SYNTHESIS OF AZO DISPERSE DYES DERIVED FROM 4-PHENOXYANILINE AND 3-CHLOROANILINE AND THEIR DYEABILITY ON POLYESTER FABRIC

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Abstract: A series of disazo disperse dyes were synthesized by the diazotization of 4-phenoxyaniline and coupling reaction of 3-chloroaniline to give an intermediate dye compound. The structure of these disperse dyes were confirmed by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy and infrared spectrometry. The ultraviolet visible absorption spectra of the dyes were measured in dimethylformamide. The maximum absorption wavelength ranged from 440 – 448 nm and some with shoulders in the near infrared region (in dyes 5a and 5c). The disperse dyes were applied to polyester fabrics and the colour fastness properties were investigated. The results show that the hue produced was brown. The wash fastness and rub fastness results were between grade 4 and 5, while perspiration fastness and sublimation fastness were between grades 3/4 and 5 while light fastness was between grades 5/6 and 6. The dyes produced in this study could be useful candidates for the dyeing of hydrophobic fibres.

Keywords: Disazo disperse dyes, polyester fabric

Introduction

A lot of interest has been shown by many researchers in recent years in the design of azo synthetic colourants (Otutu and Ossai, 2017a; Aysha *et al*., 2015; Otutu and Efurhievwe, 2013) in such a way that the components should be free as much as possible from groups that can cause environmental hazards as well as carcinogenic effects on humans. This has become necessary because as a society, we are becoming increasingly conscious over the protection of the environment and the safety of our health (Zhang and Hou, 2015; Kan *et al*., 2016; Choudhari *et al*., 2016). Azo colourants are one of the dominant classes of industrial dyes and pigments designed and synthesized for application in a variety of fields of human endeavour. The versatility of the azo dye application is based on the case of production, low cost, excellent optical properties, bright shades and fastness properties on textile fibres. The main precursors for this study is 4-phenoxyaniline. A series of Schiff bases have been synthesized from it, which were found to have the ability to disrupt the growth and development of small animals such as nematodes and plant parasites (Binder *et al*., 1992). A part from the afformentioned use of this intermediate compound, attempt has also been made to synthesize monoazo disperse dyes based on it, and the dyes obtained were observed to show promising fastness properties on nylon 6 fabric (Otutu, 2018).

Thus, encouraged by these findings, and as a continuation of an ongoing research programme based on 4-phenoxyaniline, the present paper is concerned with the synthesis and investigation of the fastness properties of disazo disperse dyes derived from 4-phenoxyaniline and 3-chloroaniline. In addition to the synthesis of the disperse dyes their spectroscopic properties and application in the dyeing of polyester fabrics were evaluated.

Materials and Methods

All the starting compounds were procured from Aldrich (USA) and Fluka Switzerland and they were used as obtained with further purification. The FTIR spectra were measured using a Shimadzu 8400S Fourier transform infrared (FTIR) spectrophotometer, with KBr disc, MB – series 100. Proton Nuclear Magnetic Resonance (^{1}H-NMR) and Carbon – 13 Nuclear Magnetic Resonance (^{13}C-NMR) spectral measurements were recorded on a Varian Geinini 2000 (200 MHz), Varian, Pelo Alto, CA USA. The spectra of the disazo disperse dyes were measured at room temperature in deuterated dimethylsulphoxide (DMSO – δ_6). Melting points were measured on a Gallenkamp melting point apparatus. The Ultraviolet visible (UV-vis) absorption spectra were recorded on a Shimadzu 1700 spectrophotometer in a dimethylformamide (DMF) at a concentration of 5X10^{-4} M.

