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Synthesis and Application of Monoazo Disperse Dyes Derived from 4-amino-*N*-hexadecyl-1, 8-naphthalimide and their Dyeing Performance on Polyester Fabrics

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ABSTRACT

A series of monoazo disperse dyes were synthesized using 4-amino-N-hexadecyl-1, 8-naphthalimide by coupling with different substituted electron rich arenes in appropriate reaction conditions. The synthesized diazo component and the dyes were purified by recrystallization method. The structures of the diazo component and the dyes were confirmed using UV-visible, FT-IR, NMR and MS spectroscopic techniques. Spectrophotometric investigations of the dyes in solvents of different polarities were carried out in order to obtain their absorption maxima, molar extinction coefficient and solvatochromic effects. These dyes were applied on polyester fabrics using High Temperature and High Pressure (HTHP) exhaust dyeing method. The dyeing characteristics such as build up on fabrics, wash, perspiration and light fastness were examined. The dyed fabric generally gave deep and bright hue ranging from light yellow, orange, maroon and neon red. The colour fastness of the dyed fabrics to washing and perspiration were examined to be very good, however, the light fastness was found to be fair to good.

Keywords: *Disperse dyes, 4-amino-N-hexadecyl-1, 8-naphthalimide, Solvatochromism, Dyeing, Polyester fabrics, Fastness properties*

INTRODUCTION

Azo dyes account for more than half of the total number of disperse dyes and cover nearly the full colour spectrum from greenish yellow to bluish green [1, 2]. They are relatively inexpensive and generally do not require numerous intermediate stages in their manufacture [2]. Disperse dyes are substantially water-insoluble dye having substantivity for hydrophobic fibres and usually applied from aqueous dispersion [3]. Disperse dyes are used mainly for dyeing polyester, secondary cellulose acetate and cellulose triacetate but they are also used in limited application for dyeing nylon and acrylic fibre [4]. The majority of disperse dyes are monoazo (50%) or anthraquinone dyes (25%) [5]. The remaining dyes are based on other dye chromophores such as benzodifuranone, courmarin, methane, naphthalimide, nitrophenylamine and quinophthalone.

Heterocyclic derivatives of naphthalimides, phenylazophthalimides and 1, 8-naphthalic anhydrides have been studied to assess their role as intermediates for dye synthesis [6]. These compounds have been investigated for the synthesis of disperse dyes, dyes for other polymer fibres, acid dyes, dyes for polymeric materials and dyes capable of copolymerization. It has been shown in the last decade that the use of diazo components such as 4-aminonaphthalimides have advantageous effects on the dyeing properties of the derived disperse azo dyes. The presence of the naphthalimide system also leads to a deep and intense colour [7]. 4-Amino-*N*-substituted-naphthalimide is a useful diazo component for the synthesis of azo dyes [8]. Naphthalimide derivatives have obtained a great industrial importance because of their excellent fastness of some of these dyes [9]. When substituted with electron donating groups, naphthalimides are useful for colour chemists, preferably in the 4-position. The substitution of an amino group into the 4-position yields brilliant greenish yellow compounds [10]. 4-Amino-*N*-(substituted)-1, 8-aphthalimides were used for synthesis of azo and non-azonaphthalimide dyes [11]. The range of applications for these dyes are very wide; alongside classical fields such as dyeing natural and synthetic textile fibres, plastics, paints and coatings, increasingly novel applications are coming to light, in which aesthetic considerations are no longer of primary importance. These include applications in solar energy collectors, light emitting diodes, liquid crystal displays, and laser active media, potential photosensitive biologically active units, as fluorescent markers in biology and in medicine as antiviral compounds or as analgesics [12]. Aminonaphthalimides are known to produce fluorescent yellow dyes for synthetic polymer fibres. In these compounds, when the *N*- substituent of naphthalimide is an aryl, most of the dyes exhibit properties similar to typical organic colorants, due to strong aggregation. The dyes with alkyl group in *N*-substituted naphthalimides can be converted into disperse dyes which are used in the colouration of synthetic fibres [13]. Generally, monoazo disperse dyes derived from naphthalimides show exceptionally good thermal stability and good dyeing fastness properties [14]. However, the 4-amino-*N*-alkyl (ester)-1, 8-naphthalimide derivatives of monoazo disperse dyes have relatively low heat fastness properties. Moreover, lack of polar groups in their structures made them hardly soluble in water which results to the milling of the dye into fine dispersion during application. This work aims to introduce amphiphiles into 4-aminonaphthalimide compound which serve as a diazo component to synthesize dyes with improved solubility, penetration, levelness and also, save time of milling which is associated to the conventional method of disperse dyes application.

EXPERIMENTAL

MATERIALS AND METHODS

All the chemicals used in the synthesis were of commercial grade and were used as received. The synthesized compounds were characterized by melting point, TLC, FT-IR, ^{1}H and ^{13}C NMR, MS and elemental analysis (CHN). Melting points were recorded on Barnstead electrothermal 9200 apparatus and are uncorrected. Infra-red were recorded using Perkin-Elmer Spectrum RX1 FT-IR Spectrometer, ^{1}H and ^{13}C NMR were carried out on 300 MHz Bruker instrument using deuterated chloroform ($CDCl_3$) and dimethylsulphoxide (DMSO-d_6) as solvent. Chemical shifts were reported in parts per million (ppm) downfield from internal tetramethysilane (TMS). Elemental analyses (CHN) were recorded on Perkin-Elmer PE 2400 series II and mass spectra were reported using Agilent Technologies 5975C VL MSD mass spectrometer.

