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Synthesis of Halogenated Disazo Disperse Dyes Derived from 2,4-Dichloroaniline and 3-Aminophenol

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ABSTRACT

This study has been motivated by two developments. Firstly by the limited literature on the use of disazo dyes for application on textile fibres that could improve the light and sublimation fastness of dyed polyester fabrics. Also the recent non-textile application of disazo dyes in such areas as organic photoconductors and non-linear optical materials. In view of these, this study described the synthesis of disazo dyes, from 2,4-dichloroaniline and 3-aminophenol. The 2,4-dichloroaniline was diazotized and coupled with 3-aminophenol and the product of this, 2,4-dichlorophenyl-azo-4'-amino-2'-hydroxybenzene was diazotized and coupled with other coupling components to yield disazo dyes. The results of the absorption maxima of the dyes were observed to be dependent upon the substituents in the diazonium and coupling components and varied from 404 to 482 nm and 751 to 767 nm in DMF. The dyes on polyester fabric showed excellent fastness to light, sublimation, washing and good rubbing fastness. The dyes were characterised, using IR, ^{1}H-NMR and UV-visible analysis. The absorption of the dyes in the near-infrared region suggests that they are capable of acting as organic photoconductors.

Key words: Diszotisation, halogenated disperse dyes, absorption maxima, sublimation fastness, polyester fibre

INTRODUCTION

In recent years, there has been a trend towards developing different types of special fibres for special application conditions (Shuttleworth and Weaver, 1990). For instance, the heat or sublimation fastness of certain dyes that are low is not desirable for certain applications such as those used in the automobile industry. The condensed polycyclic compounds such as those often found to be used as vat dyes for cellulose fibres do not find much application on polyester, although hydrophobic in nature and of potential utility as disperse dyes. The reason probably lies in their larger molecular size and hence poor diffusion rate into the compact polyester fibre structure. However, a few such derivatives have found commercial utility in the colouring of polyester, particularly in the thermosol process (Gordon, 1990).

Disperse dyes have been placed according to their heat or sublimation fastness. The trend over the years of replacing the dyes of lower fastness reflects the increased usage of polyester, the changing demands for higher heat fastness and the increased availability of pressure-dyeing equipment (Otutu, 2010).

Heat Fastness, like rate of dyeing, depends on the diffusion coefficient of the disperse dye in the polymer substrate. Thus, in general, heat fastness is increased by molecular size or increase in polarity. However, these changes tend to lower the colour yield when the dyes are applied by the exhaustion methods and high temperatures must be used to counteract this effect (Burkinshaw, 1994; Shuttleworth and Weaver, 1990).

Recently, an attempt was made to synthesize disazo disperse dyes which contain one halogen atom in the diazonium components. Thus, a series of disazo disperse dyes containing a halogen atom in the first and second diazonium components was prepared with a view to developing disperse dyes that have increased heat fastness. Those dyes gave brown, yellow colour shades and excellent light and heat fastness (Otutu, 2007).

In this study a series of disazo disperse dyes having two halogen atoms in the first benzene nucleus in the molecule were prepared. The heat or sublimation and other fastness properties of the dyes on polyester fabric were investigated. Also, the correlation between the dye structure and absorption maxima was discussed.

MATERIALS AND METHODS

Materials: 2-4-Dichloroaniline, 3-aminophenol, obtained from Aldrich Chemical Company; 1-Naphthylamine, 4-chloroaniline and 2-naphthol obtained from BDH Chemical Co. were used as received. All other chemicals used were of synthesis grade purchased from Merck. The study was conducted in the Chemistry Laboratory of Delta State University, Abraka (Nigeria) during 2010-2011.

