Synthesis and Characterization of Novel Monoazo N-ester-1,8-naphthalimide Disperse Dyestuffs

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Five novel monoazo disperse dyestuffs based on N-ester-1,8-naphthalimide were synthesized. Acenaphthene was nitrated, then oxidized to 4-nitro-1,8-naphthalic anhydride. 4-Nitro-1,8-naphthalic anhydride was reacted with methyl and ethyl glycinate in alcoholic media, followed with reduction. 4-Amino-N-methyl and ethyl glycinate-1,8-naphthalimide were obtained. These products were diazotized and coupled with appropriate aromatic amines to give bluish-red or violet dyestuffs.

All intermediates and dyestuffs were purified and characterized by ^{1}H-NMR, FTIR, DSC, UV-VIS and Elemental Analysis. Dispersion of dyestuffs was prepared in water and applied to polyester fabrics. The dyed fabrics showed that four of the synthesized dyestuffs were suitable for coloring polyester fibers, producing deep bluish red with very good build up properties.

Keywords: Disperse dyestuffs; 4-Amino-N-alkylglycinate-1,8-naphthalimide; Azo dyestuffs; Dyeing; Diazotization; Coupling.

INTRODUCTION

Consumption of disperse azo dyestuffs is more than 50% of the total amount of the production of disperse dyestuffs in the world.[1] Relatively simple synthesis method for these dyestuffs enables the production of a wide range of colours of high tensity and brightness from greenish yellow to cyan with this chromophore system.[2]

4-Amino-N-substituted-1,8-naphthalimides are useful intermediates for the synthesis of monoazo disperse dyestuffs. These dyestuffs have been considered for dyeing of polyester fibers.[3-5]

Diazotization of 4-amino-N-alkyl-1,8-naphthalimides and coupling to aryl amines or naphthols gives red to bluish red disperse dyestuffs while, similar coupling to p-aminoacetophenone produces yellow disperse dyestuffs.[4,6]

The synthesized dyestuffs have very good affinity towards polyester fibers with good color fastness properties and also they possess excellent sublimation fastness.[3,5]

In the present study, a series of novel monoazo disperse dyestuffs have been synthesized using 4-amino-N-methylglycinate-naphthalimide and 4-amino-N-ethyl glycinate-1,8-naphthalimide as diazo components and N,N-diethylaniline and N,N-diethyl-m-toluidine, as the coupling components. In this respect, acenaphthene was nitrated and further treated using different unit processes such as oxidation, imidation, reduction, diazotisation and finally coupled with selected amines (Fig. 1). The intermediates and dyestuffs were purified and characterized by analytical methods (^{1}H-NMR, FTIR, DSC, UV-VIS and Elemental Analysis). The spectrophotometric properties of the synthesized dyestuffs in various solvents were examined. These dyestuffs were applied to polyester fibers and dyeing properties were investigated.

EXPERIMENTAL

Materials and Apparatus

Acenaphthene, N,N-diethylaniline, N,N-diethyl-m-toluidine, methyl glycinate, ethyl glycinate and 3-(N,N-diethylamino)acetanilide were purchased from Aldrich Co.

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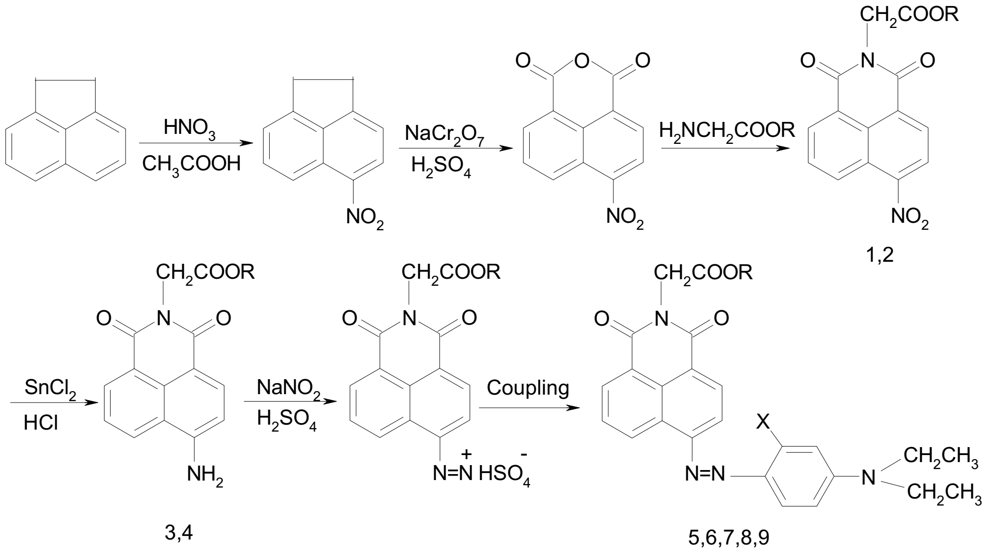