Synthesis of 5-Nitroacenaphthene

Acenaphthene **1** (15.4 g, 0.1 mol) was dissolved in hot acetic acid (57.2 cm^3) and was cooled with vigorous stirring to separate crystalline acenaphthene as fine as possible. Concentrated nitric acid (65%, d =1.40 g/cm^3) (9.84 g) was added drop wise for 1 h at 22-27 °C, then further stirred for 1 h at 25 °C. The solution was warmed gradually for 30 min to 68 °C then cooled to form the crystals which were filtered, washed with 1:1 acetic acid – water and water to give yellow needles 5-nitroacenaphthene **(2)** [15], yield 85 %, Mp: 101-102 °C.

Synthesis of 4-nitro-1, 8-naphthalic anhydride

5-Nitroacenaphthene (24.87 g, 0.125 mol) was dissolved in hot acetic acid (248.75 cm^3), sodium dichromate (158.5 g) was added for 3 hours at 65 – 70 °C. The solution was warmed gradually to 98 – 100 °C for 30 min and further refluxed for 5 h. The reaction mixture was washed out from the flask with hot water (0.6 L), cooled, filtered and the solid was washed with dilute HCl. In addition, the solid was boiled with 200 cm^3 of 5 % Na_2CO_3 solution for 30 min and filtered. The filtrate was acidified and the separated crystals dried at 120 °C for 4 hours to obtain 4- nitro -1, 8-naphthalic anhydride **(3)**, which was recrystallized from concentrated HNO_3 (65%, d = 1.40 g/cm^3) to afford colourless needles [16], yield 74%, Mp: 231-232 °C.

Synthesis of 4-nitro-*N*-hexadecyl-1, 8-naphthalimide

A suspension of 4-nitro-1, 8-naphthalic anhydride (0.02 mol, 4.86 g) and hexadecylamine (0.03 mol, 7.17 g) was stirred under reflux for 7 h in ethanol (102 cm^3). The cooled suspension was filtered out and recrystallized with ethanol to give off-white crystals of 4-nitro-*N*-hexadecyl-1, 8-naphthalimide **(4)** [17], yield 64.6 %; Mp: 99-101 °C.

Synthesis of 4-amino *N*-hexadecyl -1, 8-naphthalimide

A mixture of 4-nitro-*N*-hexadecyl-1, 8-naphthalimide (18 mmol, 8.39 g) and stannous chloride (90 mmol, 20.25 g) in ethanol (81 cm^3) was refluxed for 1hr with hydrochloric acid (10.1 cm^3) till the reaction was complete. The mixture was transferred into 100 cm^3 of water and the observed precipitate was filtered. The crude product (4-amino *N*-hexadecyl -1, 8- naphthalimide **(5)**) was purified by recrystalization from ethanol as orange crystals [17], yield 71 %; Mp: 138-139 °C;

Representative Procedure for the Synthesis of Dyes (7a-e)

Synthesis of (*Z*)-2-hexadecyl-6-((2-hydroxynaphthalen-1-yl)diazenyl)-benzo[de]isoquinoline-1,3(2*H*)-dione (7a)

Sodium nitrite (1.5 mmol, 0.104 g) was slowly added with constant stirring to cold concentrated sulphuric acid (98 %, 1.1 cm^3) at below 10 °C. The temperature of the reaction mixture was gradually increased to 65 °C using water bath until all the sodium nitrite was dissolved. The solution was then cooled externally to 5 ºC and diluted with a mixture of propionic acid and acetic acid (10 cm^3 1.5:8.5 v/v). The finely ground powder of 4-amino-*N*-hexadecyl-1, 8-naphthalimide (1.5 mmol) was added portion wise at less than 10 °C, and then the liquor was stirred for 3 h. The obtained clear diazonium salt solution **(6)** was used immediately in coupling reactions with 2-naphthol (1.5 mmol) dissolved in ethanol by adding over 30-40 min with vigorous stirring. The mixture was stirred further for 2 h, maintaining a temperature of 5 °C. The pH of the solution was adjusted to 4-5 using 10 % sodium acetate and stirred for 1 h. The resulting product was then collected by filtration, washed with warm water and then cold water and dried. The crude product was purified by recrystallization method using DMSO several times to obtained dye **7a,** Yield 71.1 %; Mp: 154–156 °C. The same procedure were used to produce dyes **7b – 7e**

Dyeing Procedure

The dyeing was carried out using KMS-IRE Laboratory Dyeing Machine – ELITE. The material to liquor ratio of 1:50 and 2 % shade was used for dyeing On Weight of the Fabric (OWF). The dye was dissolved in DMF (5 cm^3) and water (45 cm^3) was added with constant stirring, the pH was adjusted to 5 using glacial acetic acid. The dye suspension (50 cm^3) was transferred into a beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a wetted pattern of polyester fabric 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 glycerin-bath and the temperature was raised to 130 °C at the rate of 2 °C per min. The dyeing was continued for 1h, under pressure. After cooling to 70 °C the beaker was removed from the bath, the dyed pattern was removed, thoroughly washed with water and dried at room temperature [17].