Methods

Synthesis of compound 3 (Fig. 1): 2-4-Dichloroaniline (29 g; 0.1543 mole) was dispersed in 80 mL of water. Ten milliliter of concentrated H_2SO_4 was added and the amine was diazotized by treatment with sodium nitrite (10.65 g, 0.1543 mole) in 25 mL of water over 20 min. Excess nitrous acid was destroyed by using urea (0.30 g, 0.006 mole). The 3-aminophenol (16.8 g, 0.1543 mole) was dissolved in sodium hydroxide (6.17 g, 0.154 mole) in 50 mL of water. The solution obtained was cooled to 0-5°C. the diazonium solution prepared was slowly added into the coupler solution with vigorous stirring over a period of 15 min at 0-5°C. Stirring was continued at this temperature for 2 h. The dye precipitate was isolated by filtration, washed with water and air dried. The crude dye was purified by recrystallization from hot acetic acid to give compound 3 in 98 % yield.

Synthesis of dye 5: 2-4-Dichlorophenyl-azo-4-amino-2-hydroxybenzene, compound 3, (3.0 g, 0.800 mL) was dispersed in 50 mL of water. Sulphuric acid (6 mL) was added to this mixture and the amine was diazotized by treating it with sodium nitrite (3.0 g, 0.0435 mole) in 15 mL of water at 0-5°C with stirring for over 15 min.

The resultant diazonium salt solution was added slowly to a solution of 3-aminophenol (2.0 g, 0.0183 mole) in (1.0 g) $NaOH_{(aq)}$ with vigorous stirring for 2 h. The precipitated compound was

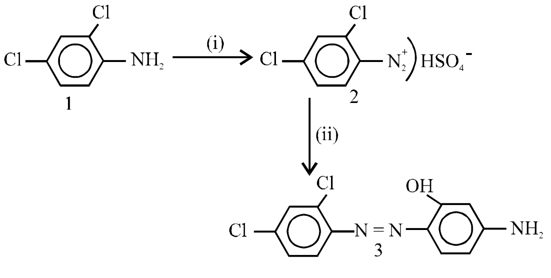

Fig. 1: Synthesis scheme for the preparation of dye 3 (i) $NaNO_2/H_2SO_4$, 0-5°C and (ii) C_6H_7O

isolated by filtration, washed with distilled water and dried. The crude product was recrystallized out of acetic acid to give a brown solid in 67% yield. This procedure was also used to synthesize compound 8 and 9.

Synthesis of dye 6: Compound 3 (3.0 g, 0.0071 mole) was mixed with 50 mL of water and diazotized with (3.0 g, 0.0183 mole) of sodium nitrite in 15 mL of water in 6 mL of sulphuric acid with stirring at 0-5°C over 15 min. 1-Naphthylamine (1.6 g, 0.0057 mole) which was dissolved in 5 mL of acetic acid, was coupled with the resultant diazonium salt solution with vigorous stirring for 2 h. The precipitate obtained was filtered, washed and dried in air. The crude product was recrystallized out of carbon tetrachloride to give a brown solid of compound 6 in 70% yield. This procedure was also used to prepare compound 7.

Chemical and instrumental analysis: Melting points were determined using a Buchi SMP-20 melting point apparatus and are uncorrected. Infrared spectra (in KBr pellets) were recorded on Nicolet Aversar 330 series spectrophotometer. The absorption spectra were measured in 1 cm quartz cells on a Genesys 10S VL 200 series spectrophotometer. 'H-NMR spectra were recorded on a Mercury 220 BB Oauife series spectrometer at 199.97 MHz using DMSO and $CDCl_3$ as solvents and tetramethylsilane as the internal standard. Thin Layer Chromatography (TLC) was used to assess the purity of the dyes.

Dye application

Dyeing of polyester fabric: The dye baths were prepared with the synthesized dyes 5-9 using Lignosulphonate (sulphite cellulose liquors) as the dispersing agent. The dyes (1.0 g) were first dissolved in DMF before adding the dispersing agent at Liquor to material ratio of 20:1. The pH of the dye Liquor was adjusted to 5 with acetic acid. Dyeing was performed and continued for 60 min at 130 to 135°C under increased pressures. The dyed polyester fabric was subjected to reduction-cleared treatment at 85°C for 10 min in a solution of sodium hydroxide (flakes) 2 g L^{-1}, sodium sulfite 2 g L^{-1} and then treated in a betaine amphoteric surfactant in water, washed with water and then dried (Giles, 1974; Burkinshaw, 1994).

