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Preparation of Dis-Azo Dyes Derived from p-Aminophenol and Their Fastness Properties for Synthetic Polymer-Fibres

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Abstract: The preparation and properties of a series of dis-azo dyes derived from p-aminophenol is described. The influence on colour, dyeing fastness properties of the dyes on synthetic polymer-fibres is reported. Most of the dyes synthesized afford better light fastness and better wet (wash, perspiration) fastness on PET than on nylon 6 fabric. The structure of each compound was confirmed by using infrared, UV-VIS and elemental analysis.

INTRODUCTION

Azo dyes are compounds containing one or more azo groups of which the nitrogen atoms are SP^3 hybridized. The azo groups form links or bridges between organic residues of which one is usually an aromatic nucleus. And being a chromophore, azo groups imparts colour to textile fibres. The depth of shade is influenced by the number of azo groups present in the structure of the azo dye. They have been found to be capable of forming hydrogen bonds with the fibre thereby enhancing dye-fibre binding forces (Francis, 2003). p-Aminophenol is an aromatic amino compound and a useful source of diazonium ions (salts) for azo coupling reactions. It has found wide applications in the synthesis of mono-azo dyes which are used commercially as dyes (David and Geoffery, 1994). Typical examples include C.I. Mordant Brown 54, Acid yellow 76, Acid Yellow 40, Sulphur green 10 and Disperse Yellow 1. However, very limited commercial dis-azo dyes derived from p-aminophenol have been reported in the literature. One example of such dye is C.I. Disperse yellow 68 where the coupling components were aniline and phenol (Ven Kataraman, 1978). Also, a series of dis-azo dyes which gave good dyeing properties on polyester and nylon substrates has been prepared from p-aminophenol (Otutu et al., 2007).

The dyeing property of any dye is dependent on the substituent(s) present on the dye molecule. Consequently a great deal of attention has been focused mainly on the substituent properties of aromatic carbocycles (Bello et al., 1994, 1995). A single azo group present in a dye is often insufficient for dye fastness whereas dis-azo compounds with two groups linked to a biphenyl system, provide excellent substantive dyes (James et al., 1982). Thus, the depth of shade is influenced by the number of azo groups present in the structure of the azo dye. In a more recent study, p-aminophenol has been used as a coupling component in the preparation of a series of azo dyes from Melanine and its benzoylated and acetylated derivative (Oyewale et al., 2001). A series of azo disperse dyes have similarly been synthesized using 1, 4-diaminobenzene as the coupling component which have good dyeing properties. The colour obtained in this case were different shades of brown (Otutu et al., 2007).

The aim of this study, therefore, was to investigate the synthesis of some dis-azo dyes used as disperse dyes and their fastness properties on polyester and nylon 6 fabrics.

MATERIALS AND METHODS

This study was conducted between 2005 and 2006 at the Organic Chemistry Laboratory, University of Benin, Benin City, Nigeria.

Materials: p-Aminophenol, p-aminobenzoic acid 3-nitrophenol, 2-hydroxybenzoic acid, 2-chloroaniline, 3-methoxy-1-aminobenzene and resorcinol were purchased from BDH Chemical Company and Aldrich Chemical Company and used without further purification. All other chemicals used in the synthesis and characterization were of laboratory reagent and analytical grade.

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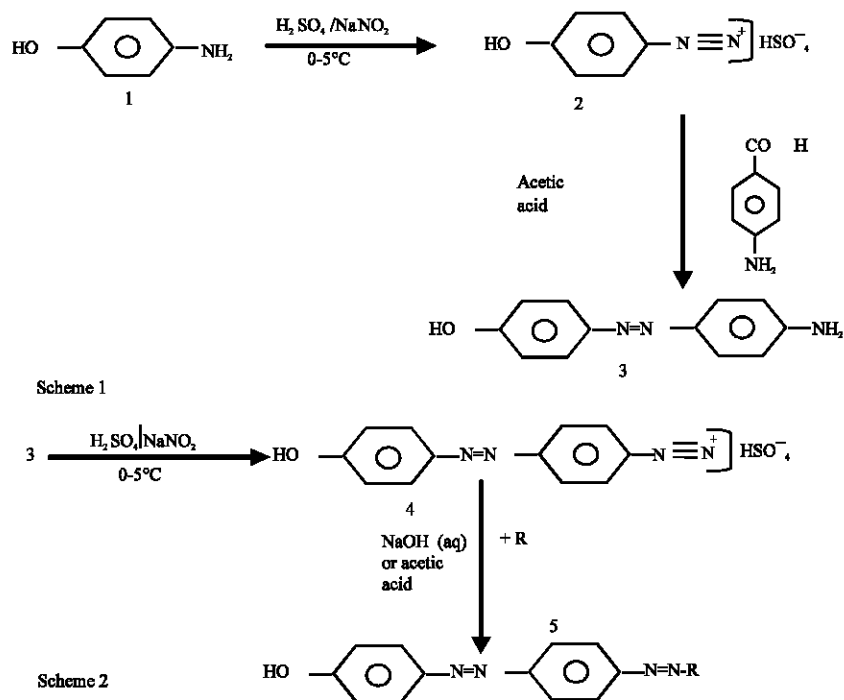Tel: +234 8033834446, +2348023320809