Reduction Clearing: The dyed fabric was treated with an aqueous solution containing sodium dithionite (2 g/L) and sodium hydroxide (2 g/L) for 45 min at 70 °C. The fabrics was then washed with water and dried.

Fastness Properties: The dyed fabrics were evaluated using a standard test methods, wash fastness (ISO 3), perspiration (ISO 105 E04:2013) and light fastness (ISO 105 B02:2014).

Synthesis of Intermediates and the Dyes

Acenaphthene **1** was reacted with concentrated nitric acid in an acetic acid media at room temperature to give yellow crystals of 5-nitroacenaphthene **2** in 85 % isolated yield. 5-Nitroacenaphthene **2** was oxidized using sodium dichromate and hot glacial acetic acid as the solvent to give colourless crystals of 4-nitro-1, 8-naphthalic anhydride **3** in 74 % isolated yield after recrystallization from nitric acid. 4-Nitro-1, 8-naphthalic anhydride **3** was reacted with hexadecylamine in absolute ethanol media under reflux condition to produce off-white crystals of 4-nitro-*N*-hexadecyl-1, 8-naphthalimide **4** in 64.6 % isolated yield. 4-Amino-*N*-hexadecyl-1, 8-naphthalimide **5** was synthesized by the reaction of 4-nitro-*N*-hexadecyl-1, 8-naphthalimide **4** with stannous chloride (II) in hydrochloric acid as a reducing agent and ethanol as solvent to give the corresponding orange crystals of **5** in 71 % isolated yield (Scheme 1). The structure of the intermediates were confirmed by various techniques which include FT-IR, NMR, elemental analysis (CHN) as shown in Tables 1 and 2, and mass spectroscopy. The IR spectra of the intermediate 4-Amino-*N*-hexadecyl-1, 8-naphthalimide **5** showed absorptions at 3352 and 3254 cm^{-1} due to NH_2 stretch, the signal at 2998 cm^{-1} is attributed to aromatic C-H stretch while the signal at 2917 indicates C-H stretch of aliphatic. The absorption at 1675 cm^{-1} and 1653 cm^{-1} are due to –N-C=O and C=O stretch respectively and the absorption band at 1636 cm^{-1} corresponding to C=C groups. The ^1H NMR spectra displayed two signals at 0.86 and 1.24-1.77 ppm corresponds to the terminal methyl ($-CH_3$) and the methylene ($-CH_2-$) groups of the hexadecylamine chain respectively. The peaks at 4.11 ppm showed a downfield correspond to (-*N*-CH_2-), the peak at 5.06 ppm was observed which account for the hydrogens associated with NH_2 substituent. The aromatic protons were showed signals at 6.86-8.57 ppm as multiplet. ^{13}C NMR spectrum showed 16 peaks at 14.1 and 22.6-40.2 ppm related to the terminal $–CH_3$ and $–CH_2$ groups of hexadecylamine carbons respectively. The peaks at 109.5-149.1 ppm correspond to the carbons at the aromatic region and the carbonyl groups appeared at 164.0 and 164.5 ppm. The elemental analysis results showed good agreement with the theory. The mass spectrometry analysis showed a molecular ion [M^+] at m/z 436.4 which is in agreement with the formula mass of **5** as shown in Table 3.

The diazotisation of 4-amino-*N*-hexadecyl-1, 8-naphthalimide was carried out using nitrosylsulphuric acid method and coupling with various electron-rich arenes produce the dyes (Scheme 1). The structures of the dyes were characterized using FT-IR, ^{1}HNMR, MS and UV spectroscopic methods. The FT-IR, ^{1}HNMR and UV- visible results were shown in the Table 3 and 4 respectively. Figures 1–4 showed the FT-IR and Mass spectra of the selected compounds **7a** and **7b.** The dye **7a** showed absorption band at 3351 cm^{-1} due to the presence of OH group. All the dyes showed absorption bands at 3060-2953 cm^{-1} and 2921-2917 cm^{-1} due to the presence of C-H stretching vibration of aromatic C-H, methyl and methylene groups. The absorption band at 1657-1647 cm^{-1} corresponding to C=O groups. The absorption band at 1646-1604 cm^{-1} confirmed the presence of C=C groups. The signal at 1589-1575 cm^{-1} is attributed to –N=N- stretch while signal at 1386-1351 cm^{-1} is due to C-N. The ^{1}HNMR spectra of the dyes displayed signals at 0.84-0.86 and 1.23-1.76 ppm for the methyl and methylene protons of the aliphatic regions. The signal at 4.09-4.18 ppm shows a downfield due to *N*-CH_2 protons of the aliphatic group. The diazo group was substituted in the alpha position of 2-naphthol in the dye **7a**. For this purpose, the dye **7a** showed signals at 17.07 ppm for OH proton in ^{1}H NMR spectra. This amount of desheilding can be attributed to the interamolecular hydrogen bonding of the diazo group and the –OH group. The aromatic protons were showed signals at 6.66 - 9.21 ppm and the number of protons is in agreement with the aromatic protons in the structure of dyes. The presence of two signals at 6.7 and 7.9 ppm as doublet in the ^{1}H NMR spectra of **7b** and **7c** exactly confirm that the diazo group substituted at para position on the *N*, *N*-(dialkyl)aniline ring. In addition mass analysis exactly confirms the molar mass of the dyes.