Fastness tests

Wash fastness: The wash fastness of all dyed samples were tested according to ISO standard method (ISO, 1994). The composite samples measuring (10×5 cm) were washed with soap solution (2 g L^{-1} Na_2CO_3, 5 g L^{-1} soap solution, Liquor ratio 50:1) for 30 min at 60°C in an Atlas Launder-Ometer. The change in colour of the treated test specimens and the degree of staining of the two adjacent undyed fabrics were evaluated using the Grey Scales. The Grey Scale for assessing change in colour consists of five pairs of pieces of Grey Cards in a frame numbered 1 to 5 where 1 indicates poor fastness and 5 excellent.

Light fastness: The light fastness of the 1% (owf) dyeings were determined using an Atlass ES 25 Weather-Ometer (Xenon arc) according to AATCC test method (ISO, 2001). The test conditions were: Blank panel temperature: 60°C, Relative humidity: 30±5%, Chamber temperature 50°C, Irradiance: 0.75 W m^{-2}, Counter setting: 54 kJ m^{-2}. The dyed samples were exposed to these conditions and the change in colour of the fabrics (2×6 cm) were rated against standard blue wool samples (grade 1-8), 1-2 (poor), 8 (excellent), were used as indications for the Grey scale for light fastness.

Sublimation: Sublimation test was determined according to ISO, 105-P01 1993 protocol (ISO, 1993). The dyed fabric samples were treated in a sublimation testing machine at 177°C for 30 sec after heat setting at 180°C for 60 sec. The tested fabrics were then rated against the standard Grey scale (grade 1-5): 1 (poor), 5 (excellent).

Rub fastness: The Rub (Crocking) fastness was evaluated using a Crock meter. The dyed fabrics were treated with the crock meter when dry and when wet and then rated against the Grey Scale for colour transfer. The results are shown in Table 4.

The fastness test is to investigate the rate of fading of the colour of the dyes on the fabrics when exposed to various agencies such as light, washing, sublimation and rubbing. Other fabric properties such as the crystallinity and chemical composition may also influence the fastness of fabrics.

RESULTS AND DISCUSSION

The five disperse dyes (5-9) were prepared by coupling the diazonium salt solutions of compound 3 with various coupling compounds as shown in Fig. 2. The dye structures were characterized using IR, 'H-NMR and UV-VIS analyses as shown in Table 1 and 2. The melting points of the dyes are quite high and did not differ considerably from each other. This is probably due to the similar substituents present in the first benzene nucleus. All the dyes gave moderate yields except dye 5 and 6 which gave relatively high yields.