1,3) R=CH_3 2,4) R=C_2H_5 5) R=CH_3 X=H 6) R=CH_3 X=CH_3 7) R=C_2H_5 X=H 8) R=C_2H_5 X=CH_3 9) R=C_2H_5 X=$NHCOCH_3$

Fig. 1. Synthesis of dyestuffs from acenaphthene.

and used without further purification. Melting points were determined by DSC using a Differential Scanning Calorimeter 2010 TA Instrument. The ^{1}H-NMR spectra were obtained with a Bruker AVANCE-300 MHZ using the appropriate deuterated solvent. FTIR absorption spectra were recorded on a Nicolet 470/670/870. UV-VIS absorption spectra were measured in a Cecil 9200 double beam spectrophotometer. The colorimetric properties of the dyeings (D65 illumination, 10° observer) were obtained using a Gretag-Macbeth 7000A spectrophotometer.

Synthesis of Intermediates

Synthesis of 5-nitroacenaphthene and 4-nitronaphthalic anhydride

5-Nitroacenaphthene and 4-nitronaphthalic anhydride were synthesized following the method of Okazaki and Taniguchi.[7]

Synthesis of 4-nitro-N-ethylglycinate-1,8-naphthalimide

3.96 g (0.02 mol) of 4-nitro-1,8-naphthalic anhydride was dissolved in 100 mL absolute ethanol with stirring and heating. 3.09 g (0.03 mol) ethyl glycinate was added and the mixture was refluxed until TLC showed no 4-nitro-1,8-naphthalic anhydride remained. This reaction was completed in 10 hours. The mixture was then poured into water. The precipitated solid was filtered off and recrystallised.

Synthesis of 4-nitro-N-methylglycinate-1,8-naphthalimide

5.94 g (0.03 mol) of 4-nitro-1,8-naphthalic anhydride was dissolved in 200 mL absolute ethanol with stirring and heating. 3.56 g (0.04 mol) methyl glycinate was added and the mixture was refluxed until TLC showed no 4-nitro-1,8-naphthalic anhydride left; this reaction was completed in 16 hours. The mixture was solidified in water, filtered off and recrystallized.

Synthesis of 4-amino-N-ethylglycinate-1,8-naphthalimide

A mixture of 6 g (18 mmol) 4-nitro-N-ethylglycinate-1,8-naphthalimide and 20.31 g (90 mmol) stannous chloride in 90 mL ethanol was refluxed for 1 hour with 22.5 mL hydrochloric acid till the reaction completed. The mixture was poured into 300 mL water and the precipitated solid was filtered off. The crude product was purified by column chromatography (eluent: acetone/toluene = 2/1).

Synthesis of 4-amino-N-methylglycinate-1,8-naphthalimide

A solution of 6 g (19 mmol) 4-nitro-N-methylglycinate-1,8-naphthalimide and 21 g (93 mmol) stannous chloride in 150 mL ethanol was refluxed 60 minutes with 30 mL hydrochloric acid and then the mixture was solidified in 300 mL water and filtered off. The crude product was purified by column chromatography (eluent : acetone/toluene = 2/1).

Synthesis of Dyestuffs

Diazotisation of 4-amino-N-ethylglycinate-1,8-naphthalimide

0.37 g (5.3 mmol) of sodium nitrite was added slowly to 2.32 mL of concentrated sulphuric acid (98%) at below 10 °C. The temperature of the reaction rose to 65 °C, where no color change occurred. The solution was then cooled to 5 °C and 1.58 g (5.3 mmol) of the powder of 4-amino-N-ethylglycinate-1,8-naphthalimide was added slowly to the solution over 40 min. The reaction mixture was stirred for 3 hours.

Diazotization of 4-amino-N-methylglycinate-1,8-naphthalimide

0.37 g (5.3 mmol) of sodium nitrite was added slowly to 2.2 mL of concentrated sulphuric acid at a temperature less than 10 °C where no color change occurred. 1.505 g (5.3 mmol) of the powder of 4-amino-N-methylglycinate-1,8-naphthalimide was added slowly to the obtained solution over 40 min. The reaction mixture was stirred for 3 hours.