RESULTS AND DISCUSSION

Table 1: The FT-IR, ^{1}H NMR and ^{13}C NMR Spectra of the Synthesized Intermediates

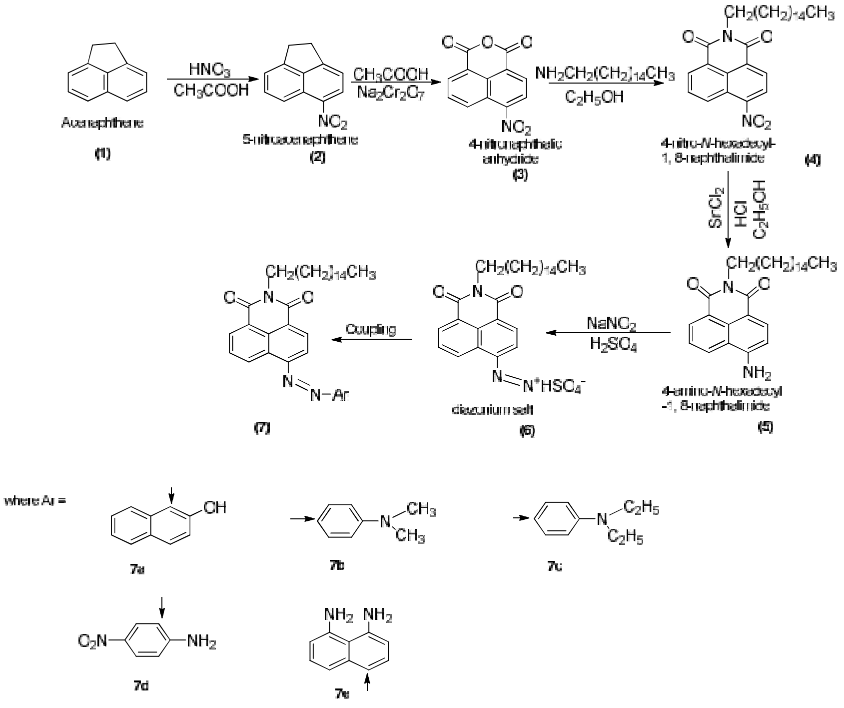
Compound	FT-IR (cm^{-1})	^{1}HNMR and ^{13}C NMR (δ ppm,$CDCl_3$)
5-nitroacenaphthene (2)	3085 (C-H str. Ar.), 2946 (C-H str. Aliphatic), 1620, 1596 (NO_2 str.), 1508 (C=C str.)	3.43 (4H, s, 2CH_2), 7.31(1H, d, *J* = 7.8 Hz, 1-H), 7.45 (1H, t, *J* = 7.0 Hz, 9-H), 7.66 (1H, dd, *J* = 6.7 and 7.1 Hz, 2-H), 8.47 (1H, d, *J* = 7.7 Hz, 8-H), 8.54 (1H, d, *J* = 8.6 Hz, 3-H); 30.6, 33.1, 117.9, 120.1, 121.2, 122.7, 124.3, 127.7, 131.7, 140.1, 146.6, 155.7
4-nitro-1, 8-naphthalic anhydride (3)	3078 (C-H str. Ar.), 2914, 2849 (C-H str. Aliphatic) 1789.1756 (C=O str.), 1624 (NO2 str.), 1526 C=C str.	(δ ppm,DMSO-d_6) 8.09 (1H, t, *J* = 7.8 Hz, 3-H), 8.54 (1H, d, *J* = 8.0 Hz, 8-H), 8.61 (1H, s, 2-H), 8.64 (1H, d, *J* = 7.5 Hz, 9-H), 8.73 (1H, dd, *J* = 8.2 and 8.7 Hz, 4-H); 120.1, 122.6, 124.0, 124.3, 129.8, 130.3, 130.6, 131.1, 133.2, 149.5, 159.4, 160.0.
4-nitro-*N*-hexadecyl-1, 8-naphthalimide (4)	3081 (C-H str.), 2947 2916 (C-H str. Aliphatic), 1699 (-N-C=O str.), 1656 (C=O str.), 1622 (C=C str.), 1593 (NO_2 str.)	0.86 (3H, t, *J* = 6.9 Hz, CH_3), 1.26-1.79 (m, 28H, Aliphatic), 4.16 (2H, t, *J* = 7.6 Hz, *N*-CH_2), 7.96 (1H, t, *J* = 7.3 Hz, 3-H), 8.40 (1H, d, *J* = 8.0 Hz, 8-H), 8.68 (1H, d, *J* = 5.7 Hz, 9-H), 8.75 (1H, dd, *J* = 8.0, 8.3 Hz, 2-H), 8.85 (1H dd, *J* = 8.7 and 8.8 Hz, 4-H); 14.1, 22.7, 27.1, 28.0, 29.3, 29.4, 29.4, 29.4, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 31.9, 40.9, 123.1, 123.7, 123.9, 127.1, 129.1, 129.2, 129.7, 129.9, 132.4, 149.5, 162.4, 163.3.
4-amino *N*-hexadecyl -1, 8- naphthalimide (5)	3254 (N-H str.), 2998 (C-H str. Ar.), 2917, 2851 (C-H str. Aliphatic), 1675 (-N-C=O str.), 1653 (C=O str.), 1636 (C=C str.)	0.86 (3H, t, *J* = 6.9 Hz, CH_3), 1.24-1.77 (m, 28H, Aliphatic), 4.13 (2H, t, *J* = 7.6 Hz, *N*-CH_2), 5.06 (2H, s, NH_2), 6.86 (1H, d, *J* = 8.2 Hz, 8-H), 7.60 (1H, t, *J* = 7.8 Hz, 2-H), 8.11 (1H, d, *J* = 8.2 Hz, 9-H), 8.38 (1H, d, *J* = 8.2 Hz, 3-H), 8.57 (1H, d, *J* = 7.2 1-H); 14.1, 22.7, 27.2, 28.2, 29.3, 29.4, 29.4, 29.4, 29.4, 29.4, 29.5, 29.5, 29.6, 29.7, 31.9, 40.3, 109.5, 112.2, 120.1, 123.2, 124.9, 126.7, 129.8, 131.4, 133.7, 149.1, 164.0, 164.5