Synthesis and spectroscopic characterization

General procedure for the synthesis of 4-amino-2-chlorophenylazo-4-phenoxybenzene derived dyes

A stirred solution of 4-phenoxyaniline (32 mmol) in concentrated sulphuric acid (5 mL) and water (20 mL) was cooled in an ice bath and then diazotized with sodium nitrite (2.24 g, 32 mmol) in water (5 mL). The cold diazonium salt solution was slowly added to a well-stirred solution of 3-chloroaniline (4.14 g, 32 mmol) with stirring over a period of 5 min. The reaction mixture was further stirred for another 3 h. The crude product was filtered off, dried and recrystallized from ethanol/acetic acid mixture to afford compound 3. The 4-amino-2-chlorophenylazo-4-phenoxylbenzene intermediate was similarly diazotized and coupled with 1-naphthylamine, 3-aminophenol, 7-methoxy-2-hydroxy-naphthalene, 3-methoxyaniline and 1,3-dihydrooxybenzene respectively to give the disazo disperse dyes (Feng *et al.*, 2017).

Methods

Preparation of dye dispersion

The pure dye was dissolved in dimethylformamide (5 mL) and then added dropwise with a stirred solution of dispersing agent (Lignin sulfonate). The mixture was transferred to a 100 mL flask and the dispersing agent was added to bring the volume of the dispersion up to the 100 mL mark (Aysha *et al.*, 2015).

Dyeing and fastness tests

Dyeing of polyester fabric

The thoroughly dispersed dye solution was added to the dye bath and the pH of the bath was adjusted to 5 by adding acetic acid. The polyester fabric was treated in a solution containing HCl (aq) to remove whitening agent and other substances that may impair the absorption of the dye into the polyester fabric. The polyester fabric was then immersed into the dye bath. Disperse dyeing of polyester fabric was performed using the high-temperature, high-pressure method in a Galvanin-Marino VI dyeing machine (Italy) with a liquor ratio of 1:30. The temperature of the dye bath was raised at a rate of 3°C/min to 135°C and then was held at this temperature for 1h before the dye bath was cooled rapidly to 50°C at 9.9°C/min. After the dyed fabrics were removed, cold water was used to rinse the dyed fabrics and then reduction-cleared in an aqueous solution containing sodium hydrosulphite (1.0 kg/m^3) and soaping agent NaOH (2.0 g/L) was used to wash it at 80°C for 20 min to improve the washing fastness (Dadras *et al.*, 2014).

