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SYNTHESIS AND APPLICATION OF MONOAZO DISPERSE DYES BASED ON ASYMMETRIC BISIMIDE ON POLYLACTIC ACID FABRICS

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ABSTRACT

A novel series of monoazo disperse dyes were prepared by diazotization of 6-amino-2-(5-methyl-1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione and coupling with *N, N*-dialkyl anilines and naphthol derivatives. To this end, acenaphthene was nitrated and several reaction steps like oxidation, amination, imidation, reduction, diazotization and coupling were carried out. The synthesized intermediates and dyes were characterized using FTIR, ^{1}HNMR, ^{13}CNMR and mass spectroscopy. The solvatochromic properties of the dyes were examined in solvents of different polarity and their molar extinction coefficient determined in DMF. The synthesized dyes were evaluated for their dyeing behaviour and fastness properties on Polylactic acid fabrics. The results showed that absorption maxima of the synthesized dyes was in the range of 450 nm to 612 nm while their molar extinction coefficient was in the range of 15,600 – 39,200 $Lmol^{-1}cm^{-1}$. Measurement of fastness properties showed that the dyes have very good wash fastness (4-5), very good perspiration fastness (4-5) and between moderate to very good light fastness (3-6). The dyes also demonstrated very good colour strength (6-28) which is an indication of good levelness and affinity for the fabrics.

Keywords: Oxidation, Imidation, Solvatochromic properties, Acenaphthene and Perspiration.

INTRODUCTION

Disperse dyes are organic colorants which are sparingly soluble in water and are applied in colloidal dispersions to hydrophobic textile fibers to produce desired colour. These dyes have found versatile applications besides dyeing of textile fibre to coloring of different substrates, biomedical studies and in advance organic synthesis (Hunger, 2003; Zollinger, 2003). Owing to their colour brilliance and wide range of excellent fastness properties, disperse dyes have become very popular and well known (Bhide *et al.,* 2016). The increase in the use of polyester fibers and their blends has brought a significant increase in the development of disperse dyes. This development has seen the use of several diazo components for the production of disperse dyes in recent time (Modi *et al.,* 1994; Racane *et al.,* 2006; Sigmundová *et al.,* 2008). Derivatives of heterocyclic naphthalimide, phenylazophthalimides and 1, 8-naphthalic anhydrides have been researched extensively to assess their performance as intermediates for dye synthesis (Peters and Bide, 1986; Khosravi *et al.,* 2005; Gharanjig *et al.,* 2007; Parvizi *et al.,* 2009). Over the years, it's being proven that the use of 4-aminonaphthalimides as diazo component has advantageous effects on the dyeing properties of the derived azo disperse dyes. The presence of the naphthalimide system brings about deep and intense colour (Wojciechowski, 1993) and higher bathochromic effects owing to the carbonyl groups on the phthalic anhydride and naphthalimide residue.

The photophysical behaviour of 1, 8-naphthalimide derivatives is dependent on C-4 substitution (Tian *et al.,* 2002; Grabchev *et al.,* 2003; Zhu *et al.,* 2003). Substitution of electron donating groups usually raises the fluorescence emission, particularly when amino and allylamino groups are situated at the C-4 position (Bojinov, 2007; Akgun *et al.,* 2012). Monoazo disperse dyes containing naphthalimide residue have been found to have acceptable dyeing and fastness properties (Szadowski *et al.,* 1985; Peters and Bide, 1986; Wojciechowski, 1988; Wojciechowski and Szadowski, 1991). They displayed excellent thermal stabilities and good dyeing fastness properties (Wojciechowski, 1993; Wojciechowski, 1997). In the present study, a novel series of monoazo disperse dyes derived from asymmetric bisimide and their dyeing properties on Polylactic acid fabric is being reported.

MATERIALS AND METHODS

All the chemicals used for the research where of analytical grade and were not subjected to further purification. The melting point were determined in an open capillary tube using Barsntead electrothermal and were uncorrected. The purity of the dyes and intermediates were determined by thin-layer chromatography (TLC) using silica gel-G-coated Al-plates. The visible absorption spectra were measured using Perkin-Elmer Lamda-25 UV-visible spectrophotometer. The infra-red spectra were recorded using Perkin-Elmer RXI FT-IR spectrometer. The ^{1}H and ^{13}C-NMR were reported on a 300 MHz Bruker avance instrument using deuterated dimethylsulphoxide (DMSO-d_6) as solvent. While the chemical shifts were reported in parts per million (ppm), the mass spectra were recorded using Agilent Technologies 5975C MSD mass spectrometer.

Synthesis of 5-Nitroacenaphthene (2)

Acenaphthene (7.7 g, 0.05 mol) was dissolved in hot acetic acid (28.6 mL) and then cooled under vigorous stirring to separate as fine as possible the crystalline acenaphthene. Concentrated nitric acid (65 %, d = 1.40 g mL^{-1}, 4.92 g) was added in drop-wise manner to the mixture over a period of 1 h at 22–27 °C and it was stirred for 1 h more at 25 °C. The solution was warmed gradually over a period 30 min. to 68 °C and was cooled to form crystals which was filtered, washed with 1:1 acetic acid–water (50% v/v) and water to give yellow needles of 5-nitroacenaphthene after purification by recrystallization (Ameuru *et al.,* 2018).

Synthesis of 6-Nitro[*de*]isochromene-1,3-dione (3)

5-Nitroacenaphthene (12.46 g, 0.0625 mol) was dissolved in hot glacial acetic acid (124.38 mL), sodium dichromate (79.25 g) was added over a period of 3 h at 65–70 °C. The solution was warmed gradually to 98–100 °C for a period of 30 min and then refluxed for 5 h. After the completion of reaction by monitoring progress with TLC, the reaction was quenched and 0.3 L of hot water was added to the mixture and cooled to room temperature and then filtered. The precipitate obtained was washed with dilute HCl (10%) after which the solid was boiled with 200 mL of 5% Na_2CO_3 solution for 30 min. cooled to room temperature and filtered. The obtained filtrate was acidified with dilute HCl (10%) and the separated crystals dried at 120 °C for 4 h to obtain 6-Nitro[*de*]isochromene-1,3-dione. This was purified by recrystallization to afford shiny yellow crystals (Ameuru *et al.,* 2018).

Synthesis 2-amino-6-nitro-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (4)

6-Nitro[*de*]isochromene-1,3-dione (1 mmol) was dissolved in 5 mL of ethyl alcohol and hydrazine hydrate (3 mmol) was added drop-wisely over a period of 10 min. The mixture was heated under reflux for 6 h. After cooling, the precipitate was filtered, washed with ethyl alcohol 10 mL three times and then dried under vacuum to afford pure product (Sidhu *et al.,* 2017).