Fig. 1: Reaction schemes 1 and 2

Methods

Synthesis of diazo component 3: p-Aminophenol (8.0 g, 0.0734 mole), distilled water (50 mL) and concentrated sulphuric acid (12 mL) were mixed. The mixture was cooled to 0°C. A solution of sodium nitrite (5.14 g, 0.0734 mole) in 15 mL of distilled water at 0°C was added to the above cold mixture with good stirring. After 20 min the diazotization was complete, which was verified by adding a solution of 4-(N,N-dimethylamine) benzaldehyde which generates colour if undiazotized aromatic amine is still present. The excess of nitrous acid was destroyed by adding 10% (W/V) of urea. The resultant diazo solution was added to a solution of p-aminobenzoic acid (10.06 g, 0.0734 mole) in 70 mL of acetic acid with vigorous stirring over 15 min. The reaction mixture was further stirred for 1 h and left to stand over night. The crude product formed was filtered, washed with distilled water, dried and purified by recrystallization from hot carbon tetrachloride to give compound (3) in 67.1% yield.

Synthesis of dyes 5a-5i: p-Hydroxyphenylazo-4-aminobenzene (3) (1.61 g, 0.06 mole) was diazotized in 8 mL of concentrated sulphuric acid (98% w/w) and 50 mL of water, by adding sodium nitrite solution (3.7 g, 0.0536 mole) in 8 mL of water at 0°C dropwise with good stirring until diazotization was complete. The excess of nitrous acid was removed by adding 10% (w/v) of urea. The diazo solution obtained was added slowly to the corresponding coupling components to obtain dis-azo dyes as follows:

- **5a:** 2-hydroxybenzoic acid (2.52 g, 0.018 mole) dissolved in 50 mL of 2.0 M sodium hydroxide solution with vigorous stirring over 15 min. After further stirring for 2 h, the dye precipitate was filtered, washed with distilled water and dried. Recrystallizing from hot carbontetrachloride gave compound (5a) in 62% yield as a brown solid, mp = 218-230°C, TLC, R_f = 0.48 (ether/acetone 5:1).
- **5b:** Two milliliters of 2-chloroaniline in 15 mL of acetic acid with vigorous stirring over 15 min. The reaction mixture was allowed to stir for further 2 h and the crude product was isolated as described for dye (5a). The dye was purified by recrystillization from hot methanol-water mixture to give dye (5b) in 50% yield, mp = 182-184°C, TLC, R_f = 0.63 (ether/acetone 5:1).
- **5c:** Two millilitres of m-anisidine dissolved in 15 mL of acetic acid with vigorous stirring over 15 min. The crude product was isolated as described for dye (5a) after further stirring for two hours. Recrystallization from carbontetrachloride gave 57% yield of compound (5c) as a brown powder, mp = 246-248°C, TLC, R_f = 0.61 (ether/acetone 5:1).
- **5d:** 1,3-dihydroxybenzene (1.07 g, 0.010 mole) in 40 mL of 2.0 M sodium hydroxide solution with vigorous stirring over 15 min. The reaction mixture was further stirred for 1 h and the dye precipitate was filtered, washed with distilled water and dried. The crude product was purified by recrystallization from

methylated spirit to give compound (5d) in 68% yield, mp = 258-260°C, TLC, R_f = 0.72 (ether/acetone 5:1).

