



Synthesis of Nitroso-Based Bis-Azo Dyes and Their Dyeing Properties for Polyethylene Terephthalate and Polyamide



Asiagwu K. Augustine and Johnson O.Otutu

Department of Chemistry, Faculty of Science, Delta State University, P.M.B.1, Abraka, Nigeria

Abstract

The aim of this work is the synthesis of new azo nitroso-based dispersed dyes with better dyeing properties on synthetic fibers. In this regard, bis-azo nitroso naphthalene dyes were synthesized via the diazo coupling reactions of 4-nitroaniline with 1-hydroxy-2-nitrosonaphthalene. Products formed were characterized by ^1H and ^{13}C NMR. Absorption values in the UV-vis spectra of the derivatives under study were quite close and they exhibited multiple maxima in the 386 – 513nm range. The dyeing process, dye exhaustion on polyethylene terephthalate (PET) and polyamide 6 (nylon 6) fabrics, and the durability of the dyes on the textile substrates were evaluated. It was found that the light fastness ratings of the dyed fabrics could reach grade 6/7 to 7, while washing fastness gave excellent values of grade 5 rubbing and perspiration fastness grades were rated at 4/5 to 5 on the International Geometric Scale. The results obtained suggested that the dyes could be used as disperse dyes on synthetic polymers fibres.

Keywords: Synthesis, nitroso dyes, characterization, fastness, synthetic substrates.

Introduction

The chemistry of nitroso dyes has attracted a lot of attentions in the last years. These have resulted in their wide applications in the areas of colloids and printing processes [1]. The nitroso dyes contain the R-N=O group, which in association with the hydroxyl groups are capable of complexing with various metals. This ability of the monoazodyes to complex with metals have been reported for the purpose of inhibiting corrosion of metals [2,3]. In addition, some nitroso dyes have been found to exhibit near infrared

properties. This has further extended their use in high technology and chemical sensing applications [4].

Furthermore, it is worthy of mention that the use of nitroso dyes in the coloration of leather materials has been reported recently [5]. Literature survey showed that there is dearth of reports on the synthesis of dyes with the nitroso moiety and their application on synthetic polymers. While literature reports of nitroso dyes containing one azo group are common, those that have two or more azo groups are rarely reported. The present paper describes the synthesis, characterization and spectroscopic properties of some nitroso based

*Corresponding author e-mail: drasiagwu@yahoo.com.

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bis-azo dyes and their dyeing abilities when applied on synthetic polymer substrates (polyamide 6 and polyethylene terephthalate (PET)), using the exhaust dyeing process.

The dyeing of polymer materials (including textile) is a major concern to industries in many countries of the world. Polyethylene terephthalate fibers are widely applied in many areas of human endeavor due to their outstanding qualities such as resistance to chemical attack, heat stability, etc. However, the compact crystalline structure of PET has made this type of polymer fibers difficult to dye with many dye types except the dispersed dyes. Hence, researchers have continued to develop different dispersed dyes with improved applications on polyester fibers. Polyamide 6, on the other hand, is one of the most versatile synthetic polymer fibers whose structure is made up of high molecular weight chains of amides. It is heat sensitive and resistant to many chemicals except strong concentrated acids. Nylon blends well with other fibers and adds strength to such blends. A good number of studies focusing on the coloration of nylon using dispersed dyes have been reported, but none has described the use of nitroso based dyes to dye nylon fibers. The present study aim to evaluate the dyeability and durability of the synthesized nitroso based dyes on polyamide 6 and PET fabrics in terms of fastness to wash, rub, light and sublimation.

Experimental

Materials and Instrumentation

1-naphthol, 4-nitroaniline and 1-naphthylamine obtained (Sigma-Aldrich, Germany) were used directly as purchased without further purification. All other chemicals used, including 8-hydroxyquinoline and 4-bromoaniline, were of