Coupling

The N,N-diethylaniline, N,N-diethyl-m-toluidine and 3-(N,N-diethylamino)acetanilide used as coupling components were:

Separately, 5.3 mmol of each coupling components was dissolved in 1 mL acetic acid. Then the clear diazonium salt solution was added to these solutions. The reaction mixture was stirred for 1 hour at below 10 °C. Then the pH of the solution was maintained between 4 and 5 by adding dropwise sodium acetate solution. Stirring was continued for 3 hours at less than 10 °C. The dyestuffs were filtered off, washed with hot water and dried. The crude products were purified with preparative TLC on silica gel (solvent: chloroform).

Preparation of dye dispersions

0.5 g of the crude dye, 1 g of the dispersing agent (Lyoprint EV, Ciba Co.) and 2 mL water were added to a mortar and milled for 60 min. Then, 20 mL water was added to this mixture. The mixture was transferred to a ball mill and treated for 20 hours. The mixture was diluted with an addition of water to 100 mL and then filtered by Micro-Prazisions Sieb Fritsch (5 μm).

Dyeing

Polyester fabric (1 g) was pretreated with a nonionic detergent (5 g/l) at 80 °C for 20 min. prior to being used for the dyeing. Dyeing was carried out in a Rotadyer apparatus (Nasaj Sanat Yazd, Ltd) using a liquor ratio of 50:1, pH = 4-5 (Acetic acid). The amounts of the dyestuff dispersion were 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2 and 4% (owf). Dyeing was performed by raising the dye bath temperature from 30 °C to 90 °C at 2 °C/min, followed by 90 °C to 130 °C at 1 °C/min, holding at this temperature for 60 min and cooling to 70 °C at 3 °C/min. The dyed fabrics were reduction cleared with 2 g/l sodium hydrosulphite, 1 g/l sodium hydroxide, 1 g/l detergent for 20 min at 50 °C, then thoroughly rinsed by cold water.

RESULTS AND DISCUSSION

Synthesis of Intermediates and Dyestuffs

The most convenient starting material for the preparation of naphthalimide dyestuffs is acenaphthene, which is reasonably cheap and easily available as a by-product of processes in the coal industry. In this work acenaphthene was utilized for preparing a number of novel naphthalimide disperse dyestuffs. Acenaphthene was reacted with nitric acid in an acetic acid media at room temperature giving yellow needle crystals having an m.p of 101-102 °C. The yield of the reaction was 85.9%. Naphthalic anhydride or substituted naphthalic anhydrides reacts with amines such as ammonia or alkyl amines to form the corresponding naphthalimides. Therefore, 4-nitro-1,8-naphthalic anhydride was reacted with methyl or ethyl glycinate. The reaction was carried out in absolute ethanol media under reflux condition, and the end point of the reaction was examined by TLC on silica gel 60. TLC showed the imidation of 4-nitro-1,8-naphthalic anhydride with ethyl and methyl glycinate completed at 10 and 16 hours, respectively. The time required for completion of the imidation reaction for 4-nitro-1,8-naphthalic anhydride with methyl or ethyl glycinate is more than for the imidation of 4-nitro-1,8-naphthalic anhydride with alkyl amines.[8,9] This can be attributed to the alkyl amines being more active than the alkyl glycinates in the nucleophilic displacement reaction in which the attacking group is amine.

The yields (Y%), melting points, the form and color of crystals of intermediate products: 4-nitro-N-alkylglycinate-1,8-naphthalimides are given in Table 1. The FTIR, ^{1}H-MNR spectra and Elemental Analysis data of 4-nitro-N-alkyl-glycinate-1,8-naphthalimides are given in Table 2.