Table 2: The Yield, Melting Point and Elemental Analysis of the Synthesized Intermediates

Compound	Yield (%)	Melting point (°C)	Found (%)			Required (%)		
			C	H	N	C	H	N
5-nitroacenaphthene (2)	85	101-102	72.18	4.57	7.04	72.3	5 4.5	7.03
4-nitro-1, 8-naphthalic anhydride (3)	74	231-232	59.17	2.02	5.75	59.27	2.07	5.76
4-nitro-*N*-hexadecyl-1, 8-naphthalimide (4)	64.6	99-101	72.39	8.79	5.91	72.07	8.21	6.00
4-amino *N*-hexadecyl -1, 8- naphthalimide (5)	71	138-139	76.91	9.33	6.23	77.02	9.23	6.42

Table 3: The FT-IR and ^{1}H NMR Spectra of the Synthesized Dyes

Dyes	FT-IR (cm^{-1})	^{1}HNMR (δ ppm,$CDCl_3$)
7a	3351 (OH str.), 3060, 2955 (C-H str.), 2920, 2849 (C-H str. Aliphatic), 1701 (-N-C=O str.), 1655 (C=O str.), 1623 (C=C str.), 1587 (N=N str.), 1382 (C-N str.)	0.85 (3H, t, *J* =6.8 Hz, CH_3), 1.25–1.72 (28H, m, Aliphatic), 4.09 (2H, t, *J* =7.7 Hz, *N*-CH_2), 6.66–8.59 (11H, m, Aromatic), 17.07 (1H, s, OH)
7b	2955 (C-H str.), 2917, 2849 (C-H str. Aliphatic), 1693 (-N-C=O str.), 1657 (C=O str.), 1604 (C=C str.), 1586 (N=N str.), 1351 (C-N str.)	0.85 (3H, t, *J* =6.9 Hz, CH_3), 1.25–1.74 (28H, m, Aliphatic), 3.15 (3H, s, CH_3), 4.15 (2H, t, *J* =7.6 Hz, *N*-CH_2), 6.76–9.21 (9H, m, Aromatic)
7c	2954 (C-H str.), 2917, 2850 (C-H str. Aliphatic), 1694 (-N-C=O str.), 1675 (C=O str.), 1636 (C=C str.), 1575 (N=N str.), 1379 (C-N str.)	0.85 (3H, t, *J* =6.9 Hz, CH_3), 1.25–1.74 (28H, m, Aliphatic), 3.48 (4H q, *J* = 7.1 Hz, 2CH_2), 4.15 (2H, t, *J* =7.5 Hz, *N*-CH_2), 6.75–9.21 (9H, m, Aromatic)
7d	3208 (NH str.), 2953 (C-H str.), 2921, 2850 (C-H str. Aliphatic), 1699 (-N-C=O str.), 1647 (C=O str.), 1589 (N=N str.), 1382 (C-N str.)	0.84 (3H, t, *J* =7.0 Hz, CH_3), 1.23–1.73 (28H, m, Aliphatic), 4.13 (2H, t, *J* =7.4 Hz, *N*-CH_2), 7.54–8.74 (9H, m, Aromatic)
7e	3353 (NH str.), 2953 (C-H str.), 2919, 2850 (C-H str. Aliphatic), 1696 (-N-C=O str.), 1614 (C=O str.), 1575 (N=N str.), 1379 (C-N str.)	0.85 (3H, t, *J* =6.9 Hz, CH_3), 1.24–1.72 (28H, m, Aliphatic), 4.14 (2H, t, *J* =7.6 Hz, *N*-CH_2), 5.02 (2H, s, NH_2), 6.85–9.08 (11H, m, Aromatic)