- **5e:** 2-naphthol (1.21 g, 0.007 mole) dissolved in 60 mL of 2.0 M sodium hydroxide with vigorous stirring, over 15 min. The dye precipitate was isolated as described for compound (5d) after further stirring for 1 h. Recrystallizing from hot carontetrachloride gave compound (5e) in 50% yield, mp = 298-300°C, TLC, R_f = 0.67 (ether/acetone 5:1).

- **5f:** 1-naphthylamine (0.99 g, 0.007 mole) dissolved in 15 mL of acetic acid with vigorous stirring over 15 min. The reaction mixture was further allowed to stir, for 1 h. Isolation and purification of the crude product were as described for compound (5e) to give 52% yield as a brown solid, mp = 208-210°C. TLC, R_f = 0.88 (ether/acetone 5:1).

- **5g:** 1-aminonaphthalene-4-sulphonic acid (1.51 g, 0.007 mole) dissolved in 60 mL of acetic acid with vigorous stirring for 20 min. The reaction mixture was further stirred for 2 h and the crude product was isolated and purified as described for dye (5b) to give 39% yield of dye (5g) as a brown solid, mp = 143-145°C, TLC, R_f = 0.85 (ether/acetone 5:1).

- **5h:** 1,2-phenylenediamine (0.80 g, 0.014 mole) dissolved in 30 mL of acetic acid with vigorous stirring for 20 min. After 1.0 h of further stirring, the crude product was isolated and purified as described for compound (5e) to give 54% yield of dye (5h) as a brown powder, mp = 286°C, TLC, R_f = 0.70 (ethanol/CCl_4 1:5)

- **5i:** 3-aminophenol (0.80 g, 0.0075 mole) was dissolved in 30 mL of 2.0 M sodium hydroxide solution with vigorous stirring for 20 min. The reaction mixture was further stirred for 1.0 h and the dye precipitate was filtered, washed with distilled water and dried. The crude product was purified by recrystallization from hot carbonterachloride to give compound 95i) in 62% yield as a brown solid, mp = 288°C, TLC, R_f = 0.32 (ether/acetone 5:1).

Chemical and instrumental analysis: The purity of the dyes was assessed by Thin Layer Chromatography. (TLC), using Whatman 250 m silica gel 60 AMK 6F plates. Ultraviolet-visible spectra were recorded in 1.0 cm quartz cells on a unicam UV-vis spectrophotometer equipped with Hilios scan software. Fourier Transform Infrared (FTIR) spectra were recorded on an ATI Wattson Genesis series spectrophotometer. Melting points were determined using Gallenkamp block melting point apparatus and are uncorrected. Elemental analysis was carried using Perkin-Elmer 240C for C, H and N. Dyeings were carried out on 100% polyester (PET) and nylon 6 fabrics, using macheasil as the dispersing agent with a nonaqueous

dyebath (using Dyemaster Dyeing Machine) at 85 and 100°C for nylon 6 and PET (using 20 g L^{-1}, 0.213 mole of phenol as a carrier) fabrics, respectively and liquor ratio 50:1.

Assessment of fastness properties: The wash fastness tests of the dyes were carried out according to ISO washing test number 3 (Nkeonye, 1987). The composite samples of PET and nylon 6 fabrics were treated with a mixture of 0.2% soap solution and 2 g L^{-1} (0.0188 mole) sodium carbonate liquor ratio 50:1 for 30 min at 60°C in a Linitest Washwheel Machine. The change in colour of the treated specimens and the degree of staining of the two adjacent undyed fabrics were evaluated using grey scales.

Light fastness: Light fastness was tested using a standard method issued by ISO (AATCC, 1992). The samples (2×6 cm) were rated against standard blue wool samples (grade 1-8).

Sublimation fastness: The sublimation fastness of the dyes on nylon 6 and PET were tested according to ISO 105-PO1 1993 protocol (ISO 105-PO1, 1993). The dyed samples were treated in a sublimation testing machine at 177°C for 30 sec. and matched against the grey scales for assessing staining.

Perspiration fastness: The perspiration fastness test was determined according to ISO 105-E04 1994 standard method (ISO 105-EO4, 1994). Both alkaline and acid perspiration fastnesses were evaluated.

