dyed fabrics exhibit very good to excellent washing fastness properties and with a little variation in the moderate to good light fastness. The nature of the substituent in the coupling components has a little influence on the visible absorption. The striking feature of the dyeing behavior of bisazo disperse dyes envisages good dye-bath exhaustion and fixation with a major amount of dye exhausted from dye-bathing in the case of polyester compared to nylon. In general, all the dyes have shown excellent to moderate fastness properties. The fastness properties of all the dyes on nylon fabrics is much more higher than on polyester fabrics, especially light fastness was good on nylon fabrics while wash fastness was better on polyester fabrics.

4. Conclusion

The striking feature of the dyeing characteristics of bisazo disperse dyes on nylon and polyester fabrics have shown the percentage dye bath exhaustion ranging from 75% to 85% but that of percentage fixation of these dyes was in the range of 80–90%. Comparison of the data of percentage exhaustion with that of percentage fixation reveals that almost all the dye exhausted from the dye bath is fixed on the fabric. For all these dyes, the light fastness and washing fastness are of moderate to excellent grade.

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