synthetic grade and purchased from commercial suppliers. The polyethylene terephthalate and polyamide 6 fabrics used for the study were purchased from commercial suppliers (Nigeria). All the chemical reactions and purity of products were monitored by thin-layer chromatography (TLC) using precoated plates of 0.25 mm E-Merck silica gel 60 F₂₅₄ size. The melting points of the dyes were recorded using Gallenkamp apparatus (Germany) and were uncorrected. The ¹H NMR spectra were run at 200 MHz on a Mercury 200 BB series NMR spectrometer (USA). ¹³C NMR spectra were recorded on a 50 MHz instrument (USA) using tetramethylsilane (TMS) as internal standard in deuterated dimethylsulfoxide (DMSO-d₆) at Obafemi Awolowo University Central Laboratory, Nigeria. Chemical shifts (δ units) were quoted in parts per million (ppm). The spectronicGenesys 2 UV-vis spectrophotometer (Thermo Electron Corporation, USA) was used to determine and record the absorption spectra of the dyes. Measurements were carried out in DMF. The IR spectra were recorded on a Shimadzu 8400S spectrophotometer (Japan) using KBr discs. The dyeing were performed in a Linitest Plus laboratory scale dyeing machine (Atlas USA) and Aluba laboratory dyeing machine (Data color, USA).

Synthesis of 1-hydroxy-2-nitrosonaphthalene (HNTN)

1-hydroxynaphthalene (50 g, 347 mmol) was added to a solution of sodium hydroxide (13.0 g, 325 mmol) in 600 mL of water and stirred until it dissolved. The solution obtained was mixed with acetic acid (141.0 mL) and stirred for 2 min. Sodium nitrite solution (25 g, 360 mmol) in 60 mL of water was added dropwise through a separating funnel for 1 hour with mechanical stirring. The precipitate formed was filtered and washed three times with water until golden yellow

crystals were obtained. The characteristic golden yellow crystals were dried in the oven and kept for further use [6].

Synthesis of Dyes 2a -2g

A mixture of 4-nitroaniline (1.50 g, 0.0108 mol), water (25 mL) and concentrated hydrochloride acid (30%, 4 mL) was heated up to 70°C until the amine dissolved. The solution was then cooled down to 0 – 5°C, after which a solution of sodium nitrite (0.75 g, 0.0108 mol) in 10 mL of water was added in drops with mechanical stirring for 20 min. The Ehrlich reagent was used to ascertain whether the diazotization reaction was completed. This was followed by the addition of a few drops of sulphamic acid to remove excess HNO₂. The coupling component, 1-naphthylamine (1.55 g, 0.0108 mol), was dissolved in acetic acid (5 mL) and the active diazonium salt solution was slowly added to it with mechanical stirring at 10 °C for over 25 min. The precipitated product obtained was isolated by filtration, rinsed with distilled water and dried. The pure compound was recrystallized from ethanol to give compound 2a. Dyes 2b - 2g were similarly obtained using 2-hydroxynaphthalene (1.57 g, 0.0108 mol), 4-bromoaniline (1.87 g, 0.0108 mol), 4-ethylbenzoate (1.63 g, 0.0108 mol), 3-aminophenol (1.18 g, 0.0108 mol), 8-hydroxyquinoline (1.58 g, 0.0108 mol) and 1,3-dihydroxybenzene (1.20 g, 0.0108 mol) as coupling components respectively [7].

Synthesis of Dyes 3a -3g

Compound 2a(4.10 g, 0.03 mol) was mixed with water (50 mL), a solution of hydrated sodium sulphide (4.90 g, 0.02 mol) and sodium hydrogen carbonate NaHCO₃(1.70 g, 0.02 mol) at 75 °C with mechanical

stirring. The reaction temperature was kept at 75 °C for 4h and the progress of the reaction was monitored using thin layer chromatography (TLC) with a solvent system of isopropanol:butanol:ethyl acetate:water 4:2:1:1 (v/v) as eluent. Acetic acid (2%) was then used to adjust the pH of the reaction mixture 5-6 to induce the precipitation of the product. The precipitated product was filtered, dried and recrystallized from hot ethanol. Dyes 3b - 3g were similarly diazotized and coupled with 1-hydroxy-2-nitroso naphthalene (2.0 g, 0.012 mol) and recrystallized from ethanol, methanol or CCl₄ to afford dyes 4a - 4g.