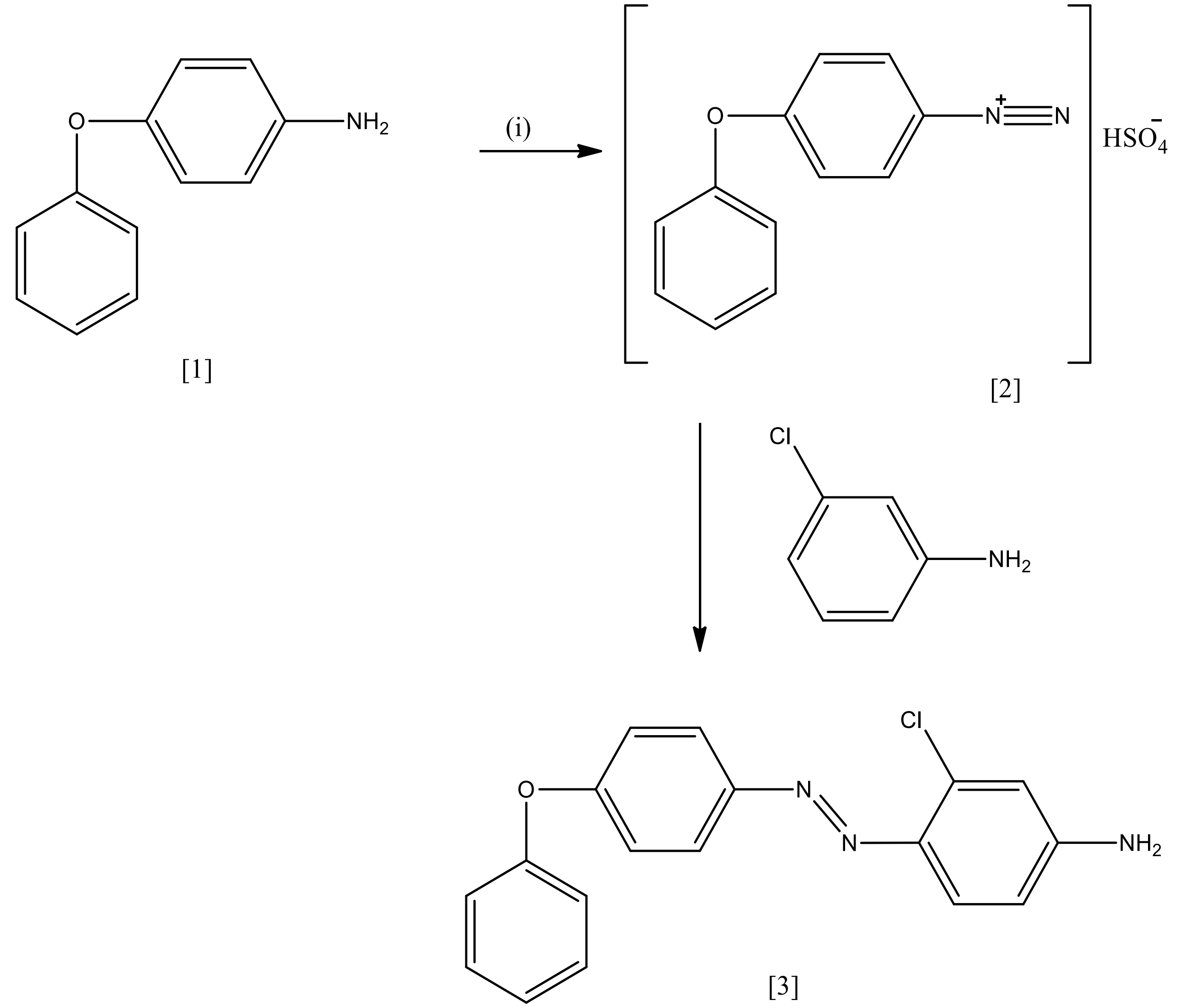
Colour fastness testing

The colour fastness of the dyes on the reduction/cleared dyed polyester fabric was carried out according to the corresponding standard methods, such as fastness to light (ISO 105 – BO2: 2013), fastness to sublimation (ISO 105 – PO1: 1993), fastness to washing (ISO 10S – CO6 A2S: 2010), fastness to perspiration (ISO 105 – EO4: 2013). The staining of the adjacent multifibre fabric and changes in shade were assessed using standard grey scales.