Table 1. Characteristics of synthesized intermediates

Series No.	Reaction conditions			Product			
	Reaction	Solvent	time (hrs.)	mp (°C)	Y (%)	Form	Color
1	Imidation	Ethanol	16	196.22	82.75	needle	fawn
2	Imidation	Ethanol	10	169.75	92.28	needle	fawn
3	Reduction	Ethanol	1	228.05	77.82	needle	orange
4	Reduction	Ethanol	1	227.55	84.97	needle	orange

Table 2. FTIR,^{1}H NMR and elemental analysis of intermediates

Intermediates	FTIR, ^{1}H NMR and elemental analysis
1	^{1}H NMR ($CDCl_3$): δ 3.82 (3H, s, CH_3), 4.96-4.98 (2H, s, NCH_2), 8.00-8.05 (1H, J = 7.4 Hz, 6-H), 8.42-8.45 (1H, d, J = 8.0 Hz, 3-H), 8.72-8.79 (2H, 2-H, 5-H), 8.87-8.89 (1H, J = 8.7 Hz, 7-H); FTIR (KBr): ν 3075.17 cm^{-1} (C-H str. Ar.), 2956.57 cm^{-1} (C-H str. Aliphatic), 1749.19 cm^{-1} (C=O str. ester), 1708.45, 1670.99 (C=O str. Carbonyl), 1583.33 (C=C str. Ar.), 1532.88, 1379.24 (NO_2 str.); Anal. Calcd for $C_{15}H_{10}N_2O_6$: C, 57.32%; H, 3.18%; N, 8.92%; Found: C, 57.4%; H, 3.3%; N, 9.1%.
2	^{1}H NMR ($CDCl_3$): δ 1.30-1.35 (3H, t, J = 7.1 Hz, CH_3), 4.24-4.31 (2H, q, J = 7.1 Hz, CH_2CH_3), 4.954 (2H, s, NCH_2), 7.98-8.03 (1H, J = 7.4 Hz, 6-H), 8.40-8.43 (1H,d, J = 8.0 Hz, 3-H), 8.70-8.77 (2H, 2-H, 5-H), 8.84-8.87 (1H, d, J = 8.7 Hz,7-H); FTIR (KBr): ν 3118.31 cm^{-1} (C-H str. Ar.), 2987.36 cm^{-1} (C-H str. Aliphatic), 1742.85 cm^{-1} (C=O str. ester), 1709.30 cm^{-1} (C=O str. Carbonyl), 1673.47 cm^{-1} (C=O str. Carbonyl), 1595.44 cm^{-1} (C=C str. Ar.), 1523.20 cm^{-1} (NO_2 str.), 1382.28 cm^{-1} (NO_2 str.); Anal. Calcd for $C_{16}H_{12}N_2O_6$: C, 68.78%; H, 4.19%; N, 9.27%; Found: C, 68.9%; H, 4.3%; N, 9.5%.
3	^{1}H NMR (CD_3COCD_3): δ 3.987 (3H, s, CH_3), 4.84 (2H, s, N-CH_2), 6.89 (2H, s, NH_2), 6.93-7.01 (1H, d, J = 8.4 Hz, 3-H), 7.68-7.73 (1H, J = 7.8 Hz, 6-H), 8.29-8.32 (1H, d, J = 8.4 Hz, 2-H), 8.51-8.52 (1H, d, J = 7.3 Hz, 5-H), 8.61-8.64 (1H, d, J = 8.3 Hz, 7-H); FTIR (KBr): ν 3364.98, 3258.08 cm^{-1} (N-H str. Primary amine), 2927.51 cm^{-1} (C-H str. Aliphatic), 1734.82 cm^{-1} (C=O str. ester), 1685.45, 1642.62 (C=O str. carbonyl), 1577.96 (C=C str. Ar.); Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38%; H, 4.23%; N, 9.86%; Found: C, 63.5%; H, 4.4%; N, 9.6%.
4	^{1}H NMR (CD_3COCD_3): δ 1.24-1.29 (3H, t, J = 7.1 Hz, CH_3), 4.16-4.23 (2H, q, J = 7.1 Hz, CH_2CH_3), 4.84 (2H, s, NCH_2), 6.89 (2H, s, NH_2), 6.99-7.02 (1H, d, J = 8.3 Hz, 3-H), 7.68-7.73 (1H, J = 7.7 Hz, 6-H), 8.29-8.32 (1H, d, J = 8.4 Hz, 2-H), 8.51-8.54 (1H, d, J = 7.3 Hz, 5-H), 8.61-8.64 (1H, d, J = 7.4 Hz,7-H); FTIR (KBr): ν 3367.89, 3256.39 cm^{-1} (N-H str. Primary amine), 2924.08 cm^{-1} (C-H str. Aliphatic), 1730.04 cm^{-1} (C=O str. ester), 1686.12 cm^{-1}, 1643.14 cm^{-1} (C=O str. carbonyl), 1577.56 cm^{-1} (C=C Ar.); Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.43%; H, 4.7%; N, 9.39%; Found: C, 65%; H, 4.9%; N, 9.3%.