Table 1: (Z)-4-hydroxynaphthylazophenylazo-4'-amino-3-nitrosophthalene (4a)

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{\max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{\max}$ (cm ⁻¹)	¹ H NMR (DMSO-d ₆) δ_{H} ppm	¹³ C NMR (DMSO-d ₆) δ_{C} ppm (All C)		
Solid	349	3456	3091	2.42 (s, 1H, ArNH)	135.4	127.7
Brown color	394	2970	2862	4.00 (s, 1H, ArOH)	133.7	127.0
Yield = 56%	442	2771	2222	6.21 (d, J=8Hz, 4H, ArH)	131.9	126.3
M p. 210 °C		2162	1670	6.85 (s, 1H, ArH)	131.2	122.9
		1626	159	7.25 – 7.63 (m, 4H, naphthyl H)	130.9	120.6
		1521	1402	8.10 (m, 1H, ArH)	129.9	116.8
		1338	1093	8.41 – 8.68 (m, 2H, ArH)	129.7	41.4
		1066	796	9.18 (m, 1H, naphthyl H)	128.7	40.9
			680	420		127.9
					40.2	39.7
					39.3	38.9
					130.2	

Table 2: (Z)-2-hydroxynaphthylazophenylazo-4'-hydroxy-3-nitrosophthalene (4b)

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{\max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{\max}$ (cm ⁻¹)	¹ H NMR (DMSO-d ₆) δ_{H} ppm	¹³ C NMR (DMSO-d ₆) δ_{C} ppm (All C)		
Solid	513	3446	1298	3.61 (s, 1H, ArOH)	133.7	41.3
Brown color		3234	1111	6.40 (d, J= 8.7Hz, 4H,ArH)	132.7	40.2
Yield = 58%		3084	516	6.85 (d, J= 8Hz,4H, ArH)	131.9	39.8
M pt 230 °C		2862	418	6.93 (s, 1H, naphthyl H)	130.8	39.6
		2220	1683	7.10 (m, 1H, ArH)	130.2	39.3
		2166	1647	7.42 – 7.61 (m, 4H, nahthyl H)	128.7	38.6
		1398		7.85 (m, 2H, ArH)	129.7	38.5
				8.22 (m, 1H, naphthyl H)	127.5	38.2
			8.67 – 8.95 (m, 1H, naphthyl H)	126.9	41.6	
				122.8	41.9	

Table 3: (Z)-2-amino-5-bromophenylazophenylazo-4'-hydroxyl-3-nitrosophthalene (4c)

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{\max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{\max}$ (cm ⁻¹)	¹ H NMR (DMSO-d ₆) δ_{H} ppm	¹³ C NMR (DMSO-d ₆) δ_{C} ppm (All C)		
Solid	386	3454	1527	2.45 (s, 2H, ArNH)	133.6	38.9
Brown color	439	3093	1317	3.81 (s, 1H, ArOH)	132.7	39.3
Yield = 46%	531	2970	1301	6.33 (d, J= 8.8Hz,4H,ArH)	131.9	39.7
M.p200 oC		2862	1072	6.86 (s, 1H, naphthyl H)	130.2	39.5
		2222	1031	7.50 – 7.41 (m, 2H, ArH)	127.4	40.2
		2102	711	7.61 – 7.86 (m, 2H, naphthyl H)	127.0	40.6
		1957	427	8.00 – 840 (m, 2H, naphthyl H)	41.4	
			1687	1577	8.80 – 9.10 (m, 2H, ArH)	

Table 4: (Z)-2-amino-5-acetylphenylazophenylazo-4'-hydroxy-3-nitrosophthalene

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{max}$ (cm ⁻¹)		1H NMR (DMSO-d ₆) δ H ppm	13C NMR (DMSO-d ₆) δ C ppm (All C)	
Crystals	423	3485	1254	2.24 (s, 2H, NH)	201.3	130.5
Brown color	444	3020	1095	3.24 (t, 3H, CH ₃)	136.4	130.2
Yield = 49%	448	2932	1394	3.93 (s, 1H, OH)	135.5	128.9
M. p. 101 oC		2873	1496	4.31 (q, 2H, CH ₂)	133.9	127.6
		2355	556	6.70 (d, J= 8.7Hz, 4H, ArH)	133.8	121.8
		1670	660	7.23 – 7.75 (m, 2H, ArH)	132.8	41.9
			866	7.80 (m, 2H, ArH)	131.0	41.7
				8.00 (m, 1H, naphthyl H)	41.4	39.8
				9.11 (m, 1H, naphthyl H)	39.5	39.0
					38.8	38.5
					38.3	

Table 5: (Z)-2-amino-4-hydroxyphenylazo-phenylazo-4'-hydroxy-3-nitrosophthalene (4e)