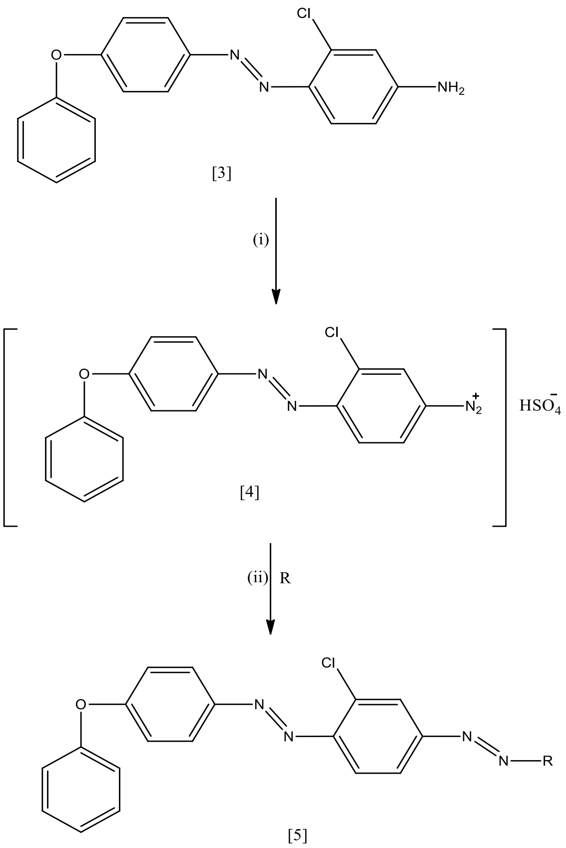
Results and Discussion

Synthesis

Scheme 1 illustrates the synthesis of the intermediate dye 3. In the first step, 4-phenoxyaniline reacted with cold sodium nitrite in a diazotization reaction under acidic condition to obtain a diazonium salt 2 which was coupled with 3-chloroaniline to afford 4-amino-2-chlorophenylazo-4-benzyloxbenzene. In the next step, this intermediate was similarly diazotized and coupled with solutions of 1-naphthylamine, 3-aminophenol, 7-methoxy-2-naphthol, 3-methoxyanoline and 1,3-dihydroxylbenzene respectively to afford the disazo disperse dyes. The crude dyes obtained were purified by recrystallization from ethanol/acetic acid mixture until a constant thin layer chromatography purity were obtained. All the disperse dye compounds were synthesized in moderate yield (40 – 72%). The chemical structures were confirmed with FTIR, ^{1}H-NMR and ^{13}C-NMR analyses. The chemical shifts, multiplicities and integration of the corresponding proton groups are in accordance with the structures of the dye molecules (Bruice, 2001).



Scheme 1: Synthesis of 4-amino-2-chlorophenylazo-4-benzyloxybenzene



Scheme 2: Synthesis of dyes 5a to 5e

(i) NaNO$_2$, H$_2$SO$_4$, 0 – 5^{O}C

(ii) CH$_3$COOH or NaOH$_{(aq)}$

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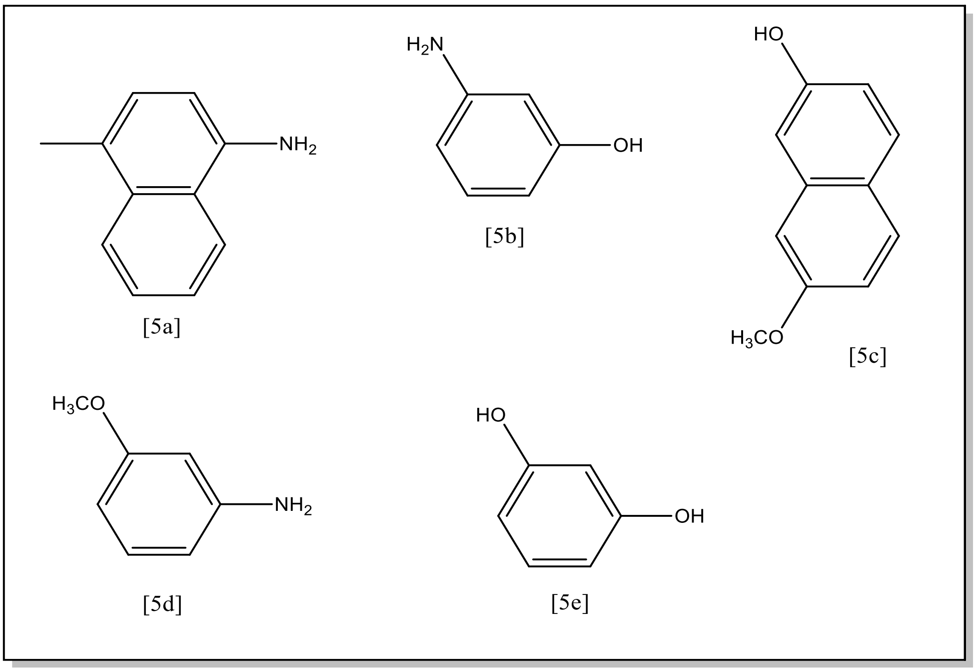

Characterization

4-amino-naphthaleneazo-2-chlorophenylazo-4-benloxybenzene (5a)