4-Amino-1,8-naphthalimides have been prepared by reduction of the 4-nitro group of the appropriate naphthalic anhydride or imide. Therefore, 4-amino-N-alkylglycinate-1,8-naphthalimides were synthesized by the reaction of 4-nitro-N-alkylglycinate-1,8-naphthalimide with stannous chloride(II) in hydrochloric acid as reducing agent and ethanol as solvent. Purification of product was carried out by column chromatography on silica gel G (60-120) using acetone and toluene (2/1) mixtures as eluent. The yields (Y%) of obtained products: 4-amino-N-alkylglycinate-1,8-naphthalimides, their melting points and the form and color of crystals are given in Table 1. The FTIR, ^{1}H-NMR spectra and elemental analysis of 4-amino-N-alkylglycinate-1,8-naphthalimides are given in Table 2.

The general method of diazotisation of 4-amino-1,8-naphthalimide derivatives uses nitrosyl sulphuric acid.[10,11] Thus 4-amino-N-alkylglycinate-1,8-naphthalimide was reacted with nitrosyl sulfuric acid. This reaction was completed in 3 hours. The obtained diazonium salts were reacted with various coupling components such as N,N-diethylaniline, N,N-diethyl-m-toluidine and 3-(N,N-diethylamino)acetanilide in weak acid media (pH = 4-5) (Fig. 1). All analytical data of the synthesized dyestuffs (the yields (Y%), DSC, FTIR, ^{1}H-MNR spectra and Elemental Analysis) are shown in Table 3.

Electronic Absorption Spectra

It is a well-accepted fact that the constitution of dyestuffs have a fundamental role in producing desired color over substrate. The correlation between the colour and constitution is a highly interesting aspect of dyestuff development and commercialization. Due to the abovementioned points, the subject has attracted the attention of the companies producing commercial azo disperse dyestuffs.[12,13] The wavelength of maximum absorption (λ_{max}) and the molar absorption coefficients (ε_{max}) are all equally important for dyestuffs.[14] The absorption spectra of the dyestuffs 5-9 were determined in toluene, chloroform and DMF solvents, respectively, and are summarized in Table 4. Comparing the λ_{max} of dyestuffs in chloroform for 5 and 6 with 7 and 8 shows that the nature of imide residue CH_2COOR (R=CH_3, C_2H_5) is not very significant in the context of color change. This finding is in good agreement with work of other research groups.[4] It is well known that the color of dyestuffs is influenced by the introduction of additional donor groups into the coupling component. One can easily deduce from Table 4 that the presence of a methyl group in the 3-position of N,N-diethyl-m-toluidine related to N,N-diethylaniline was caused by the bathochromic effect (~ 8-10 nm) in dyestuffs 6 and 8.

The introduction of a –$NHCOCH_3$ group into the coupling component of the dye 7 caused bathochromic shifts, which is seen in dye 9 (~ 26 nm). The bathochromic shift of the –$NHCOCH_3$ group is particularly large. This bathochromic shift has been reported for other azo heterocyclic compounds.[12]

The measurement of absorption at λ_{max} in toluene and DMF showed that the lowest $\Delta\lambda_{max}$ belongs to the dye 9. Absorption maxima in Table 4 revealed that the solvatochromism shifts between toluene and DMF of the acetylamino derivatives related to toluidine-based dyestuffs are smaller.[12] Comparing λ_{max} of dyestuffs showed that for dyestuffs lacking acetylamino substituents (dyestuffs 5-8) the solvatochromism shifts are ~24-32 nm, while for dyestuff containing an acetylamino group (dyestuff 9), it is less than 19 nm. This difference can be attributed to the weaker solvatochromism of the acetylamino derivatives, despite the fact that the acetylamino group of these dyestuffs causes the dyestuff to be bright and bathochromic as a result of intramolecular hydrogen bonding.[12]

The measurement of λ_{max} in toluene and DMF showed that λ_{max} of the intramolecular charge transfer bands exhibit a marked red shift on transfer from nonpolar to polar solvents. This behavior indicates that the polar excited states of the synthesized dyestuffs are stabilized by polarization interaction forces as the polarizibility of the solvent is increased.[15]

Dyeing and Fastness Properties

The dyestuffs 5-9 were applied to polyester fabric under high temperature dyeing conditions at concentrations of 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2 and 4 percent of dyestuffs based on the weight of fabric. 0.5% Acetic acid (pH = 4.5-5) was added and the dyeing was carried out according to Fig. 2. Dyed fabric was reduction cleared in an aqueous solution containing 2 g/l of sodium hydrosulphite, 1 g/l of sodium hydroxide and 1 g/l detergent for 20 min at 50 °C. The treated polyester was then rinsed with hot and cold water.