Synthesis of 2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-6-nitro-1*H*-benzo[*de*] isoquinoline-1, 3(2H)-dione (5)

2-amino-6-nitro-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (1 mmol) and 5-methylisobenzofuran-1,3-dione (1.1 mmol) was heated in 15 mL glacial acetic acid for 6 h. under reflux. After cooling, the solution was poured in ice water and the resulted product was collected by filtration, washed with water and dried. Analytically pure products was obtained by recrystallization from aqueous DMF (Al-Salahi and Marzouk, 2014).

Synthesis of 6-amino-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*] isoquinoline-1, 3(2*H*)-dione (6)

2-(5-methyl-1, 3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-6-nitro-1*H*-benzo[*de*]isoquinoline-1,3(2H)
-dione (6.25 mmol) was dissolved in 2 mL of concentrated hydrochloric acid, and 15 g of tin II chloride in 3 mL of hydrochloric acid was added drop-wisely. After 2 h. of reflux, precipitates were filtered off and washed with water and ethyl alcohol followed by diethyl ether. The obtained orange-coloured product was dried under vacuum to get the desired product (Sidhu *et al.,* 2017).

Synthesis of dyes

Synthesis of 6-(2-Hyroxy-naphthalen-1-ylazo)-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-isoindol-2-yl)-benzo[*de*]isoquinoline-1, 3-dione (1a)

A salt of sodium nitrite (1.5 mmol, 0.104 g) was added slowly under constant stirring to a cold concentrated sulphuric acid (98 %, 1.1 mL) at below 10 °C in such a way that yellow fume was not evolved. The temperature of the reaction mixture was raised gradually to 65 °C until the sodium nitrite dissolved completely. The solution was then cooled to 5 °C by addition of ice and diluted with a mixture of propionic acid and glacial acetic acid (10 mL, 1.5:8.5). Finely ground powder of 6-amino-2-(5-methyl-1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (1.5 mmol) was added portion wise below 10 °C, and then the mixture was stirred for 3 h. The clear diazonium salt solution obtained was used immediately in coupling reactions with 2-naphthol (1.5 mmol) dissolved in ethanol and was added over a period of 30–40 min under vigorous stirring. The mixture was stirred further for 2 h. at 0-5 °C. The pH of the solution was adjusted to 4–5 using 10 % sodium acetate and stirred for 1 h. more. 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 from DMSO several times.

Synthesis of 6-(4-Dimethylamino-phenylazo)-2-(5-methyl-1, 3-dioxo-1,3-dihydro-isoindol-2-yl)-benzo[*de*]isoquinoline-1,3-dione (1b)

The same procedure as in (1a) was followed except that N, N-dimethylaniline was used for coupling. Yield = 89%; Mp: 397 – 399 ºC; FT-IR (KBr, cm^{-1}) 3100, 3051, 2922, 2855, 1792, 1744, 1634, 1529, 1480, 1426, 1357, 1380; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.48 (1H, t, J = 4.1 Hz, -CH_3), 6.90-8.75 (m, 13H, Aromatic); MS(EI): m/z 503 (M^+), 401, 371, 327,195, 169, 141, 118, 90, 63, 40.

Synthesis of 6-(4-Diethylamino-phenylazo)-2-(5-methyl-1, 3-dioxo-1,3-dihydro-isoindol-2-yl)-benzo[*de*]isoquinoline-1,3-dione (1c)

The same procedure as in (1a) was followed except that N, N-diethylaniline was used as a coupling component.

Synthesis of 6-(4-Amino-naphthalen-1-ylazo)-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-isoindol-2-yl)-benzo[*de*]isoquinoline-1,3-dione (1d)

The same procedure as in (1a) was followed except that 1-Naphthylamine was used as a coupling component.

Synthesis of 6-(2-Amino-naphthalen-1-ylazo)-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-isoindol-2-yl)-benzo[*de*]isoquinoline-1,3-dione (1e)

The same procedure as in (1a) was followed except that 2-Naphthylamine was used as a coupling component.

Synthesis of N-{4[2-(5-Methyl-1,3-dioxo-1,3-dihyrdo-isoindo-2-yl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-ylazo]-phenyl}-acetamide (1f)

The same procedure as in (1a) was followed except that acetanilide was used as a coupling component.

Synthesis of 6-(4-Hydroxy-naphthalen-1-ylazo)-2-(5-methyl-1,3-dihydro-isoindol-2-yl)-benzo[*de]*isoquinoline-1,3-dione (1g)

The same procedure as in (1a) was followed except that 1-Naphthol was used as a coupling component.

Dyeing Procedure

The dyeing test was performed using KMS-IRE– ELITE dyeing master. The dye-bath was prepared using material to liquor ratio of 1:50 at 2 % shade on the weight fabric (OWF) and a dispersing agent (Avolan IS). The dye-bath pH was adjusted to 5 using glacial acetic acid and the wetted pattern of polylactic acid fabric was rolled in and the temperature 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 dyed pattern was removed, washed thoroughly with water and dried at room temperature

Reduction clearing
Treatment of the dyed fabrics was carried out by stirring in aqueous solution containing sodium dithionite (2 g/L) and sodium hydroxide (2 g/L) for 50 min at 70 °C. The Polylactic acid fabrics were then washed with water and dried.

Colour measurement
An X-rite Colour-Eye 7000A spectrophotometer was used for colour measurement of the dyed polyester fabrics using a D65 source, 10° collection angle and a small area view aperture (3×8 mm).

Fastness properties of the dyed polyester fabrics
Wash fastness: The wash fastness test of the dyed samples were carried out according to the standard procedure specified by International Standards Organization (ISO 3). The composite samples were treated with a solution containing 5 g/L detergent, 2 g/L sodium carbonate at liquor ratio 50:1 for 30 min. at 60 °C. The change in colour of the tested samples and the degree of staining of the adjacent undyed fabrics were evaluated using grey scale.
Light fastness: The photostability of the dyed Polylactic acid fabrics were evaluated following ISO 105 B02:2014.
Perspiration fastness: Colour fastness to perspiration was determined according to ISO 105 – EO4, 2013 by treating the dyed fabrics (10 cm× 4 cm) in an alkaline solution of freshly prepared 0.5 g/L histidine monohydrochloride monohydrate, 5 g/L, sodium chloride, 2.5 g/L disodium hydrogen orthophosphate and 0.1 M sodium hydroxide at a volume ratio of 50:1. The acid perspiration test solution contained 0.5 g/L histidine monohydrochloride monohydrate, 5 gL sodium chloride, 2.2 g/L disodium hydrogen orthophosphate and 0.1 M acetic acid solution. The tested fabrics were rinsed, dried and then rated against the grey scales for colour changes.