Brown crystals, yield: 57%, mp=110°C, UV-vis (ʎ$_{max}$ in DMF), 440, 603 nm IR (KBr) v_{max} (cm^{-1}), ^{1}H-NMR (DMSO-d$_6$, 200MHz) δ_H (ppm): 1.81 (2H, s, NH$_2$), 2.45 (1H, s, Ar-H), 3.83 (1H, s, OH), 5.85 (5H, s, OAr-H), 6.25 (d, J=8z, 2H, Ar-H), 6.65 (d, J=9H$_z$ 2H, Ar-H), 7.22 – 7.45 (2H m, Ar-H), 7.67 (2H, Ar-H), 7.82 (2H, m, Ar-H), ^{13}C-NMR, 50 MHz), δ_C (ppm): 161.0, 159.0, 150.4, 134.2, 131.1, 130.6, 115.8, 112.3, 109.6, 105.5, 99.2, 41.2, 40.7, 40.3, 39.9, 39.5, 39.1, 38.7. IR (KBr) v_{max} (cm^{-1}): 3708 – 3776 (Ar-NH$_2$), 2974 (ArC-H), 2387) Ar-OArH), 1467, 1524 (Ar C=C), 817 (substituted aromatic ring).

2-amino-4-hydroxyphenylazo-2-chlorophenylazo-4-benzyloxybenzene (5b)

Brown solid, yield: 65%, mp=150°C, UV-vis (ʎ$_{max}$ in DMF): 448 nm, ^{1}H-NMR (DMSO – d$_6$, 200 MHz) δ_H (ppm): 2.41 (2H, s, NH_2), 4.84 (1H, s, OH), 6.85 – 7.00 (d, J=8H$_2$, 2H, Ar-H), 7.10 – 7.80 (3H, m, Ar-H), 8.56 – 8.62 (3H, m, Ar-H), 8.96 (1H, s, Ar-H). ^{13}C-NMR, ($CDCl_3$, 50 MHz) δ_C (ppm): 162.1, 133.0, 131.5, 128.8, 128.4, 127.7, 127.4, 126.4, 125.0, 124.7, 123.8, 121.0, 120.2, 41.2, 40.8, 40.3, 39.9, 39.5, 38.9, 38.7. IR (KBr), v$_{max}$ (cm^{-1}); 3776, 3708 (Ar-NH$_2$, OH$_{str}$), 2974 (Ar-C-H$_{str}$), 1652, 1524 (Ar-C=C$_{str}$), 1467 (Ar-C=C$_{str}$), 1380, 1052 (C-O$_{str}$), 817 (disubstituted aromatic ring), 719 (mono substituted aromatic ring C-C).

7-methoxy-2-hydroxy-naphthaleneazo-2-chlorophenylazo-4-benzyloxybenzene (5c)

Brown solid, yield: 55%, mp=180°C, UV-vis (ʎ$_{max}$ in DMF): 424, 602 nm, ^{1}H-NMR (DMSO-d$_6$) δ_H (ppm): 3.80 (3H, s, OCH_3), 4.79 (1H, s, OH), 6.22 (d, J=8.2 H2, 2H, ArH), 6.86 (2H, m, Ar-H), 7.25 – 7.39 (1H, m, Ar-H), 7.46 – 7.57 (2H, m, Ar-H), 8.40 (1H, m, Ar-H). ^{13}C-NMR ($CDCl_3$ 50 MHz) δ_C (ppm): 161.5, 132.8, 132.3, 131.8, 130.7, 124.7, 124.3, 115.9, 98.9, 55.9, 55.7, 41.9, 41.4, 40.7, 40.3, 39.9, 39.5, 39.0, 38.6. IR (KBr) v$_{max}$ (cm^{-1}): 3795 (), 2883 – 2948 (Ar-OH$_{str}$), 2391 (C-H$_{str}$), 1592, 1461 (ArC=C$_{str}$), 1379 (Ar-OCH$_3$), 817 (disubstituted aromatic ring), 722 (monosubstituted aromatic ring C-Cl).