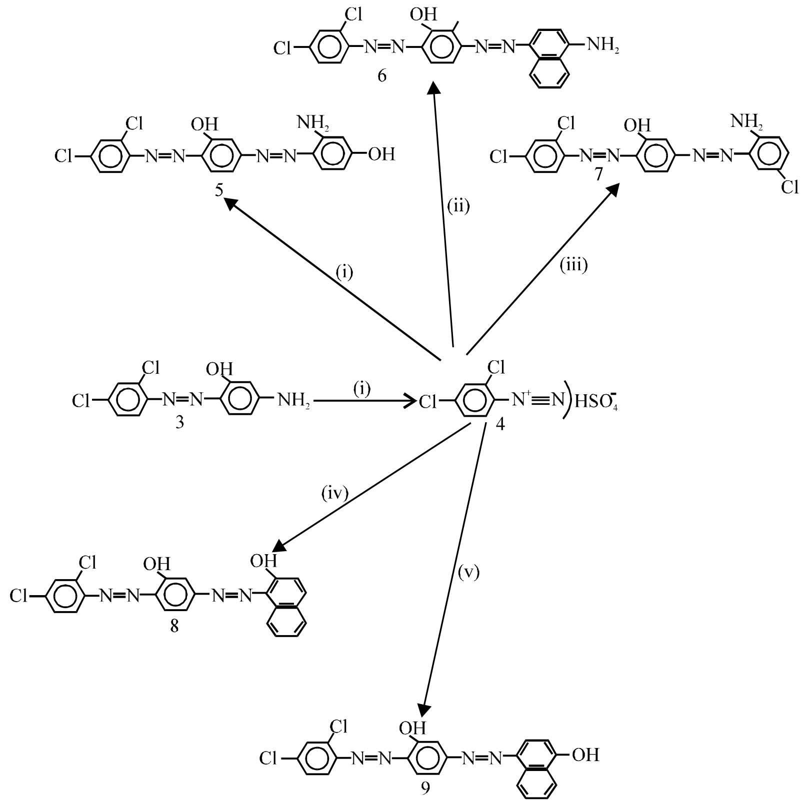

Fig. 2: Synthesis scheme for the Preparation of disazo dyes 5-9, (i) NO_2/H_2SO_4, 0-5 °C, (ii) $C_{10}H_9N$, (iii) p-C_6H_6NCl, (iv) β-$C_{10}H_8O$ and (v) α-$C_{10}H_8O$

Table 1: IR and ^{1}H-NMR data of dyes 5-9

Dye	IR (KBr, νcm^{-1})	^{1}H-NMR, δ(ppm)	Solvent
5	3452 (OH, NH_2)	2.42-3.43 (S, 2H, NH_2)	DMSO
	1508 (Ar-ring)	6.68-7.62 (m, 6H, Ar-H)	
	1418 (N = N)	7.68 (m, 1H, Ar-H)	
	1100 (C-O)	7.77 (m, 1H, Ar-H)	
	619 (C-Cl)	7.85 (d, 1H, Ar-H)	
		8.43 (d, 1H, Ar-H)	
		12.20 (S, 1H, bonded OH)	
6	3451 (OH, NH_2)	2.51-3.45 (S, 2H, NH_2)	DMSO
	1575 (Naphthalene-ring)	6.79-7.66 (M, 6H, Naphthalene)	
	1507 (Ar-ring)	7.70 (m, 1H, Ar-H)	
	1417 (N = N-)	7.79-8.22 (m, 2H, Ar-H)	
	1198 (C-O)	8.25 (d, 1H, Ar-H)	
	771 (C-Cl)	8.42 (dd, 1H, Ar-H)	
		12.10 (S, 1H, bonded OH)	
7	3455 (OH, NH_2)	619 (C-Cl)	$CDCl_3$
	1578 (Naphthalene ring)	2.40-3.45 (S, 2H, NH_2)	
	1507 (Ar-ring)	6.76 (m, 1H, Ar-H)	
	1415 (N = N-)	7.10 (m, 1H, Ar-H)	
	1116 (C-O)	7.45 (m, 1H, Ar-H)	
		7.56 (m, 1H, Ar-H)	
		7.62 (m, 1H, Ar-H)	
		7.87 (m, 1H, Ar-H)	
		8.20 (m, 1H, Ar-H)	
		8.36 (dd, 1H, Ar-H)	
		8.42 (d, 1H, Ar-H)	
		13.10 (S, 1H, bonded OH)	
8	3452 (OH)	6.85-7.75 (m, 6H, naphthalene-H)	$CDCl_3$
	1553 (Naphthalene-ring)	7.80 (m, 1H, Ar-H)	
	1506 (Ar-ring)	7.85 (m, 1H, Ar-H)	
	1414 (N = N-)	7.96 (d, 1H, Ar-H)	
	1233 (C-O)	8.12 (dd, 1H, Ar-H)	
	716 (C-Cl)	8.40 (d, 1H, Ar-H)	
		8.45 (s, 1H, Ar-H)	
		12.25 (S, 1H, bonded OH)	
9	3446 (OH)	6.75-7.60 (m, 6H, Naphthalene-H)	$CDCl_3$
	1554 (Naphthalene ring)	7.69 (m, 1H, Ar-H)	
	1506 (Ar-ring)	7.80 (m, 1H, Ar-H)	
	1415 (N = N-)	7.85 (m, 1H, Ar-H)	
	1206 (C-O)	7.92 (m, 1H, Ar-H)	
	7.59 (C-Cl)	8.20 (dd, 1H, Ar-H)	
		8.35 (d, 1H, Ar-H)	
		12.20 (S, 1H, bonded OH)	