RESULTS AND DISCUSSION

Table 1: The Melting Point, Percentage Yield and IR Spectra of Synthesized Intermediates

Compounds	Melting Point (°C)	Yield (%)	FT-IR (cm^{-1})
5-nitroacenaphthene	101 – 102	92.1	3085 (C-H str. Ar.), 2947, 2938, 2809 (C-H str. Aliphatic), 1508 (NO_2 str.), 1620 (C=C str.)
6-nitro[*de*]isochromene-1,3-dione	232 – 233	75.4	3094, 3079, 3045 (C-H str. Aro.), 2922, 2868 (C-H str. Aliphatic), 1787, 1756 (C=O str.), 1526 (NO_2 str.), 1626 (C=C str.)
2-amino-6-nitro-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione	216 – 218	59.3	3335 (NH str.), 1620, 1650 (C=C), 3076, 3064 (C-H str. Ar.), 2955, 2919, 2850 (C-H str. Aliphatic), 1763, 1693 (C=O str.), 1523 (NO_2 str.)
2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-6-nitro-1*H*-benzo[*de*] isoquinoline-1,3(2H)-dione	312 – 313	60.4	3113, 3079 (C-H str. Ar.), 2925, 2859 (C-H str. Aliphatic), 1616 (C=C str.), 1532 (NO_2 str.)
6-amino-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione	>400	58.93	3501, 3356 (NH str.), 3110 (C-H str. Aromatic), 2916, 2708 (C-H str. Aliphatic), 1741, 1699 (C=O str.), 1673, 1633 (C=C str.), 1356 (C-N str.)

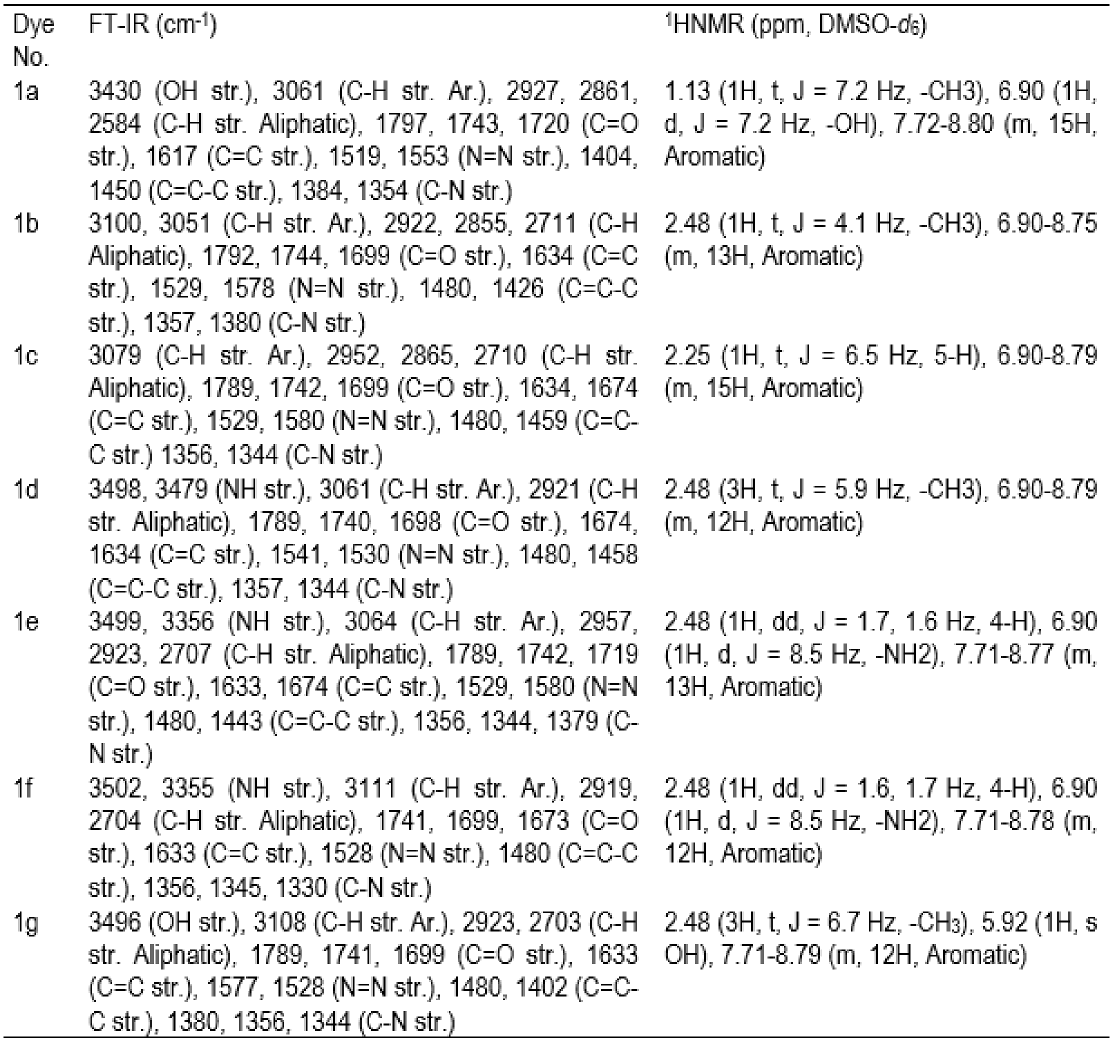
Table 2: ^{1}HNMR and ^{13}CNMR of Synthesized Intermediate