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{max}$ (cm ⁻¹)		1H NMR (DMSO-d ₆) δ H ppm	13C NMR (DMSO-d ₆) δ C ppm (All C)	
Solid	421	3780	1443	1.25 (s, 2H, NH)	133.9	128.3
Brown color	419	3490	1393	4.16 (s, 1H, ArOH)	133.6	127.9
Yield = 45%	430	3050	1254	6.75 (d, J= 8Hz, 2H, ArH)	132.4	127.5
M. p. 195 oC		2932	1094	7.26 (m, 2H, ArH)	131.7	122.8
		2873	866	7.56-7.83(m, 4H, naphthyl H)	131.5	116.5
		2351	659	8.05 (m, 1H, naphthyl H)	130.3	41.9
		1671	551		128.7	41.6
		1496			128.3	41.0
					40.8	39.7
					40.4	39.1
					38.9	38.6

Table 6: (Z)-4-hydroxyquinolylazophenylazo-4'-hydroxy-3-nitrosophthalene (4f)

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{max}$ (cm ⁻¹)		1H NMR (DMSO-d ₆) δ H ppm	13C NMR (DMSO-d ₆) δ C ppm (All C)	
Solid	430	3488	1445	4.20 (s, 1H, OH)	133.8	41.9
Brown color	441	3081	1395	6.85 (d, J= 8.8hZ, 4H, ArH)	132.6	41.6
Yield = 66%	443	2932	1254	7.10–7.42 (m, 2H, naphth H)	131.8	40.8
M. p. 110 oC		2868	1094	7.88–8.22 (m, 4H, naphth H)	131.6	40.5
		1671	864	8.35 (m, 2H, ArH)	130.9	40.2
		1496	659	9.10 (m, 1H, naphthyl H)	130.7	40.0
			551		128.6	39.7
					127.5	39.5
					127.2	39.3
					126.8	38.6
					122.7	38.4

Table 7: (Z)-2,4-dihydroxyphenylazophenazo-4'-hydroxy-3-nitrosonaphthalene (4g)

Physical Properties of Dye (4a – 4g)	UV-visible (λ_{max} , DMF) (nm)	IR (KBr) $\bar{\nu}_{\text{max}}$ (cm ⁻¹)		¹ H NMR (DMSO-d ₆) δ H ppm	¹³ C NMR (DMSO-d ₆) δ C ppm (All C)		
Solid	418	3493	1496	3.35 (s, 1H, ArOH)	133.9	128.3	
Brown color	422	3080	1393	6.68 (d, J=8.6Hz, 2H, ArH)	133.8	41.6	
Yield = 63%	424	2931	1254	6.85-7.10 (m, 4H, naphthyl H)	133.0	40.9	
M p 121 oC		2868	1093	7.25-7.67 (m, 2H, ArH)	131.8	40.7	
		2352	861	7.56-7.83 (m, 4H, naphthyl H)	130.9	40.5	
			1671	659	8.22 (m, 4H, ArH)	127.5	39.8
				548	8.32 (m, 2H, naphthyl H)	127.4	39.5
					9.00 m, 1H, naphthyl H)	121.6	38.7
					116.6	38.5	
					41.9	39.9	

*Application of Dyes on PET and Nylon 6 Fabrics**Dyeing of PET Fabric (100% terylene)*

Each of the pure powdered 4a – g dyes (1.0 g) was mixed with dimethylformamide (5 mL). Dispersing agent (Materil DA-N (1.0 gL⁻¹) (ICI company, UK) and water were mixed with the solution to obtain a homogenous dye dispersion. The pH of the dye dispersion was adjusted to 5 using 2% acetic acid. Polyester fabrics (4.0 g) were immersed into the dye bath with liquor ratio 1:56 and dyeing was carried out at an elevated temperature of 130°C at a rate of 2.5 min⁻¹ in a high pressure – high temperature dyeing machine. The dyed substrates were then removed after cooling to 50°C, rinsed with water and treated with sodiumdithionite solution (2.0 gL⁻¹) and sodium carbonate (2.0 gL⁻¹) at 60°C for 15 min (liquor ratio 50:1). The reduction-cleared samples were rinsed with water and later neutralized in 1.0 gL⁻¹ acetic acid at 40°C for 5 min. Finally, the samples were rinsed in tap water and air-dried [8].

Dyeing of Polyamide6 Fabric

The dye dispersion (100 mL) was mixed with distilled water (100 mL) and the pH of the dye dispersion was brought up to 5 using 2% acetic acid.