IR: Infrared, ^{1}H-NMR: Proton nuclear magnetic resonance measured in potassium bromide (KBr) pellets, PPM: Parts per million, ν: Wavelength

The IR spectra are shown in Table 1. The broad bands in the region 3442-3455 cm^{-1} of dye 5-7 are typical of the OH and the aromatic NH stretching vibrations.

However, the hydroxyl stretching vibration bands were observed to overlap in the region 3442-3455 cm^{-1} with the aromatic NH stretching bands in dyes 5, 6 and 7 (Kirkan and Gup, 2008). The

Table 2: Wavelength (λ_{max}), molar extinction Co-efficient (ε), Intensity (Log ε), % yield of synthesized dyes 5-9

Dye	λ_{max} ^{a}(nm)	Absorbance	ε_{max} ^{a}(1 mol^{-1} cm^{-1})	Intensity (Log ε)	Yield (%)	M.p. (°C)
5	495	0.835	85204	4.93	67	208-210
	752	0.500				
6	428	0.756	41311	4.62	70	205-207
	751	0.420				
7	458	0.425	22368	4.33	51	207-209
	753	0.356				
8	482	0.719	39289	4.59	57	203-205
	767	0.462				
9	404	0.724	39562	4.59	51	206-208
	762	0.620				

^{a}Measured in DMF Concentration = 1.9×10^{-5} M

reason for the O-H bands overlapping with the N-H bands is attributed to intra-molecular hydrogen bonding. Thus, the N-H bands appear obscured as a result of the overlapping effect.

In addition, the primary amine group bands are usually weak-medium in intensity and can easily be overshadowed by their very strong bands such as the O-H group.

Absorption spectra: The absorption maxima (λ_{max}) in the visible spectra of the dyes recorded in DMF were as shown in Table 2.

The value of the logarithm of the molar extinction coefficient (Log ε) of the dyes was 4.93, 4.62, 4.33, 4.59 and 4.59 that are consistent with their high absorption intensities. Moreover, the presence of electron donating or electron withdrawing groups did not bring about any marked increase or decrease in the λ_{max} in the visible region and Log ε remains nearly the same except for dye 7 which gave Log ε of 4.33. However, electron donating or withdrawing substituents such as OH, NH_2 and Cl present in both the diazonium component and coupler component increase the polarizability. These tend to bring about a decrease in the energy gap between the highest occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) and therefore π(HOMO)-π^*(LUMO) electronic transition occurs with lower frequency photons, leading to a bathochromic shift of the visible absorption bands (Dixit *et al.*, 2007).

All the dyes showed very broad adsorption curves in the range 350-800 nm leading to a large tinctorial strength. Thus, this is a very important desirable feature both from the consideration of the economics of polyester dyes. All dyes showed a multiplet of absorption bands corresponding to bands in the region of 404-495 nm and 751-762 nm. This is attributed to the presence of many benzene rings and auxochromes leading to a highly conjugated aromatic dye structures.

The bands on the absorption curve which appeared in the region 751-767 nm, are said to be in the near infrared region which suggests that these dyes could act as organic photoconductors.