Compound	^{1}HNMR and ^{13}CNMR (ppm, DMSO-d_6)
5-nitroacenaphthene	3.32 (4H, s, CH2-CH2), 7.46 (2H, dd, J = 7.2, 7.3 Hz, 4-H), 7.71 (2H, m, J = 7.60 Hz, 8-H), 8.34 (1H, d, J =8.5 Hz, 2-H), 8.48 (1H, d, J = 7.7 Hz, 2-H); 10.58, 30.33, 118.70, 119.17, 121.59, 122.79, 123.56, 128.16, 132.22, 139.58, 147.32, 156.62.
6-nitro[*de*]isochromene-1,3-dione	8.07 (1H. t, J = 7.7 Hz, 3-H), 8.52 (1H, d, J = 7.9 Hz, 2-H), 8.61 (2H, t, J = 7.8 Hz, 3-H), 8.7 (1H, d, J = 8.7 Hz, 2-H); 120.12, 122.89, 124.53, 129.93, 130.42, 130.67, 131.22, 133.36, 149.65, 159.60, 160.22.
2-amino-6-nitro-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione	5.84 (2H, s, -NH2), 8.04 (1H, t, J = 7.5 Hz, 3-H), 8.51 (1H, d, J = 7.9 Hz, 2-H), 8.58 (2H, dd, J = 5.6, 6.3 Hz, 4-H), 8.66 (1H, d, J = 8.7 Hz, 2-H); 122.55, 122.83, 124.47, 126.43, 127.16, 129.07, 129.80, 130.27, 131.91, 149.36, 159.40, 160.38.
2-(5-methyl-1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-6-nitro-1*H*-benzo[*de*] isoquinoline-1,3(2H)-dione	2.48 (3H, t, J = 1.5 Hz, $-CH_3$), 7.85 (1H, d, J = 7.7 Hz, 2H), 7.98 (1H, s), 8.01 (1H, d, J = 7.7 Hz, 4-H), 8.15 (1H, t, J = 8.4 Hz, 3-H), 8.60 (1H, d, J = 8.0, 2-H), 8.75 (2H, dd, J = 3.6, 2.6 Hz, 4-H), 8.82 (1H, d, J = 8.6 Hz, 2-H); 21.56, 121.04, 123.25, 124.40, 125.09, 126.27, 128.60, 129.24, 130.42, 131.87, 133.70, 136.53, 147.62, 150.53, 159.63, 160.25, 163.51.
Synthesis of 6-amino-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*] isoquinoline-1,3(2*H*)-dione	2.48 (3H, t, -CH3), 6.90 (1H, d, J = 8.5 Hz, -NH2), 7.71 (1H, t, J = 7.8 Hz, 3-H), 7.81 (1H, t, J = 7.6 Hz, 3-H), 7.93 (1H, s, 3-H), 8.01 (1H, d, J = 7.6, 2-H), 8.17 (1H, d, J = 7.4 Hz, 4-H), 8.51 (1H, d, J = 6.8 Hz, 4-H), 8.76 (1H, t, J = 8.3 Hz, 3-H); 21.53, 105.05, 108.90, 119.64, 120.27, 124.39, 125.03, 126.52, 129.49, 130.25, 131.83, 131.67, 135.48, 136.21, 147.21, 153.19, 154.48, 159.73, 161.32, 163.96, 164.12.

Table 3: Mass Spectrometry of Synthesized Intermediates and the Dyes

Dye No:	Empirical formula	Experimental values of m/z fragments	Corresponding positive charge fragment	Theoretical value
(6)	$C_{20}H_{10}ClN_3O_4$	43.2, 63.1, 90.1, 118.1, 141.1, 169.1, 195.1, 327.2, 371.2	$CHNO^+$, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{20}H_{27}N_2O_2^+$, M.	371.35
1a	$C_{31}H_{18}N_4O_5$	40.1, 63.1, 90.1, 118.1, 141.1, 169.1, 195.1, 371.1, 401.1, 526.3	$C_3H_4^+$, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{23}H_{35}N_2O_2^+$, $C_{25}H_{41}N_2O_2^+$, M.	526.50
1b	$C_{29}H_{21}N_5O_4$	40.1, 63.1, 90.1, 118.1, 141.1, 169.1, 195.1, 327.2, 371.2, 401.0, 503.2	$C_3H_4^+$, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{20}H_{27}N_2O_2^+$, $C_{23}H_{35}N_2O_2^+$, $C_{25}H_{41}N_2O_2^+$, M.	503.51
1c	$C_{31}H_{25}N_5O_4$	40.1, 63.1, 90.1, 118.1, 141.1, 169.1, 195.1, 327.2, 371.2, 529.2	C_3H_4+, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{20}H_{27}N_2O_2^+$, $C_{23}H_{35}N_2O_2^+$, $C_{36}H_{69}N_2^+$, M.	531.56
1d	$C_{31}H_{19}N_5O_4$	40.1, 63.0, 90.1, 118.1, 141.1, 169.1, 195.1, 327.2, 371.2, 525.3	$C_3H_4^+$, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{20}H_{27}N_2O_2^+$, $C_{23}H_{35}N_2O_2^+$, M.	525.51
1e	$C_{31}H_{19}N_5O_4$	43.1, 63.1, 90.1, 118.1, 154.1, 199.0, 312.2, 357,2, 401.0, 523.6, 525.6	$CHNO^+$, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_{10}H_{20}N^+$, $C_{10}H_{19}N_2O_2^+$, $C_{20}H_{26}NO_2^+$, $C_{22}H_{33}N_2O_2^+$, $C_{25}H_{41}N_2O_2^+$, $C_{36}H_{63}N_2^+$, M.	525.51
1f	$C_{29}H_{19}N_5O_5$	40.1, 75.1, 110.0, 141.1, 169.1, 195.1, 347.1, 391.1, 517.1	$C_3H_4^+$, $C_3H_9NO^+$, $C_5H_4NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{22}H_{23}N_2O_2^+$, $C_{24}H_{43}N_2O_2^+$, M.	517.1
1g	$C_{31}H_{18}N_4O_5$	40.1, 63.1, 90.1, 118.1, 141.1, 169.1, 195.1, 371.1, 401.1, 526.3	$C_3H_4^+$, $C_2H_7O_2^+$, $C_3H_8NO_2^+$, $C_5H_{12}NO_2^+$, $C_6H_9N_2O_2^+$, $C_8H_{13}N_2O_2^+$, $C_{10}H_{15}N_2O_2^+$, $C_{23}H_{35}N_2O_2^+$, $C_{25}H_{41}N_2O_2^+$, M.	526.50