The polyamide 6 fabric (2.0 g) was wetted and immersed into the dye bath (liquor ratio 1:40) at 40 °C. The temperature of the bath was raised to 100°C at the rate of 2°Cmin⁻¹ as dyeing progressed in an Ahiba laboratory dyeing machine (Datac USA). Dyeing was allowed to continue at this temperature for 1 h. After cooling the dye bath and the dyed fabric was removed and rinsed with distilled water then treated with a solution (materials of liquor ratio 1:2) containing iodet T (2.0 gL⁻¹) for 15 min at 40 °C. The reduction-cleared samples were thoroughly rinsed with cold water and air dried [9].

*Colour Fastness Tests**Colour Fastness to Light*

The test for light fastness was assessed using the ISO 105-BO2: 2013 test method [10], using a xenon arc lamp and continuous light for 35 h. The effect of light on the tested dyed fabrics was measured with reference to the standard blue wool scale to observe change in colour.

Colour Fastness to Washing

Colour fastness to washing was determined using the ISO 105-CO6: 2010 test protocol [11]. The dyed samples measuring 5cm x 2cm were sewed between two pieces of white polyester and cotton

fabrics and then dipped into an aqueous solution of nonionic detergents (5.0 gL^{-1}) at a liquor to goods ratio 1:50. The test was carried out in a bath at 60°C for 30 min. The tested samples were removed from the dye bath rinsed three times with water and dried. The standard grey scale was then used to evaluate and establish the wash fastness for colour change as well as staining of adjacent undyed fabrics.

Colour Fastness to Crocking

The crocking fastness to rubbing of the dyed samples was carried out according to ISO 105-X12: 2016 standard protocol [12]. The test was performed on dry and wet fiber samples. The degree of colour transfer from the surface of the dyed fabric to another surface was established by comparing with the standard grey scale for colour change.

Colour Fastness to Perspiration

The test for perspiration fastness was carried out based on acidic and alkaline media in accordance with the International Organization Standardization (ISO.105-E04, 2016) [13]. The alkaline perspiration fastness test was performed in a solution containing 1-histidine monohydrochloride monohydrate (0.5 gL^{-1}), sodium chloride (5.0 gL^{-1}), disodiumhydrogen orthophosphate (2.5 gL^{-1}) and sodium hydroxide (0.1M) dissolved in water (liquor ratio 50:1). The acidic perspiration test was performed with a solution containing 1-histidine monohydrochloride monohydrate (0.5 gL^{-1}), sodium chloride (5.0 gL^{-1}) and sodium hydrogen orthophosphate (2.2 gL^{-1}). The pH of this solution was adjusted by adding 1% acetic acid. The dyed textile samples (5cmx4cm) were immersed into the solutions respectively and allowed to remain with squeezing and agitation from time to time for 15 – 30 min. after which, the treated samples were removed from test solution and the excess liquid was allowed to flow out, and the sample was dried in an oven set at $37 \pm 2^\circ\text{C}$ for 4 h. The colour

change of the tested sample was assessed by comparing with standard grey scale

Results and Discussion

Synthesis and Characterization

New nitroso-based bis-azo dyes were successfully prepared. The synthesis of all prepared compounds were based on diazo coupling reactions. The synthesis of the dyes was carried out by a three-step process, as outlined in Schemes 1 and 2. In the first step, the intermediate nitroso coupling compound 1-hydroxy-2-nitrosophthalene (HNTN) was prepared by diazotization reaction using sodium nitrite in acetic acid medium [14-16]. The second step involved the diazotization of 4-nitroaniline and coupling with various coupling agents to give compounds 2a to2g. In the third step, the nitro groups of the intermediate dye compounds 2a to2g were converted to primary amino groups using $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and sodium carbonate to obtain compounds 3a to3g. These intermediate dyes were diazotized under hydrochloric acid medium using very low temperature with sodium nitrite solution. The resulting active diazonium solutions were reacted with 1-hydroxy-2-nitrosophthalene (HNTN) under alkaline medium to afford nitroso-disazo dyes 4a – g. All the reactions were monitored using TLC.

The electronic absorption spectra were measured in DMF at room temperature for all prepared dyes 4a to4g. The azo nitroso compounds showed HOMO – LUMO multiple absorption bands except compound 4b which had only one absorption band. All the compounds exhibited absorption bands in the visible region. The multiple absorption bands observed could be attributed to the presence of different chromophores in the compounds. Also, the variation in the positions of absorption bands exhibited by the compounds could be attributable to the structure of the system (aryl) and substitution pattern in the aryl rings.