For elaborating on the buildup of the synthesized dyestuffs, the K/S was calculated by using the Kubelka-Mank Equation (Eq. 1):

$$K/S = (1 - R)^2/2R; \qquad (1)$$

where K, S and R are absorption coefficient, scatter coeffi-

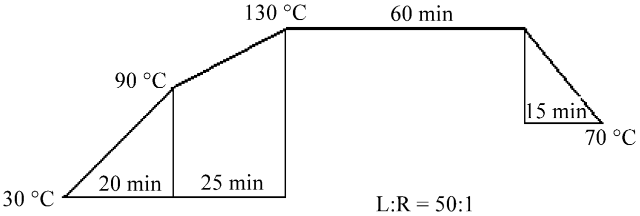

Fig. 2. Conditions of dyeing, L:R, liquor to goods ratio, the volume of liquor employed on the weight of fabric.

Table 3. FTIR, ^{1}H-NMR and elemental analysis of dyestuffs

Dyestuffs	FTIR, ^{1}H NMR and elemental analysis
5	^{1}H NMR ($CDCl_3$): 1.276-1.346 (6H, CH_2CH_3), 3.50-3.57 (4H, q, J = 7.1 Hz, CH_2CH_3), 3.81 (3H, s, $COOCH_3$), 4.98-4.999 (2H, s, NCH_2), 6.786-6.82 (2H, 3′-H, 5′-H), 7.83-7.88 (1H, J = 8.2 Hz, 6-H), 7.97-8.06 (3H, 2″-H, 6′-H, 5-H), 8.66-8.699 (2H, 2-H, 7-H), 9.28-9.30 (1H, d, J = 8.7 Hz,3-H); FTIR (KBr): ν 2948.17 (C-H str. Ar.), 2929.34 cm^{-1} (C-H str. Aliphatic), 1738.74 cm^{-1} (C=O str. ester), 1688.95 cm^{-1}, 1652.05 cm^{-1} (C=O str. Carbonyl), 1585.44 cm^{-1} (N=N str.); Anal. Calcd for $C_{25}H_{24}N_4O_4$: C, 67.57%; H, 5.4%; N, 12.6%; Found: C, 67.2%; H, 5.1%; N, 12.8%.
6	^{1}H NMR ($CDCl_3$): 1.275-1.347 (6H,CH_3), 2.79 (3H, s, Ph-CH_3), 3.48-3.56 (4H, q, J = 7.0 Hz, $N(CH_2CH_3)_2$, 3.82 (3H, s, $COOCH_3$), 4.98 (2H, s, NCH_2), 6.69-6.78 (2H, 3′-H, 5′-H), 7.83-7.89 (1H, J = 7.4 Hz, 6-H), 7.97-8.05 (2H, 6′-H, 5-H), 8.65-8.698 (2H, 2-H, 7-H), 9.27-9.31 (1H, J = 8.5 Hz, 3-H); FTIR (KBr): ν 2970.25 cm^{-1} (C-H str. Ar.), 2928.32 cm^{-1} (C-H str. Aliphatic), 1748.91 cm^{-1} (C=O str. ester), 1693.74, 1649.56 cm^{-1} (C=O str. carbonyl), 1589.74 cm^{-1} (N=N str.); Anal. Calcd for $C_{26}H_{26}N_4O_4$: C, 68.12%; H, 5.68%; N, 12.22%; Found: C, 68.25%; H, 5.27%; N, 12.56%.
7	^{1}H NMR ($CDCl_3$): 1.27-1.34 (9H, t, CH_2CH_3), 3.50-3.57 (4H, q, J = 6.9, $N(CH_2CH_3)_2$), 4.24-4.31 (2H, q, J = 7.1 Hz, $COOCH_2CH_3$), 4.98 (2H, s, N-CH_2), 6.79-6.82 (2H, 3′-H, 5′-H), 7.83-7.89 (1H,J = 8.3, 6-H), 7.97-8.06 (3H, 2′-H, 6′-H, 5-H), 8.66-8.70 (2H, 2-H, 7-H), 9.28-9.31 (1H, d, J = 8.6 Hz, 3-H); FTIR (KBr): ν 2960.77 (C-H str. Ar.), 2924.95 cm^{-1} (C-H str. Aliphatic), 1748.4 cm^{-1} (C=O str. ester), 1698.61 cm^{-1}, 1662.05 cm^{-1} (C=O str. Carbonyl), 1596.4 cm^{-1} (N=N str.); Anal. Calcd for $C_{26}H_{26}N_4O_4$: C, 68.12%; H, 5.68%; N, 12.2%; Found: C, 68.1%; H, 5.6%; N, 11.5%. mp = 201.27 °C