Table 4: FT-IR and ^{1}HNMR of Synthesized Dyes

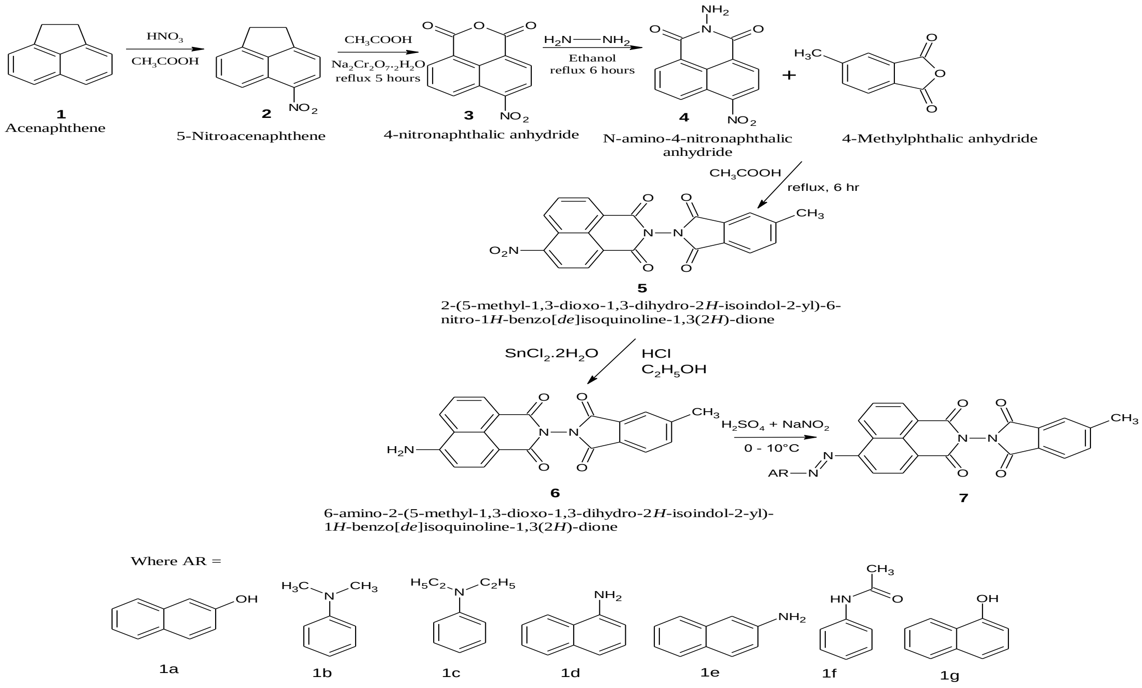


Dye No.	FT-IR (cm^{-1})	^{1}HNMR (ppm, DMSO-d_6)
1a	3430 (OH str.), 3061 (C-H str. Ar.), 2927, 2861, 2584 (C-H str. Aliphatic), 1797, 1743, 1720 (C=O str.), 1617 (C=C str.), 1519, 1553 (N=N str.), 1404, 1450 (C=C-C str.), 1384, 1354 (C-N str.)	1.13 (1H, t, J = 7.2 Hz, -CH3), 6.90 (1H, d, J = 7.2 Hz, -OH), 7.72-8.80 (m, 15H, Aromatic)
1b	3100, 3051 (C-H str. Ar.), 2922, 2855, 2711 (C-H Aliphatic), 1792, 1744, 1699 (C=O str.), 1634 (C=C str.), 1529, 1578 (N=N str.), 1480, 1426 (C=C-C str.), 1357, 1380 (C-N str.)	2.48 (1H, t, J = 4.1 Hz, -CH3), 6.90-8.75 (m, 13H, Aromatic)
1c	3079 (C-H str. Ar.), 2952, 2865, 2710 (C-H str. Aliphatic), 1789, 1742, 1699 (C=O str.), 1634, 1674 (C=C str.), 1529, 1580 (N=N str.), 1480, 1459 (C=C-C str.) 1356, 1344 (C-N str.)	2.25 (1H, t, J = 6.5 Hz, 5-H), 6.90-8.79 (m, 15H, Aromatic)
1d	3498, 3479 (NH str.), 3061 (C-H str. Ar.), 2921 (C-H str. Aliphatic), 1789, 1740, 1698 (C=O str.), 1674, 1634 (C=C str.), 1541, 1530 (N=N str.), 1480, 1458 (C=C-C str.), 1357, 1344 (C-N str.)	2.48 (3H, t, J = 5.9 Hz, -CH3), 6.90-8.79 (m, 12H, Aromatic)
1e	3499, 3356 (NH str.), 3064 (C-H str. Ar.), 2957, 2923, 2707 (C-H str. Aliphatic), 1789, 1742, 1719 (C=O str.), 1633, 1674 (C=C str.), 1529, 1580 (N=N str.), 1480, 1443 (C=C-C str.), 1356, 1344, 1379 (C-N str.)	2.48 (1H, dd, J = 1.7, 1.6 Hz, 4-H), 6.90 (1H, d, J = 8.5 Hz, -NH2), 7.71-8.77 (m, 13H, Aromatic)
1f	3502, 3355 (NH str.), 3111 (C-H str. Ar.), 2919, 2704 (C-H str. Aliphatic), 1741, 1699, 1673 (C=O str.), 1633 (C=C str.), 1528 (N=N str.), 1480 (C=C-C str.), 1356, 1345, 1330 (C-N str.)	2.48 (1H, dd, J = 1.6, 1.7 Hz, 4-H), 6.90 (1H, d, J = 8.5 Hz, -NH2), 7.71-8.78 (m, 12H, Aromatic)
1g	3496 (OH str.), 3108 (C-H str. Ar.), 2923, 2703 (C-H str. Aliphatic), 1789, 1741, 1699 (C=O str.), 1633 (C=C str.), 1577, 1528 (N=N str.), 1480, 1402 (C=C-C str.), 1380, 1356, 1344 (C-N str.)	2.48 (3H, t, J = 6.7 Hz, -CH$_3$), 5.92 (1H, s OH), 7.71-8.79 (m, 12H, Aromatic)