4-amino-2-methoxyphenylazo-2-chlorophenylazo-4-benzyloxybenzene (5d)

Brown solid, yield: 74%, mp=198 °C, UV-vis (ʎ$_{max}$ in DMF): 425 nm, ^{1}H-NMR (DMSO-d$_6$) δ_H (ppm): 256 (2H, s, NH_2), 3.74 (3H, s, OCH_3), 6.62 – 6.89 (d, J=8.4H$_2$, 2H Ar-H), 7.31 (1H, m, Ar-H), 7.40 (2H, m, Ar-H), 7.58 – 7.88 (2H, m, Ar-H), 8.67 (2H, m, Ar-H). ^{13}C-NMR (DMSO-d$_6$, 50 MHz) δ_C (ppm): 161.0, 145.2, 133.3, 132.4, 130.8, 125.7, 124.8, 114.7, 89.2, 66.8, 66.5, 42.0, 41.8, 40.3, 38.6, 38.5, 38.4, 38.1. IR (KBr) v$_{max}$ (cm^{-1}) 3782 (ArN-H$_{str}$), 2875 – 2952 (C-H$_{str}$), 2394 (), 1378, 1463, 1587 (ArC=C$_{str}$), 812 (disubstituted aromatic ring), 713 (C-Cl$_{str}$).

2,4-dihydroxyphenylazo-2-chlorophenylazo-4-benzyloxybenzene (5e)

Brown crystals, yield: 72%, mp=195°C, UV-vis (ʎ$_{max}$ in DMF): 445nm ^{1}H-NMR (DMSO-d$_6$) δ_H (ppm): 4.32 (1H, s, OH), 6.89 (d, J=7.9H$_2$, Ar-H), 7.25 (1H, m, Ar-H), 7.56 (2H, m, Ar-H), 7.62 (2H, m, Ar-H), 7.83 – 8.52 (3H, m, Ar-H), 8.65 (1H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) dC (ppm): 162.0, 132.3, 130.8, 131.2, 125.9, 125.7, 123.5, 122.8, 120.7, 41.8, 41.5, 40.9, 40.6, 39.7, 38.7, 38.4. IR (KBr) v$_{max}$ (cm^{-1}): 3777 (ArO-H$_{str}$), 3708 (O-H$_{str}$), 2975 (C-H$_{str}$), 1526 (C=C$_{str}$), 1463 (ArC=C$_{str}$), 1370 (C=C$_{str}$), 817 (disubstituted aromatic ring), 718 (C-Cl$_{str}$).

The FTIR spectra (in KBr) of the dye compounds showed two characteristic sharp bands within the range 3776 - 3708 cm^{-1}, corresponding to primary amine on the benzene ring for dye 5a, 5b and 5d. the absorption bands of O-H stretching vibrations in the FTIR spectra were observed within the range 3887 - 3660 cm^{-1} for dyes 5b, 5c and 5e. The strong absorption bands at the 2948 - 2883 cm^{-1} region were assigned to aromatic C-H stretching vibrations. The FTIR bands observed at 2391 cm^{-1} region were attributed to those of C-O-C of aryl ethers. For compounds 5c and 5d. The absorption bands appearing at 1592 - 1370 cm^{-1} region indicate the presence of C=C stretching vibrations of aromatic rings (Carey, 2003). Absorption bands of C-O stretching in the FTIR spectra were observed at 1080 - 1060 cm^{-1} range for compounds 5b, 5c and 5e. The presence of C-Cl stretching vibration at 722 - 719 cm^{-1} range was also found in the FTIR spectra of all the dye compounds.

In the ^{1}H-NMR spectra, protons close to the electronegative atoms gave signals at the downfield side 6.50 – 8.98 ppm, respectively while the -OCH_3 protons appeared at 3.70 – 3.74 ppm. The singlet OH proton signal was also observed at 3.80 – 4.82 ppm. Similarly, the ^{1}H-NMR spectra depicted in the experimental section indicate that the dyes showed multiplets at 7.00 – 8.98 ppm. This is attributed to aromatic proton and the singlet at 3.70 – 3.74 ppm of -OCH_3 protons. The characteristic doublet for the aromatic proton appeared at 6.25 – 6.89 ppm for dyes 5a to 5e.