8	^{1}H NMR ($CDCl_3$): 1.27-1.34 (9H, CH_3), 2.79 (3H, s, Ph-CH_3), 3.48-3.55 (4H, q, J = 7.0 Hz, $N(CH_2CH_3)_2$), 4.24-4.31 (2H, q, J = 7.1 Hz, $COOCH_2CH_3$), 4.98 (2H, s, NCH_2), 6.60-6.65 (2H, 3′-H, 5′-H), 7.82-7.87 (1H, J = 7.4 Hz, 6-H), 7.96-8.03 (2H, 6′-H, 5-H), 8.65-8.69 (2H, 2-H, 7-H), 9.32-9.35 (1H, d, J = 8.4 Hz, 3-H.); FTIR (KBr): ν 2972.25 cm^{-1} (C-H str. Ar.), 2932.22 cm^{-1} (C-H str. Aliphatic), 1752.02 cm^{-1} (C=O str. ester), 1695.59, 1659.37 cm^{-1} (C=O str. carbonyl), 1588.21 cm^{-1} (N=N str.); Anal. Calcd for $C_{27}H_{28}N_4O_4$: C, 68.64%; H, 5.93%; N, 11.86%; Found: C, 68.8%; H, 6%; N, 11.8%. mp = 202.38 °C
9	^{1}H NMR ($CDCl_3$): 1.27-1.34 (9H, CH_3), 1.61 (1H, $NHCOCH_3$, D_2O exchangeable), 2.35 (3H, $NHCOCH_3$), 3.52-3.59 (4H, q, J = 6.7 Hz, $N(CH_2CH_3)_2$), 4.24-4.31 (2H, q, J = 6.9 Hz, $COOCH_2CH_3$), 4.98 (2H, N-CH_2), 6.54-6.56 (1H, d, J = 7.7 Hz, 5′-H), 7.82-7.96 (3H, 6-H, 5-H, 6′-H), 8.18 (1H, s, 3′-H), 8.65-8.70 (2H, 2-H, 7-H), 9.12-9.15 (1H, d, J = 8.0 Hz, 3-H). FTIR (KBr): ν 2976.64 cm^{-1} (C-H str. Ar.), 2930.82 cm^{-1} (C-H str. Aliphatic), 1747.05 cm^{-1} (C=O str. ester), 1697.99, 1658.53 Cm^{-1} (C=O str. Carbonyl), 1588.77 cm^{-1} (N=N str.); Anal. Calcd for $C_{28}H_{29}N_5O_5$: C, 65.24%; H, 5.63%; N, 13.59%; Found: C, 65.1%; H, 5.8%; N, 13.4% mp = 276.11 °C

cient and reflectance of dyed sample, respectively. Fig. 3 (K/S vs. concentration) shows the synthesized dyestuffs had very good buildup on polyester fabric except for dyestuff 5. K/S is taken as criteria for dyeability of polyester fibres. As is clear from Fig. 3, they generally reached saturation at concentrations of 1-1.5% owf. The rate and degree

Table 4. Spectral data of synthesized dyestuffs

Dyestuffs	Chloroform		Toluene	DMF	$\Delta\lambda_{max}$ (nm)
	λ_{max} (nm)	∈ (l/mol.cm)	λ_{max} (nm)	λ_{max} (nm)	
5	529.7	37637	515.1	539.7	24.6
6	536.6	38233	524.1	549.0	24.9
7	528.5	36983	514.8	547.0	32.2
8	538.7	33196	523.6	554.7	31.1
9	554.6	49080	544.5	563.4	18.9

of exhaustion of dyestuffs (5-8) were good, but dyestuff 9 had poor exhaustion. The introduction of an acetyl group at the 3-position on N,N-diethylaniline produced a pronounced bathochromic shift but had little effect on the exhaustion.