Synthesis of intermediates and dyes

Acenaphthene **(1)** was reacted with concentrated nitric acid in an acetic acid media at room temperature to give yellow crystals of 5-nitroacenaphthene after recrystallization from ethyl alcohol with a yield of 92%. 5-Nitroacenaphthene **(2)** was oxidized using sodium dichromate and hot acetic acid under a reflux condition of 5 h to give 6-Nitro[*de*]isochromene-1,3-dione **(3)** in 75% yield after recrystallization from concentrated nitric acid. 6-Nitro[*de*]isochromene-1,3-dione was reacted with hydrazine hydrate in ethyl alcohol as solvent and then refluxed for 6 h. to give 2-amino-6-nitro-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione **(4)**. The yield obtained was 59% after purification by washing three times using ethyl alcohol. The compound **4** was subjected to imidation by reacting with 5-methylisobenzofuran-1, 3-dione under acetic media and refluxed for 6 h. The precipitate obtained was purified by recrystallization from aqueous DMF to give 2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-6-nitro-1*H*-benzo[*de*]isoquinoline-1, 3(2H)-dione **(5)** with a yield of 60%. 6-amino-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*]isoquinoline-1, 3(2*H*)-dione **(6)** was synthesized by reduction of 2-(5-methyl-1, 3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-6-nitro-1*H*-benzo[*de*]isoquinoline-1,3(2H)-dione using tin (II) chloride in the presence of ethyl alcohol and concentrated hydrochloric acid. The precipitate obtained was purified by recrystallization from aqueous DMF to obtain orange crystals in 58% yield. The reaction sequence is shown in scheme 1. The structure of the intermediates and dyes were characterized using FTIR, ^{1}H NMR, ^{13}C NMR and mass spectroscopic techniques as shown in Table 1, 2, 3 and 4. The infra-red (KBr, cm^{-1}) spectral of the intermediate; 6-amino-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*]isoquinoline-1, 3(2*H*)-dione **(6)** showed absorption peaks at 3501 and 3356 which correspond to N-H stretch. The peak found at 3110 is due to aromatic C-H stretch while that found at 2916 and 2708 correspond to C-H stretch aliphatic. The carbonyl (C=O) stretch shows absorption at 1741 and 1699 while carbon carbon double bond (C=C) stretch shows absorption at 1673 and 1633. The ^{1}H-NMR spectrum shows peak at 2.48-2.55 ppm which correspond to the three (3) protons on the methyl group (CH$_3$) at the aliphatic region of the spectrum. The peak at 6.90 ppm is due to the amino group (NH$_2$) on the compound while the peaks at 7.21-8.78 ppm shows the (8H) at the aromatic region on the spectrum. The ^{13}C-NMR spectrum shows peak at 21.53 ppm which correspond to the carbon of the methyl group (CH_3) at the aliphatic region. The peaks at 105.05-164.12 ppm correspond to the aromatic carbons on the spectrum. The MS analysis shows a molecular ion [M^+] at m/z 371.2 which is in agreement with formula mass 371.35 g/mol as seen on Table 3.

The diazotization of 6-amino-2-(5-methyl-1, 3-dioxo-1, 3-dihydro-2*H*-isoindol-2-yl)-1*H*-benzo[*de*]isoquinoline-1, 3(2*H*)-dione was carried out using nitrosylsulphuric acid being a weakly basic amine and was coupled with various naphthols and electron-rich arenes to produce the dyes as shown in Scheme 1. The structures of the dyes were characterized using FT-IR, ^{1}H NMR and MS spectroscopic techniques. The results of the characterization are shown in Table 3 and 4. Figures 1–4 showed the FT-IR and Mass spectra of some selected dyes.