Scheme 1: Synthesis of the Intermediates and the Dyes

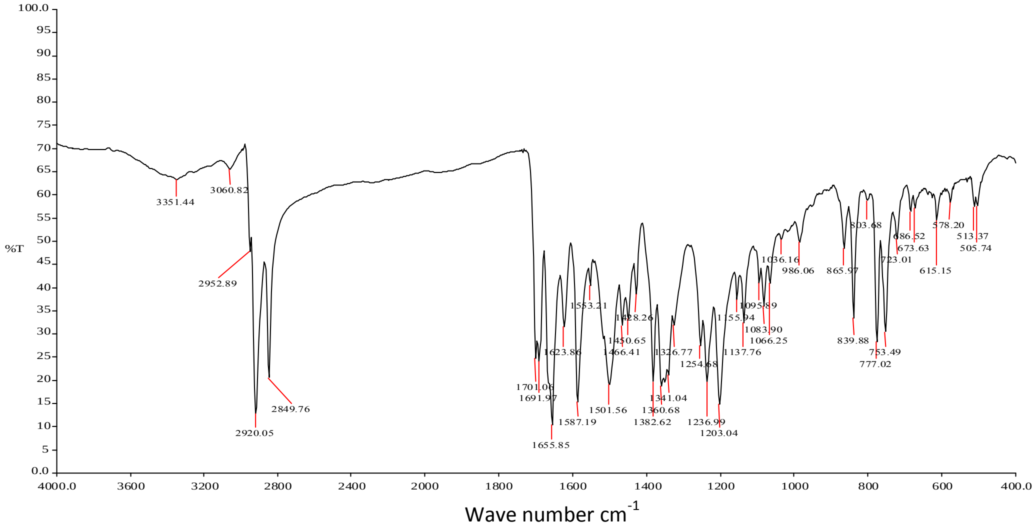


Figure 1: FT-IR for the dye 7a

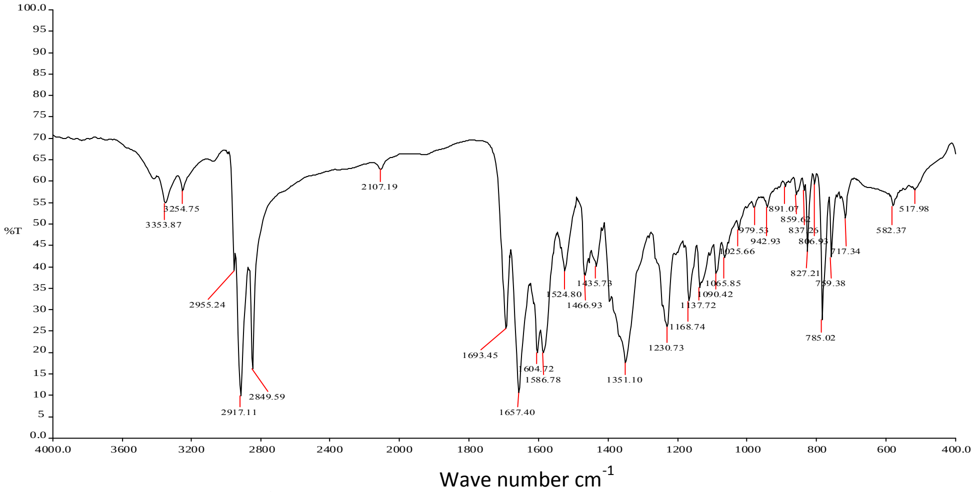


Figure 2: FT-IR for dye 7b

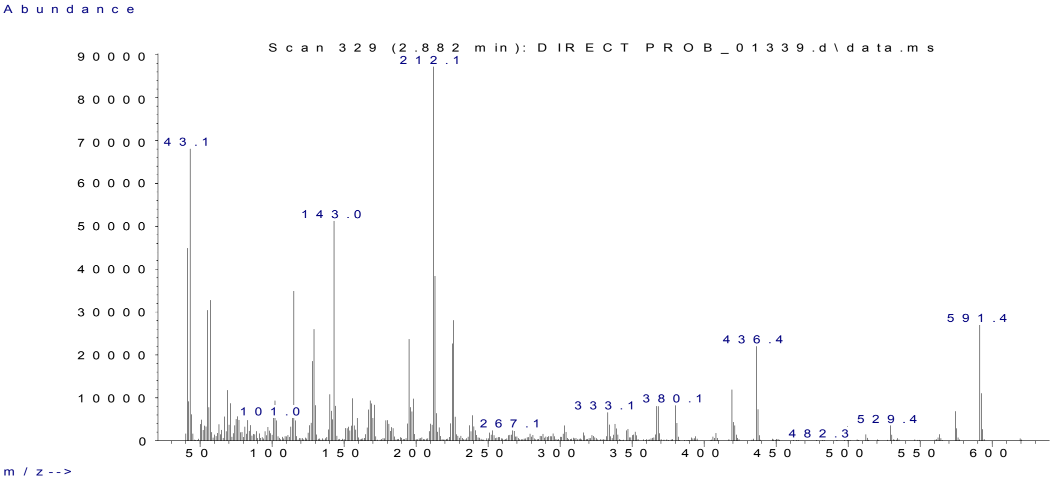


Figure 3: Mass Spectra of the dye 7a

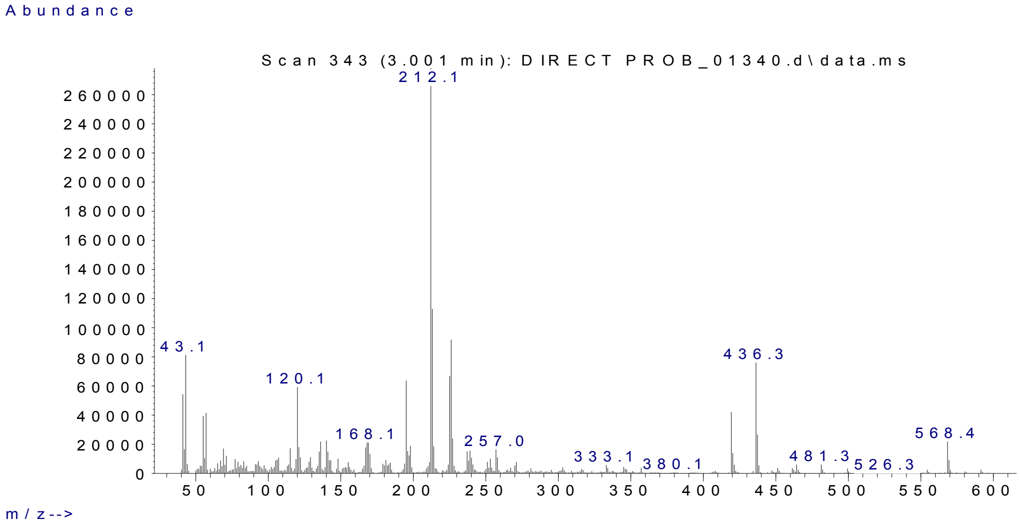


Figure 4: Mass Spectra of the dye 7b

Spectral Characteristics of the Synthesized Dyes

The absorption spectra of the synthesized dyes were measured in various solvents. Absorption maxima, molar extinction coefficients of each dye in various solvents are listed in Table 4. Wavelengths of maximum absorption (λ_{max}) and molar extinction coefficient ranged from 440-610 nm and $1.06x10^4$-$3.18x10^4$ l/mol cm for the synthesized dyes in DMF respectively. The wavelength (λ_{max}) shifts in different solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvent. In many dyes, however, the ground state is less polar than the excited state, thus a polar solvent will tend to stabilize the excited state more than the ground state, giving rise to bathochromic shift [18]. It was observed that in chloroform, ethanol and ethanol plus a drop of HCl, the absorption spectral of the dyes did not change significantly.

Dye **7a** which was obtained by diazotised 4-amino-*N*-hexadecyl-1, 8-naphthalimide and coupled with 2-naphthol gave maximum absorption wavelength of 520 nm in DMF and when the coupling component was changed to *N, N*-dimethylaniline give dye **7b**, the resulting dye gave maximum absorption wavelength of 540 nm in the same solvent. It is well known that the colour of dyes is influenced by the introduction of additional donor groups into the coupling component. The presence of *N, N*- dimethyl in the coupling component of dye **7b** resulted in the bathochromic effect of 20 nm when compared with dye **7a** which may attribute to the present