NMR and IR Spectroscopy

The ^1H NMR spectra of the dyes displayed a characteristic doublet localized at chemical shifts of 8.0 – 8.7 ppm and could be attributable to the aromatic hydrogen protons. The ^{13}C NMR spectrum of compound 4d showed the presence of sp^2 (C=O) carbon atom at $\delta = 201$ ppm [17]. The FTIR spectra (in KBr) of the synthesized dyes showed a strong absorption band between 3446 and 3494 cm^{-1} , corresponding to O-H or N-H stretch of aromatic compounds. The absorption band of C-H in FTIR spectra were observed in the range between 3020 and 3093 cm^{-1} . The absorption bands which appeared in the range between 1670 and 1671 cm^{-1} suggested the presence of N=O chromophoric group in the structure of the compounds [18]. Absorption bands of C=C in the FTIR spectra were observed in the range between 1393 and 527 cm^{-1} . The band at 1093 cm^{-1} , assigned to C-O stretching vibrations, confirmed the presence of O-H group in the compounds. Inspection of the FTIR spectra also showed the appearance of C-H bending vibrations between 861 and 866 cm^{-1} [19]. However, the carbonyl (C=O) chromophore band appear to be obscured in the FTIR spectrum of dye 4d. The reason for this observation is not immediately understood.

Dyeing Properties of the Dyes on PET Fibers and Polyamide6 Fibers

All the synthesized dyes were applied to PET and polyamide 6 fibers. The PET fabrics dyed with dyes 4d, 4e and 4f gave reddish brown hues,

whereas PET fabrics dyed with dyes 4a, 4b, 4e and 4g gave brown shades. All the dyes gave brown shades with nylon 6 fabrics. The fastness properties of the nitroso-based bis-azo dyes 4a to 4g on PET fibers and nylon 6 fibers were determined. The washing fastness, rubbing fastness, perspiration fastness and light fastness properties are shown in Tables 1 and 2 for the two textile substrates used in the study.

Fastness-to-washing

The fastness-to-washing tests showed the dyes had excellent ratings; grade 5 for PET and grade 4/5 - 5 for nylon 6 fabrics, which was attributed to an increase in the large molecular size of the dye molecules as well as the good diffusion of the dye molecules inside the fabrics. All the dyes exhibited a good level of dyeing on the two textile substrates used in the study (grade 4/5 to 5) (Table 1 and 2).

Fastness to Rubbing

The rubbing fastness (wet and dry) gave very good-to-excellent results, indicating that the extent of diffusion of the dye molecules into the fabrics was adequate.

Fastness to Perspiration

The high rating for change of colour (grade 4/5 - 5) of the perspiration fastness of the dyes under both acid and alkaline conditions implied that the dyes were relatively stable in relation to pH changes.

Fastness to Light

Table 1: Fastness Properties of Dyes 4a-g on nylon 6 fibers

Compound	Washing Fastness			Rubbing Fastness		Perspiration Fastness		Light Fastness	Colour on Fabric
	Change	Cotton	Polyester	Dry	Wet	Acid	Alkaline		
4a	4/5	5	5	5	5	4/5	4/5	6/7	Brown
4b	4/5	5	5	5	4/5	5	5	7	Brown
4c	4/5	5	5	5	4/5	5	5	6/7	Brown
4d	4/5	5	5	5	4/5	5	4/5	6/7	Brown
4e	4/5	5	5	5	5	5	4/5	7	Brown
4f	5	5		5	5	5	4/5	6/7	Brown
4g	5	5	5	4/5	5	4/5	5	7	Brown

Table 2: Fastness Properties of Dyes 4a-g on PET Fibers

Compound	Washing Fastness			Rubbing Fastness		Perspiration Fastness		Light Fastness	Colour on Fabric
	Change	Cotton	Polyester	Dry	Wet	Acid	Alkaline		
4a	5	5	5	5	5	4/5	4/5	7	Brown
4b	5	5	5	5	5	5	5	6/7	Brown
4c	5	5	5	4/5	4/5	5	4/5	7	Brown
4d	5	5	5	5	5	5	4/5	7	Reddish brown
4e	5	5	5	4/5	4/5	5	4/5	6/7	Reddish brown
4f	5	5	5	4/5	5	4/5	5	7	Reddish brown
4g	5	5	5	5	5	5	5	6/7	Brown

The light fastness of any dyed polymer fiber depends on a number of factors, and most importantly, on the concentration of the dye molecules in the fiber and the substituent groups present in the molecules of the dye. The substituent's groups could interact with the fiber or with the hydroazo groups, thereby increasing or decreasing the electron density around it. The high light fastness of dyes 4b, 4e and 4g on nylon 6 fabric may be due to the electron-donating OH group around the hydroazo group, whereas the light fastness of these dyes exhibited lower ratings on PET fabrics (Table 1 and 2). This is in agreement with the view that azo dyes containing electron-donating substituent's adjacent to the hydroazo group are more resistant to photo fading in nylon fabrics than in PET fabrics [20]. In general, the prepared dyes exhibited satisfactory resistance to photo fading (grade 6/7 – 7) according to the International Geometric Grey Scale. [21].