The wash fastness properties (ISO 105 C06C2S) of dyestuffs 5-9 expressed as colour change of the fabric samples and staining on cotton and polyester were excellent (4-5 to 5). The presence of the ester group on naphthalimide moiety was not an influencing parameter in determining wash fastness performance.[16] Also there is the possibility of the hydrolyzing ester group in alkaline washing media, which produces alkali-soluble carboxylic acid dyestuffs.

The dry heat fastness and light fastness were measured according to ISO standards 105 X11:1994(E) and ISO 105 B02, respectively. The synthesized dyestuffs showed moderate to very good dry heat fastness at 180 °C and moderate light fastness.

The color of the dyed fabrics was assessed by a reflectance spectrophotometer (Table 5). The results showed that introducing the electron donor substituents in the ring of the coupling components also considerably affect the color of the dyeings. The presence of strongly electron donor substituents in dyestuff 9 caused a color shift towards bluish. The color hues of the dyestuffs 6 and 8 on polyester fabrics are shifted towards bluish red or violets, but less than with dyestuff 5. The methyl group in the 3-position of

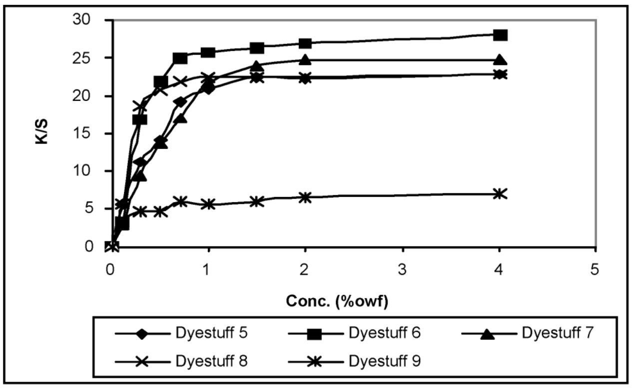

Fig. 3. Build up of the synthesized dyestuffs, K/S: Approximate concentration of each dye in the substrate.

Table 5. Colour fastness of the synthesized dyestuffs

Dyestuffs	Wash fastness			Light fastness	Heat fastness
	P[a]	C[a]	Change		180 °C
5	5	5	4-5	4	4-5
6	5	5	5	4	3-4
7	4-5	4-5	5	3-4	4
8	5	5	5	3-4	4
9	4	4	4-5	3-4	5

a: Staining, P: Polyester, C: Cotton, b: Staining on polyester, Washfastness and Heatfastness: 1 to 5 shows poor to excellent fastne-ss, respectively.
Lightfastness: 1 to 8 represents poor to ideal light fastness, spectively.

Table 6. Spectrophotometric data of synthesized dyestuffs

Dyestuff	(% owf)	L*	a*	b*
1	0.3	31.895	40.856	-10.684
	0.7	27.233	37.388	-7.514
	2	24.321	33.938	-4.665
2	0.3	49.508	35.316	-25.340
	0.7	19.153	25.239	-9.002
	2	17.499	18.816	-4.833
3	0.3	36.443	39.405	-11.352
	0.7	29.980	38.371	-7.780
	2	21.655	29.129	-1.919
4	0.3	40.909	33.793	-25.188
	0.7	22.413	28.763	-16.419
	2	21.575	26.817	-14.945
5	0.3	43.727	27.037	-30.686
	0.7	39.833	27.450	-28.519
	2	38.010	25.980	-23.282

L* = Lightness, a* and b* = chromaticity coordinate

N,N-diethylaniline in dyestuffs 6 and 8, which is a weak electron donor, caused a shift less than dyestuff 9. The spectrophotometric data showed that the nature of the ester residue in N-substituted-1,8-naphthalimide had little effect on colour dyeings.

CONCLUSIONS

A series of novel monoazo disperse dyestuffs based on N-ester-1,8-naphthalimide were synthesized from acenaphthene as a starting material. Acenaphthene was nitrated and further reacted such as with oxidation, imidation, reduction, diazotization and coupling. Data obtained by various analytical techniques proved the synthesizing of the claimed novel dyestuffs. The spectral characteristics of the synthesized dyestuffs on polyester fabrics showed that they give bluish-red with a relatively weak buildup for dyestuff 9, while the rest of the dyestuffs were very good on polyester fabrics. For all the synthesized dyestuffs the wash fastness properties were generally very good, whereas the light fastness was moderate.

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