of dimethyl. Dye **7c** was obtained by coupling *N, N*-diethylaniline with the same amine gave a maximum absorption wavelength of 440 nm in DMF and is hypsochromic by 80 nm and 100 nm when compared with dyes **7a** and **7b** respectively in the same solvent. Replacement of coupling component (*N, N*-diethylaniline) in dye **7c** with 4-nitroaniline gave dye **7d** which absorbed at 440 nm and showed a bathochromic shift of 100 nm and 0 nm when compared with dyes **7b** and **7c** respectively. Similarly, dye **7e** was obtained by coupling 1, 8-diaminonaphthalene with the diazo component. The dye **7e** showed a strong bathochromic shift of 90 nm when compared with dye **7a** which may be attributed to the presence of electron donor (NH_2) in the coupling component.

Dyeing and Fastness Properties of the Synthesized Dyes

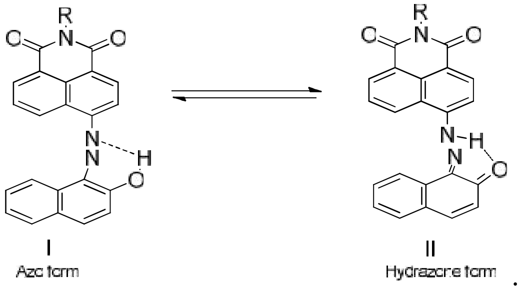
The synthesized dyes were applied onto polyester fabrics and their dyeing properties such as light fastness, wash fastness and perspiration fastness were examined. The dyes were applied by the high temperature and high pressure dyeing method. Visual evaluation of the dyeing on polyester fabrics showed that the nature of the alkyl residue in the amine group of the coupling component affects both the intensity of dyeing and their shade obtained. The highest intensity is shown by the dyes which contain *N, N*-dimethyl and *N, N*-diethyl groups. These substituents bring about an increase in the nucleophilic character of the tertiary nitrogen atom and the stability of polar forms [19] especially when there are no substituents in the phenyl ring causing steric effects. The electron donor substituent (-OH) in the ring of the coupling components in ortho position to the azo band also considerably affects the colour of the dyeing in **7a**. This phenomenon is described in terms of structures I and II.