Mechanism of dyeing

The polyester fabric is known to consist of a very high crystalline structure which makes it difficult to dye. Thus, the high temperature and pressure used in dyeing the polyester fabric was intended to loosen up the crystalline structure of the fabric. The mechanism of dyeing involves the transfer of dye molecule from solution to the fabric surface, a process known as adsorption. The adsorbed dye molecules diffused mono-molecularly into the already loosened fabric structure and could be fixed there by non – polar Van der Waal's forces. In the case of nylon fabric dyeing, the mechanism involves the fixation of the dye molecules via non – polar Van der Waal's forces and also through hydrogen bonding. Thus, the presence of the –OH and NH groups in the dye structure could form H- bonds with the amide groups of the nylon polymer.

Reaction Scheme

Figure 1: Synthesis of 1-Hydroxy-2-nitrosophthalene (HNTN)

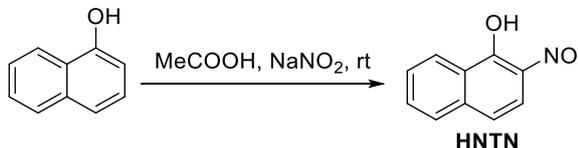
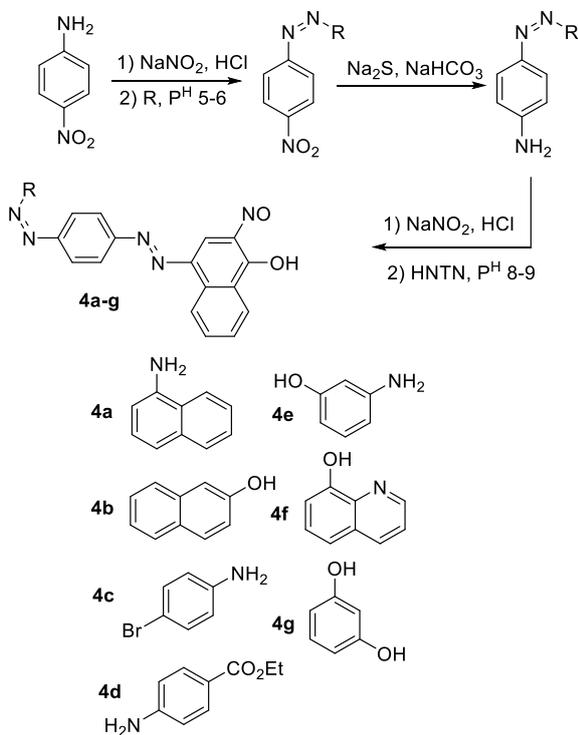


Figure 2: Synthesis of Dyes 4a-4g



Conclusion

The study described the synthesis and application of nitroso-based azo dyes 4a-g as disperse dyes onto PET fibers and polyamide 6 fibers. The dyes showed outstanding characteristics on textile substrates and washing fastness properties. There was little variation in rubbing and perspiration fastness properties. The photo stability of the dyes was observed by the influence of the substituent groups around the hydroazo group. The chromophoric

structure of the nitroso dyes suggest to the fact that they could be potential dyes for the textile industry and for corrosion control when they are complexed with metal ions such as iron.