RESULTS AND DISCUSSION

The dye intermediate (1) for the synthesis of dis-azo dyes was obtained and used without further purification and (3) (scheme 1) was prepared. The p-aminophenol was diazotized (Bryan, 1961; Paula, 1995) and the diazonium salt solution obtained was coupled with p-aminobenzoic acid to give compound (3) which was purified by recrystallization from carbon tetrachloride to give 67% yield. It was observed that the normal coupling position of the p-aminobenzoic acid is occupied by the carboxyl substituent. Thus, during the coupling process, the carboxyl group was eliminated. The elimination of the carboxyl group was assisted by the electrons provided by the amino group of the benzoic acid. The coupling reaction was carried out under acidic conditions. Compound (3) was diazotized and the diazonium salt solution was coupled with several arylamines and aryloxy compounds to give dis-azo dyes (scheme 2). The synthesised dyes were characterized using IR, UV-VIS and elemental analysis.

The introduction of substituents having different groups in the ring gave relatively moderate yields except compounds 5c, 5f, 5g, 5h and 5g. The reason for the average yield of compounds 5c, 5f, 5g and 5h and 5i is not entirely understood, however, the presence of electron-withdrawing groups such as Cl^-, $-SO_3H$ and $-NH_2$ are believed to account for the low yield obtained for compound (5c), (5g) and (5i).

In the synthesis of compound (5b) the ring deactivating effect of the chloride group in the 2-position relative to the second azo group appear to have been off-set by the +1 effect of the $-NH_2$ in the 1-position, thereby rendering the 2-chloroaniline of similar chemical reactivity to aniline (Finar, 1973). Thus, the yield obtained for dye (5b) was good.

The electronic spectral data of the dyes are shown in Table 1. All the dyes showed a multiplied of absorption bands corresponding to bands in the region of 300-420 nm and 400-600 nm. The introduction of substituents into the dye structure does not bring out a significant shift in the position of these bands. As expected, the molar absorptivities of the dyes are higher when compared with those of anthraquinone dyes (Ukponmwan *et al.*, 1999).

From Table 1, the IR spectral data of the dyes showed absorption frequencies of -OH and -NH stretching vibrations and asymmetric and symmetric $-NO_2$ vibrations for dye (5a). All these agree with that reported in the literatures (James *et al.*, 1982; Cross and Allen, 1966).

Fastness properties: The light fastness testing data of the dyes (Table 2) showed that all the dyes have moderate light fastness on PET with a rating of 5 except dyes (5b) and (5h) which have a rating of 4. The lower light fastness rating of dyes (5b) and (5h) is due to the presence of the carboxyl and sulphonate groups in the molecules. This agrees with the work of Giles and Co-workers (Ven Kataraman, 1978) who examined the way in which the surface activity of an azo dye, as determined by the salphonation pattern, affects the light fastness. They proposed that if a dye contained sulphonate group at one end or along one edge of a planar molecule (unsymmetrically substituted), the surface activity so generated would increase the proportion of dye in the dispersed state, thereby lowering the light fastness. The light fastness of the dyes on nylon 6 fabric showed ratings of 3 except dyes (5h), (5d) and (5e) with ratings of 4. Thus, compared with PET, nylon 6 fabric showed lower light fastness ratings because it is less crystalline in structure than PET.

The wash fastness test results showed no change in colour and staining of adjacent undyed fabric for all the dyes except dye (5b) and (5h). The presence of the carboxyl and sulphonate groups are believed to account for the low wash fastness of these two dyes.

The wash fastness test results of the dyes on nylon 6 fabric again showed lower ratings than PET. However, dyes (5b) and (5h) gave excellent ratings. This excellent performance of these two dyes on nylon 6 substrate is

Table 1: Spectroscopic data for dyes (*Ar, aromatic s; strong, b, broad, w; weak, m, medium)