Fastness properties: All the dyeing for the fastness tests were carried out at pH 5 and the dyed polyester fabrics were assessed with grey scales. The grey scale for the alteration of colour consisted of grades 1-5, Table 3 and 4.

Light fastness: Table 4 shows the light fastness Test results of the dyes on polyester fabric. The light fastness varied from grades 5/6 to 6.

Table 3: The wash fastness of dyes 5-9 (2% owf) on polyester fabric

		Staining				
Dye	Change	Acetate	Cotton	Nylon	Polyester	Acrylic
5	5	5	5	4/5	5	5
6	5	5	5	4/5	5	5
7	5	5	5	4/5	5	5
8	5	5	5	4	5	5
9	5	5	5	4	5	5

Table 4: The light, sublimation and rubbing fastness of dyes 5-9 (2% OWF) on polyester fabric

			Rubbing/Staining			
Dye	Light	Sublimation	Dry	Wet	Pick up	Colour on dyed polyester fabric
5	6	5	4/5	4/5	3	Brown
6	5/6	5	4/5	4/5	4	Brown
7	6	5	4/5	4	3	Yellow
8	5/6	5	4/5	4	4	Yellowish brown
9	5/6	5	4/5	4	4	Yellowish brown

Grey scale grading ranges from 1 (poor) to 5 (excellent), For light fastness, grey scale grading ranges from 1-2 (poor) to 8 (excellent)

The dyes 6, 8 and 9 showed a good light fastness of grade 5/6. Dyes 5 and 7 had a very good light fastness of grade 6.

These results appear to be contrary to recent findings that electron donating groups such as-OH and -NH_2 ortho to the azo group lowers light fastness (Otutu, 2008; Giles *et al.*, 1978). But the results of this study showed increase in light fastness probably because of the presence of the electron withdrawing-Chloro group also ortho to the azo group in the dye structure. Thus, the effect of the -OH and -NH_2 groups is counteracted by the -CI group.

Sublimation fastness: The results of the sublimation fastness of the dyes on polyester fabric is summarised in Table 4, the sublimation fastness results of the dyes showed excellent performance of grade 5 on polyester fibre. This is attributed to the relatively large molecular size and the substitution of the first benzene nucleus by two similar electron withdrawing groups, thereby increasing the polarity of the dyes and hence its sublimation fastness. This is in agreement with previous findings (James *et al.*, 1982; Karci, 2005).

Rubbing fastness: The dyes 5-9 showed a very good dry rubbing fastness (grade 4/5). Dyes 5 and 6 showed a very good wet rubbing fastness of grade 4/5. Dyes 7, 8 and 9 had a good wet rubbing fastness of grade 4.

Wash fastness: The results of the wash fastness tests for dyes 5-9 on polyester fibre are summarised in Table 3 and they all showed excellent wash fastness of grade 5 which is a strong indication of their affinity for polyester fibre. Thus most of these dyes showed excellent to good dyeing properties. The reason for the high wash fastness is due to the relatively large molecular size of the dye molecules. A remarkable degree of level in surface area after washing was observed. This may be attributed to the good penetration and affinity of the dyes to the fibre structure. This is in support of the work done in previous studies (Chakraborty *et al.*, 2010; Otutu *et al.*, 2008).

CONCLUSIONS

Disazo disperse dyes of 2,4-dichlorophenyl azo-4'-amino-2'-hydroxybenzene derivatives were synthesized and their application on polyester substrate was examined. The results of the spectral studies of each dye were consistent and hence confirm the predicted structures.

The synthesized dyes showed very good fastness to light, excellent fastness to sublimation, washing with very good to good fastness to rubbing. The very high light and sublimation fastness of the dyes showed that they can find use in the automobile industry.

The dyes also showed remarkable levelness after washing. The nature of the substituents in the diazonium and coupling components showed little influence on the visible absorption and shade of the dyeings. The very high absorption of the dyes in the near-infrared region suggests that they are capable of acting as organic photoconductors.

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