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References

- Djinovic, C. O., Rizzi, K., Castellani, C. B., Studies on Metal Complexes of Ortho-Quinone Monooximes. Part 9. Analysis of the Charge Distribution within the o-Quinone Monooxime Ligands through Crystallo-graphic Data. *Journal of the Chemical Society, Dalton Transactions*, 55, 1255-1258. (1991).
- Otutu, O.J. and A.K. Asiagwu, Synthesis and application to polyester and nylon 6 fabrics of hetarylbis-azo disperse dyes based on 6-amino-2, 4-dihydropyrimidine and 4-methoxy-2-nitroaniline moieties. *Journal of Scientific Research.*, 11: 215-224 (2019).
- Verdoom, T. A., Johnson, T. H., Drejor, J., and Nielson, E. O. J., Selective Block of Recombinant Glur6 Receptors by NS-102, a Novel Non-NMDA Receptor Antagonist. *European Journal of Pharmacology: Molecular Pharmacology*, 269, 43-49 (1994).
- Otutu, J.O., A.K. Asiagwu, I.E. Onyesom, J.K. Ebigwai and P.O. Itoya, Improving the efficiency of *Nesogordoniapapaeverifera* (Danta) as a natural dye in textile making industry. *Bulletin of the Chemical Society Ethiopia*, 33: 415-424 (2019).
- Ameuru, U. S., Yakubu, M. K., and Bellow, K. A., Synthesis and Characterization of

- Nitrosonaphthol Dyes Based on 1-Naphthol and Their Dyeing Properties on Tanned Leather. *Open Journal of Applied Sciences*, **4**, 354-359 (2014).
6. Deng, Y., Tang, B, Zhao, H., Xu, J., Xiao, J., Zhang, X., Xu, H. and Zhang, S.. Dyeing method and properties of polymaleic acid dyes on cotton. *Coloration Technology*, 129(2): 144-149(2013).
 7. Maruszewka, A., and Podsiadly, R., Synthesis and ultraviolet-visible spectroscopic and electrochemical analyses of dyes derived from 2-aminobenzothiazole, and study of their adsorption on titanium dioxide. *Coloration Technology* 130(4):243–249 (2014).
 8. Park, J.M., Jung, C.Y., Yao, W., Song, C.J. and Jaung, J.Y., Synthesis of yellow pyridonylazo colorants and their application in dye pigment hybrid colour filters for liquid crystal display. *Coloration Technology*, 133(2): 158-164 (2016).
 9. Otutu, J. O., Ossai, E. K., and Yakubu, M. K., Synthesis and Application of N-phenylmethylanilinedisazo disperse dye derivatives on polyester fiber and nylon 66 fiber *Journal of Science Research*, **2**:97-106 (2012).
 10. ISO 105-B02: 2013 Textiles: Tests for colour fastness part B02: colour fastness to artificial light: xenon arc fading lamp test (2013).
 11. ISO 105-C06: 2010 Textiles: Tests for colour fastness, part C06: colour fastness to domestic and commercial laundering (2010).
 12. ISO 105-X12: 2013 Textiles: Tests for colour fastness part X12: colour fastness to rubbing (2013).
 13. ISO 105-E04: 2016 Textiles: Tests for colour fastness. Part E04: colour fastness to perspiration (2016).
 14. Choi, J.H., Choi, J.Y., Kim, E.M., Kim, J.P., Andrew, D.T. and Yoon, C., Coloration properties and clearability of phthalimide-derived monoazo disperse dyes containing ester. *Coloration Technology*, 129(5): 352-259 (2013).
 15. Karci, F., Synthesis of disazodyes derived from heterocyclic compounds. *Coloration Technology*, 121(5): 275-286 (2005).
 16. Bruice, P. Y., Organic chemistry, 3rd Ed., pp. 572-575, Prentice-Hall Inc., New Jersey, (2001).
 17. Morrison, R. T., Boyd, R. N., Bhattacharjee, S. K. Organic chemistry, Dorling Kindersly Pvt Ltd., New Delhi, 7th Ed., pp. 845 (2011).
 18. Carey, F. A., Organic chemistry, McGraw-Hill, New York, 5th Ed., pp. 738 (2003).
 19. Metwally, M. A., Bondock, S., El-Desauky, E. S. L., and Abdou, M. M., A facile synthesis and tautomeric structure of novel 4-arylthiazono-3-(2-hydroxyphenyl)-2-pyrazolin-5-ones and their application as disperse dyes. *Coloration Technology*, 129: 418-424 (2013).
 20. Otutu, J.O. and E.K. Ossai, Colourants extracted from the bark of Iroko plant (*Milicia excels*) and their application as natural dyes on polyester and polyamide 6 fabrics Mambilla. *Journal of Sciences and Environment*, **4**: 28-37. (2017).
 21. Otutu, J.O., Preparation of azo disperse dyes from 1, 4-diaminobenzene and 4-amino-3-nitrotoluene and their application on polyester fibre using the thermosol and aqueous dyeing methods. Niger. *Journal of Sciences and Environment*. **12**: 160-166 (2013).

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