Table 3: Mass Spectroscopy of the Intermediate and the Synthesized Dyes

Dye No.	Empirical Formula	Experimental Values of m/z Fragment	Corresponding Positive Charge Fragment	Theoretical Value
(5)	$C_{28}H_{40}N_2O_2$	43.2, 212.2, 295.1, 391.3, 436.4	CNO^+, $C_{12}H_7N_2O_2^+$, $C_{18}H_{33}NO_2^+$ $C_{27}H_{38}NO^+$, M	436.63
7a	$C_{38}H_{45}N_3O_3$	43.1, 143.0, 212.1, 436.4, 591.4	CNO^+, $C_{10}H_7O^+$, $C_{12}H_7N_2O_2^+$, $C_{28}H_{40}N_2O_2^+$, M	591.78
7b	$C_{36}H_{48}N_4O_2$	43.1, 120.1, 212.1, 436.3, 568.4	CNO^+, $C_8H_{10}N^+$, $C_{12}H_7N_2O_2^+$, $C_{28}H_{40}N_2O_2^+$, M	568.79
7c	$C_{38}H_{52}N_4O_2$	43.1, 212.1, 596.5	CNO^+, $C_{12}H_7N_2O_2^+$, M	596.85
7d	$C_{34}H_{43}N_5O_4$	43.1, 212.2, 436.4, 586.4	CNO^+, $C_{12}H_7N_2O_2^+$, $C_{28}H_{40}N_2O_2^+$, M	585.74
7e	$C_{38}H_{47}N_5O_2$	43.2, 212.2, 436.4, 605.4	CNO^+, $C_{12}H_7N_2O_2^+$, $C_{28}H_{40}N_2O_2^+$, M	605.81

Table 4: The UV- Visible Spectroscopic of the Dyes

Dye No.	ε_{max} in DMF $\times 10^4$ $lmol^{-1}cm^{-1}$	DMF λ_{max} (nm)	Chloroform λ_{max} (nm)	Ethanol λ_{max} (nm) a	Ethanol + HCl λ_{max} (nm) b	Change in λ_{max} (nm) (b-a)
7a	3.06	520	465	520	520	0
7b	1.06	540	440	440	440	0
7c	1.76	440	460	440	435	-5
7d	3.18	440	410	435	435	0
7e	2.35	610	520	430	440	+10



Scheme 2: Structure of Azo form and Hydrazone form

Table 5: Dyeing Properties of the Synthesized Dyes on Polyester Fabrics

Dye No.	Light	Fastness Washing	Perspiration Acid	Alkaline
7a	2	3	3	3
7b	3	3	4	4
7c	6	5	4	5
7d	2	4	4	4
7e	3	4	3	4

The fastness properties results are summarized in Table 5, the dyes gave good levelness and fibre penetration on polyester. The wash fastness rating is good to excellent with rating of 3-5. The good wash fastness obtained on polyester is due to the crystalline structure of the polyester which disallowed the migration of dye out of the fabric when this has entered the fabric. The dye **7c** gave very good light fastness rating of 6 whereas other have poor to moderate light fastness rating as shown in Table 2. Disperse dyes have a tendency to deposit on the fibre surface during dyeing as well as during cooling [20] and therefore in order to obtain a satisfactory combination of light and sublimation fastness, a judicious choice of substituent is required. The fading of azo dyes is mainly a consequence of decomposition of the –N=N– moiety either by oxidation, reduction or photolysis. The rates of these processes should be sensitive to the chemical structure of the dye, the type of substrate and treatment conditions [21]. The dyed substrate employed in this study is polyester fabric, the fading process likely occur by oxidation [22]. The ease of oxidation of azo linkages should be a function of electron density. Therefore, electron donating substituents on this moiety should increase the fading rate while electron withdrawing groups should decrease the rate. This is in agreement with the observed results (Table 5) which demonstrate that the presence of a hydroxyl group in the dye **7a** causes decrease of light fastness to 2. The introduction of polar groups can adversely affect the dyeing properties of a dye but the hydroxyalkyl group appears to be particularly useful in increasing polarity without excessive undesirable side effects. The free hydroxyl group and also short alkyl chain favour formation of compact aggregates of dyes, which confers low surface activity and this causes dye to spread as multilayer on the surface of the fabric; the multilayer is less susceptible to fading. This may account for why the dyes from *N, N*-dimethylaniline and *N, N*-diethylaniline have acceptable results in light fastness.

CONCLUSION

A series of monoazo disperse dyes derived from amphilphilic naphthalimide have been synthesized in good yields. The structures of the intermediate and the dyes were confirmed using elemental analysis (CHN), FTIR, ^{1}H-NMR, ^{13}C NMR, UV-visible, and mass spectroscopic techniques. Spectrophotometric investigations of the synthesized dyes in solvents of different polarities were determined in order to obtain their absorption maxima, molar extinction coefficients and solvatochromic effects. The dyes were applied on polyester fabrics using high temperature dyeing method without addition of dispersing agent and their fastness properties were examined. The wash and perspiration fastness properties were generally very good. Dyes 7a and 7b showed poor light fastness whereas, dyes 7b, 7e and 7c showed a moderate to very good respectively.

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