The SP^2 carbons in ^{13}C-NMR spectra which are close to the electronegative atoms such as Cl and Oxygen gave signals at the downfield side of the spectra.

The UV-vis absorption data for dyes 5a to 5e measured in dimethylformamide (DMF) showed that dye 5a having the nitrogen atom at the para – position of the naphthalene ring caused significant bathochromic shifts and had a great influence on the ʎ$_{max}$ of the dye.

Generally, the greater strength of the electron donating nitrogen and -OCH_3 group at the naphthalene ring resulted in a more significant bathochromic shift with a shoulder at 603nm (in dye 5a) and 602 nm (in dye 5c) (Karci, 2005; Metwally *et al*., 2013).

Fastness properties

The fastness properties (Tables 1 and 2) of the disazo disperse dyes 5a – 5e on polyester fabric were evaluated. The results of the wash fastness tests of dyes 5a to 5e on the polyester fabrics are summarized in Table 2 and showed excellent wash fastness. The results also show that the staining of the adjacent multi-fibres were grade 5, indicating that there was no staining. Table 1 shows the results of light, rub, perspiration and sublimation fastness tests. The perspiration fastness for acid and alkaline conditions were observed to be good to excellent (grade 4 to 5). Rubbing fastness for dry samples was very good to excellent (4/5 to 5) while that for wet samples was moderate to very good (grade 3/4 to 4). Sublimation fastness of the dyes was rated at very good (dyes 5a and 5c) to excellent (dyes 5c to 5e).

Table 1: Fastness properties on polyester fabric

Dye	Perspiration		Rubbing		Sublimation	Light
	Acid	Alkali	Dry	Wet	180°C	
5a	5	5	4	4/5	3/4	6
5b	4/5	4/5	4/5	3/4	3/4	5/6
5c	4/5	4/5	4/5	3/4	4	6
5d	4/5	4/5	4/5	3/4	5	5/6
5e	4	4	4	4	5	5

Table 2: Washing fastness of dye 5a to e on polyester fabric

Dye	Change	Nylon	Polyester	Cotton acetate
5a	5	5	5	5
5b	5	5	5	5
5c	5	5	5	5
5d	5	5	5	5
5e	5	5	5	5

The results obtained in this study for the sublimation fastness of the dyes tend to be better compared to those of the monoazo dyes in a previous study (Otutu, 2018). This is attributed to the inclusion of polar groups such as –Cl and –OH groups in the dye molecules. The light fastness of dyes 5a and 5c was very good (grade 6), that of dyes 5b and 5d was good (grade (5/6) and dye 5e showed moderate light fastness. The reason for the moderate light fastness performance of dye 5e could be attributed to the presence of electron-donating OH group at the proximity of the hydrazo group (-N=N-). The rate of photo-fading of a dyed fabric are not only the position and nature of the substituent groups in relation to the hydrazo group but also to the interaction of the dye itself with the substrate and the effect of aggregation of dyes (Otutu and Ossai, 2017a). Thus, the light fastness results are generally in line with those obtained from previous study (Manian *et al*., 2016) in which case, a dye that contains electron-donating groups close to an azo chromaphore or a more sterical group tend to exhibit low light fastness as in the case of anthraquinones disperse dyes. The molecular size (or weight) and symmetry of dye structure have influence on the photostability of dye compounds (Otutu and Ossai, 2017b).

Conclusion

A series of 4-amino-2-chlorophenylazo-4-benzyloxybenzene disazo disperse dye derivatives were synthesized and applied to polyester fabrics. The spectra and dyeing properties were investigated. The dyes showed outstanding characteristics: very good to excellent washing and perspiration fastness, there is however, a little variation in their rubbing fastness. The sublimation fastness was good to excellent and the light fastness of the dye compounds was found to depend in the nature and position of the substituents influencing the electron density around the hydrazo group. Overall, the dyes produced in this study could be important especially in the area of transfer printing due to the moderate to good sublimation fastness properties.

Conflict of Interest

The author declares that there is no conflict of interest related to this study.

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