Dye	R	IR cm^{-1} (KBr)	(%)	Elemental analysis (%) found (calculated)	λ_{max} (nm) (in DMF)	ε_{max} (L mol^{-1} cm^{-1})	MP (°C)
5a	CO₂H/OH	3382 (bAr-OH),	1525 (Ar NO₂) 763 (s, Ar ring)	C59.49 (59.50); H3.59 (3.61), N19.29 (19.28)	420,580	19,200	56
5b	NH₂/Cl	3446 (b,Ar-OH), 721(s, Ar-ring)	1660 (C = O)	C62.96 (62.98), H3.91 (3.89), N15.40 (15.46)	420,580	26,500	62
5c	NH₂/OCH₃	3446 (b, Ar-OH), 721 (s, Ar-ring)	3198 (m, Ar-NH)	C61.41 (61.46), H4.01 (4.01), N19.89 (19.91)	378,580	25,500	50
5d	OH/OH	3388 (b, Ar-OH), 721 (s,Ar-ring),	3169 (s, Ar-NH) 1290 (w, C-O-C)	C65.67 (65.69), H4.91 (4.93), N20.13 (20.16)	396,580	23,100	57
5e	OH	3528 (b, Ar-OH),	721 (s, Ar-ring)	C64.66 (64.67), H4.21 (4.22), N16.75 (16.76)	326,580	29,500	68
5f	NH₂	3329 (b, Ar-OH),	722 (s, Ar-ring)	C71.70 (71.73), H4.35 (4.38), N15.20 (15.21)	494,580	15,900	50
5g	NH₂/SO₃H	3435 (b, Ar-OH),	3186 (s, Ar-NH)	C71.90 (71.92), H4.65 (4.66), N19.04 (19.06)	494,580	20,000	52
5h	NH₂/NH₂	3436 (b, Ar-OH), 722 (vs, Ar-ring)	3170 (m, Ar-NH)	C59.04 (59.05); H3.81 (3.83), N15.63 (15.65)	494,580	23,500	36
5i	OH/NH₂	3443, (b. Ar-OH), 721 (m, Ar-ring)	3203 (s, Ar-NH)	C65.03 (65.05), H4.83 (4.85), N25.27 (25.29)	494,580	14,500	54

Table 2: Fastness properties of dyed fabrics

	Light	Fastness	Wash fastness				Sublimation fastness				Perspiration alkaline				Fastness acidic			
			Polyester		Nylon 6		Polyester		Nylon 6		Polyester		Nylon 6		Polyester		Nylon 6	
Dye	Polyester	Nylon 6	CC	ST	CC	ST	CC	ST	CC	ST	CC	ST	CC	ST	CC	ST	CC	ST
5a	5	3	5	5	4	5	5	5	5	5	5	5	5	4-5	5	5	5	5
5b	4	4	4	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5
5c	5	3	5	5	4	4	5	5	5	5	5	5	4	4	5	5	5	5
5d	5	4	5	5	4	5	5	5	5	5	5	5	4	4	5	5	5	5
5e	5	4	5	5	4	4-5	5	5	5	5	5	5	4	4-5	5	5	5	5
5f	5	3	5	5	3	3-4	5	5	5	5	5	5	4	4-5	5	5	5	5
5g	5	3	5	5	5	5	5	5	5	5	5	5	4	4	5	5	5	5
5h	4	3	4	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5
5i	5	3	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5

CC: Change in colour, ST = staining of adjacent undyed fabrics, Grey scale ratings ranged from 1(poor) to 5 (excellent) with a grey scale of 3 deemed a passing score. The grey scale ratings for light fastness range from 1-2 (very poor), 3 (poor) to 8 (excellent)

probably due to its high affinity for the hydrogen ion in the dye molecules (Bird and Boston, 1975). This tends to corroborate the recent work done on dye affinity (Otutu, 2005).

The sublimation fastness results (Table 2) demonstrate that the dyes on PET and nylon 6 fabrics showed, that both change in shade and staining were satisfactory. The reason for this, is attributed to the presence of polar groups such as -OH and -NH$_2$ which tend to reduce the vapour pressure of the dyes (David and Geoffery, 1994) as well as the high molecular weight of the dyes. This assertion was also in agreement with that of Yakubu (2000).

Also the acid and alkaline perspiration fastness test results showed excellent performance in both change in shade and staining of adjacent undyed fabrics on both substrates except the alkaline perspiration fastness on nylon 6 fabric which showed slight change in shade and colour transfer to the adjacent undyed fabrics.

CONCLUSIONS

The light fastness properties of the prepared dyes are significantly affected by the chemistry of the substituents as well as the nature of the substrates. The wet fastness properties (wash and perspiration) were generally higher on PET than on nylon 6 substrate due to the lower moisture regain of PET. The sublimation fastness of the dyes on both PET and nylon 6 fabrics showed an all round excellent performance in both change in shade and colour transfer due to the high molecular weight and the increase in the polarity of the dye molecule. It is therefore possible that these dyes will achieve commercial importance in the textile industry and can also be used in the automobile industry for upholstery purposes, thermoplastic resins and many other appliances that require excellent sublimation fastness.

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