Scheme 1: Synthesis of intermediates and dyes

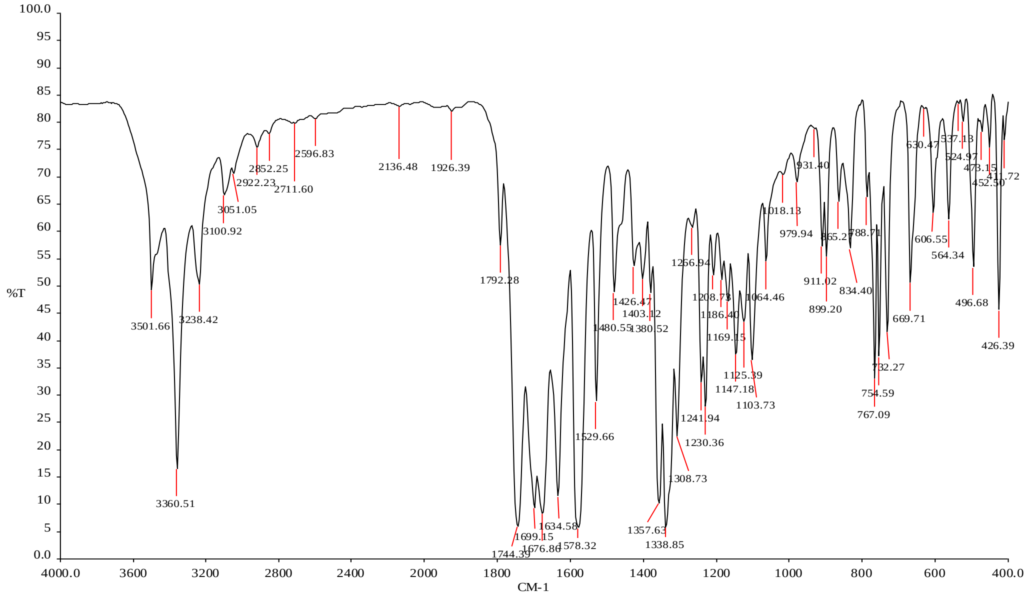


Figure 1: FT-IR spectra of dye 1b

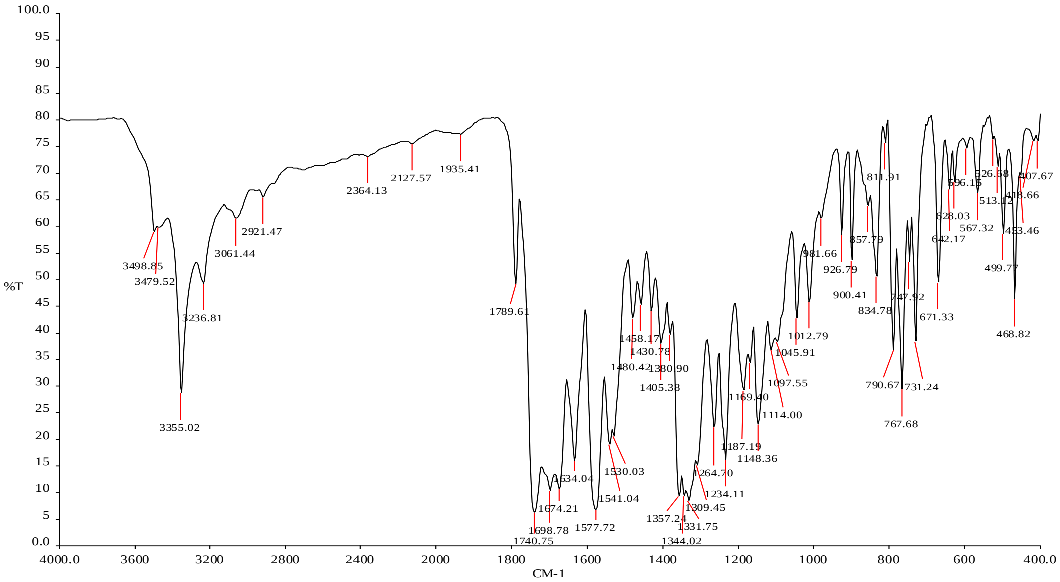


Figure 2: FT-IR spectral of dye 1d

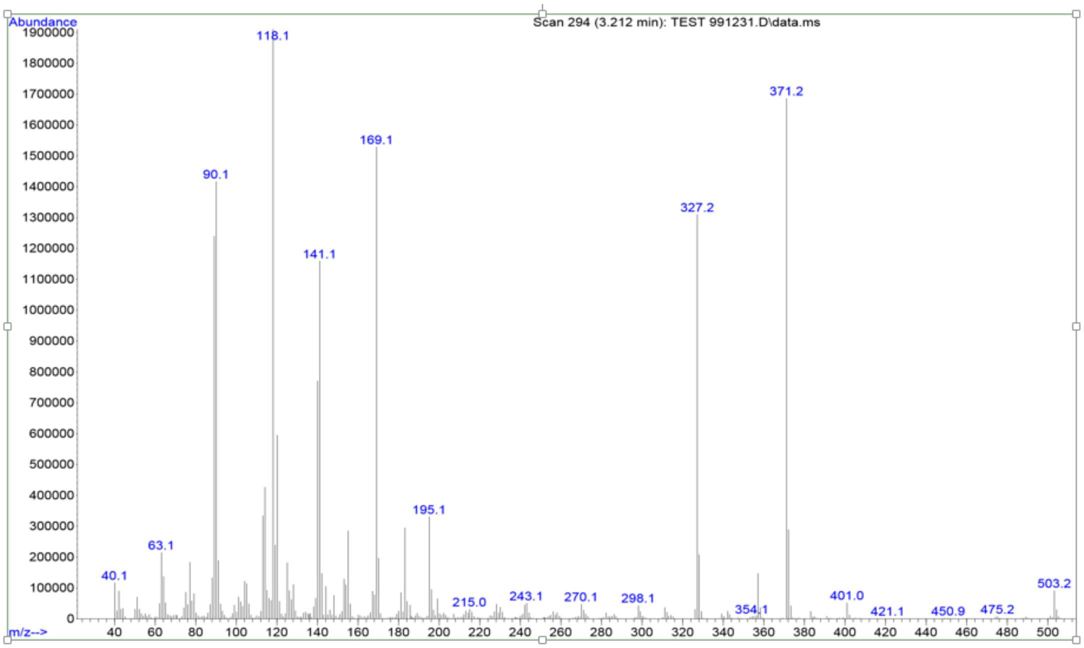


Figure 3: Mass spectral of dye 1b

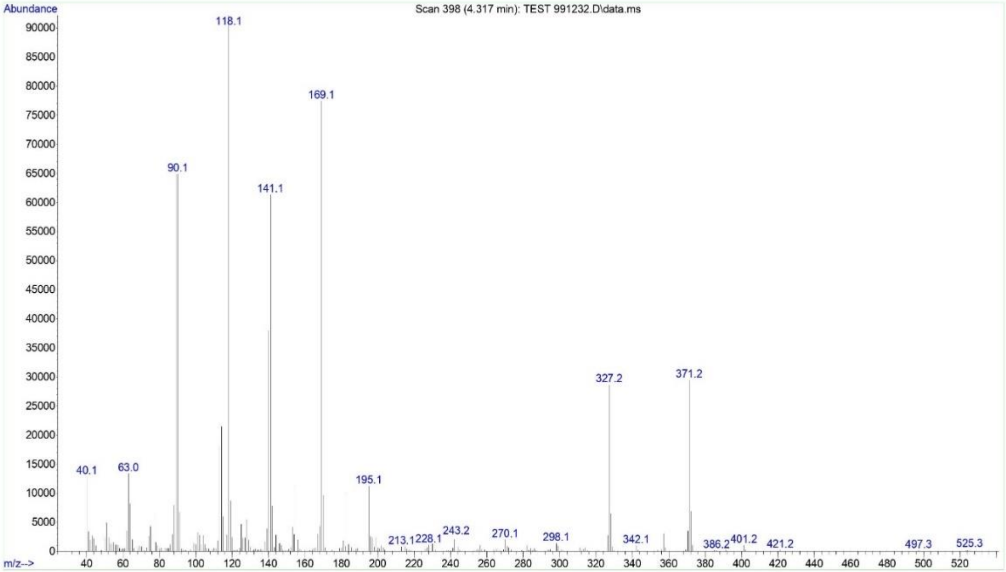


Figure 4: Mass spectral of dye 1d

Spectral characteristics of the synthesized dyes
The absorption spectra of the synthesized dyes were measured in solvents of different polarity in order to study their solvatochromic behaviour. The wavelength of maximum absorption and molar extinction coefficient of the dyes as shown in Table 4 ranged from 450 – 612 nm and 15,600 – 39,200 Lmol^{-1}cm^{-1} respectively in DMF. The shift in the wavelength of maximum absorption is brought about by the solvatochromic effect resulting from change in the dielectric constant of the solvents. It was observed from the results obtained that as the solvent changes from dipolar aprotic solvent to polar solvent and non-polar solvent, the absorption maxima changes significantly and this can be attributed to changes in the solvent polarity.

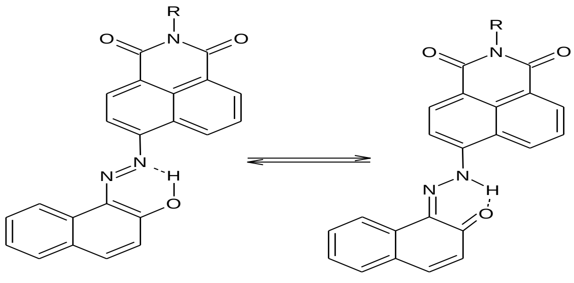
Table 5: UV-visible absorption spectroscopy of the dyes

Dye No:	ε_{max} in DMF X 10^4 (Lmol^{-1}cm^{-1})	DMF λ_{max} (nm)	Toluene λ_{max} (nm)	Ethanol λ_{max} (nm) a	Ethanol + HCl λ_{max} (nm) b	Change in λ_{max} (nm) (b-a)
1a	3.47	540	466	472	475	+3
1b	2.52	561	521	553	551	-2
1c	3.56	598	506	569	581	+12
1d	2.75	565	511	542	552	+10
1e	3.48	580	517	547	561	+19
1f	3.94	612	461	572	587	+15
1g	2.63	532	482	526	529	+3

Dye **1a** shows absorption at 540 nm and when compared with dye **1g** which absorbed at 532 nm, it will be said that dye **1a** is bathochromic by 8 nm and this can be attributed to the presence of hydroxyl (-OH) group ortho to the azo linkage in dye **1a**, thus, making it possible to form hydrogen bond which enhances the absorption band unlike dye **1g** whose hydroxyl group (-OH) is para to the azo linkage and cannot form hydrogen bond with the azo linkage. Dye **1b** gave absorption at 561 nm which shows bathochromism when compared with dye **1a** and **1g**. However, comparing dye **1b** with dye **1c**, shows that **1c** is bathochromic by 37 nm and this can be attributed to the presence of additional electron donor group on the coupling component. This is in agreement with the findings of other researchers (Khosravi *et al.,* 2006; Ameuru *et al.,* 2018). Similarly, dye **1d** absorbed at 565 nm as a result of the electron donor group (-NH_2) on the coupling component but when the position of the amino group was change from para to ortho position in 2-naphthylamine, a bathochromic shift of 15 nm was observed with dye **1e** as it shows absorption at 580 nm when compared with dye **1d**. Dye **1f** shows absorption at 612 nm and when compared with dye 1h which absorbed at 465 nm, it will be said that dye **1f** gave a strong bathochromic effect of 147 nm and this can be attributed to the presence of acetamido group which is a strong electron donor substituent.

Dyeing and fastness properties of the synthesized dyes

Using high temperature high pressure techniques, the synthesized dyes were applied on Polyester and their dyeing properties evaluated. Visual examination revealed that the nature of substituent on the coupling component affect both the intensity and the shade obtained. Dyeings with highest intensity were seen with dyes containing the methyl and the ethyl groups. This is because, these substituents increase the electron density on the tertiary nitrogen atom and stabilize the polar forms, especially when there are no substituents on the phenyl ring causing steric effects (Wojciechowski, 1990). The introduction of electron donor substituent on the coupler ring also brings about considerable effects on the colour of the dyeing, especially those containing a substituent at the ortho position to the azo linkage, such as dye **1a** and **1e**. This phenomenon is best described in terms of structures I and II.



I
Azo form

II
Hydrazone form

The colour fastness of the synthesized dyes on polyester were examined and the results presented on Table 6. The synthesized bisimide based dyes showed good levels of colour fastness to washing and perspiration as shown on Table 6. The rating of the colour fastness were between 3 and 4 for both washing and perspiration. The high degree of levelness and brightness obtained after washing is an indication of excellent dye penetration and affinity of the dyes for the fabrics. This can be attributed to the crystalline nature of polyester which make it difficult for the dyes to migrate once dyed. The absence of solubilizing groups is another factor as they aid the solubility and wash-ability of the dyes out of the fabrics.

The dyed fabrics showed fair to very good light fastness ratings. It can be seen from Table 6 that dye **1a** and **1g** show a poor light fastness rating of 2 and this can be attributed to presence of hydroxyl groups on the dye structure as they are known to have a negative effect on light fastness. This is in agreement with the findings of previous researchers (Ameuru *et at.,* 2018; Nasar, 2015). Dye **1b**, **1c, 1d**, and **1e** gave a moderate fastness rating ranging between 3 and 4 while dye 1f gave a good light fastness rating of 5 and this can be as a result of the strong acetamido group on the coupler ring of the dye structure. Because disperse dye is characterized with tendency to deposit on fibre surface during dyeing, it becomes imperative to make a judicious choice of substituents so as to have a satisfactory combination of light and sublimation fastness.

A lot of researchers have suggested that fading of azo dyes is mainly a consequence of decomposition of the –N=N– moiety, either by oxidation, reduction or photolysis (Al-Etaibi *et al.,* 2012). The rates of these processes should be sensitive to the chemical structure of the dye, the type of substrate and treatment conditions (Ameuru *et al.,* 2020). The dyed substrate employed in this study is Polylactic acid fabrics and the fading process is likely to occur by oxidation. The ease of oxidation of azo linkages should be a function of electron density.

Table 6: Fastness properties of the synthesized dyes on Poly(lactic acid) fabrics

Dye No:	Light Fastness	Wash Fastness	Perspiration Fastness	
			Acid	Alkaline
1a	2	3	4	3
1b	4	4	3	3
1c	4	4	4	4
1d	3	3	4	4
1e	4	4	4	3
1f	5	3	4	4
1g	2	3	3	4

Colour measurement of the synthesized dyes

The colour characteristics of the dyed polyester fabrics were measured using reflectance spectrophotometer (X-rite colour eye 7000A) under illuminant D65, with a 10° standard observer. The dyed Polylactic acid fabrics were assessed in terms of tristimulus colorimetry were the following CIELAB coordinates were measured; lightness (L^*), chroma (C^*), hue angle from 0º to 360º (h), a^* value represents the degree of redness (positive) and greenness (negative), and b^* represents the degree of yellowness (positive) and blueness (negative). The K/S values which corresponds to the dye uptake and given by the reflectance spectrophotometer was calculated at λ_{max} using the Kubelka-Munk equation as shown below.

K/S = $(1-R)2/2R$

Where K = absorption coefficient, S = scattering coefficient and R is the reflectance value.

The hue of the synthesized dyes on Polylactic acid fabrics shifted to the reddish direction on the red-green axis and yellowish direction on the yellow-blue axis according to the positive values of a^* and b^* respectively with the exception of dye 1b that shifted to the bluish direction on the yellow-blue axis according to the negative values of b^* for this dye. The high values of the colour lightness values (L^*) obtained for the dyes shows the excellent brightness of the dyes under investigation on Polylactic acid fabrics.

Table 7: Colorimetric and spectrophotometric data of the synthesized dyes on Poly (lactic acid) fabrics

Dye No:	L^*	a^*	b^*	C^*	hº	K/S
1a	52.02	29.24	24.91	38.41	40.43	7.41
1b	42.81	11.88	5.41	13.05	24.48	14.62
1c	51.23	13.2	7.43	15.15	29.39	17.59
1d	62.05	24.3	43.51	49.10	60.82	12.34
1e	43.15	6.59	15.14	16.51	66.50	5.23
1f	74.06	1.26	40.04	40.05	88.20	24.22
1g	54.20	16.35	17.93	24.27	47.65	9.01

The colour strength (K/S)$_{\lambda mass}$ of the dyes as seen on Table 7 showed that bisimide dyes have excellent build-up with high affinity for Polylactic acid fabrics.

Conclusion

A new series of monoazo disperse dyes based on asymmetric bisimide have been synthesized in good yields. The intermediates and the dyes were characterized using FT-IR, ^{1}HNMR, ^{13}CNMR and mass spectroscopic techniques. The absorption maxima and molar extinction coefficient were determined in solvent of different polarity. The dyes were applied on Polylactic acid fabric by exhaust dyeing techniques and their dyeing properties investigated. The wash and perspiration fastness vary from moderate to very good (3-4) while the light fastness vary from poor to very good (1-5). The exhaustion and leveling of the dyes on Polylactic acid fabrics were generally good and the K/S which is representative of the colour strength was calculated and the value obtained showed that the dyes had a very good build-up and high affinity for Polylactic acid fabrics.

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