

Synthesis, spectral properties and application of novel monoazo disperse dyes derived from *N*-ester-1,8-naphthalimide to polyester

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Abstract

A series of novel monoazo disperse dyes based on *N*-ester-1,8-naphthalimides were synthesized using 4-amino-*N*-methylglycinate-1,8-naphthalimide and 4-amino-*N*-ethylglycinate-1,8-naphthalimide, as diazo components, with various couplers. The spectrophotometric properties of the dyes were examined in different solvents and their solvatochromism effects were investigated. The dyes displayed λ_{\max} of between 515 and 563 nm and the molar extinction coefficient of the dyes varied from 25,863 to 49,080 l mol⁻¹ cm⁻¹. Most of the dyes showed acceptable build up properties on polyester fibres under high temperature conditions and displayed moderate light fastness and very good wash and dry heat fastness on polyester fibres. The results indicated that the presence of an ester group within the dye molecule provided alkali-clearable potential.

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1. Introduction

The development of polyester as a textile fibre and its use in fibre blends, particularly with cotton, pose many problems in terms of its dyeability for both the dye chemist and dyer. Polyester is the most hydrophobic of all common fibres and is usually dyed with disperse dyes. The majority of disperse dyes are azo dyes due firstly, to the ease with which an extraordinary number of molecular combinations can be generated by varying the diazo and coupling components; secondly, the dyes enjoy relatively simple manufacturing processes [1] and finally, they provide a very wide colour gamut of high colour strength [2].

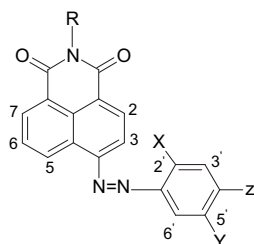
In recent years, much research has focused on naphthalimide derivatives as fluorescent materials [3,4] and disperse dyes [5–8]. These dyes show very good substantivity to

polyester fibres on which substrate they display good fastness properties in yellow to bluish-red shades [9,10].

The synthesis, characterization and spectral properties of azo-*N*-alkyl-1,8-naphthalimide disperse dyes have been reported [5,7,8,11]. To the best of our knowledge, the synthesis and spectral properties of novel monoazo-1,8-naphthalimide disperse dyes containing an ester group have not been investigated. The presence of an ester group within a dye molecule may impart alkali-clearability to the dyes. Due to the hydrolysis capability of such an ester group in alkaline solution, the synthesized dyes can be converted to water soluble products without cleavage of the azo group(s) in the dye, under relatively mild alkaline conditions. Therefore, it is possible to replace the traditional reduction clearing process that is used for disperse dyes on polyester with an environmentally friendly, alkali-clearable method which prevents the production of potentially harmful amines as a result of reduction clearing. Furthermore, the elimination of the reduction

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| DYE | R | X | Y | Z |
|-----|--|---------------------|-------------------|--|
| 1 | CH ₂ COOCH ₃ | H | H | N(CH ₂ CH ₃) ₂ |
| 2 | CH ₂ COOCH ₃ | CH ₃ | H | N(CH ₂ CH ₃) ₂ |
| 3 | CH ₂ COOC ₂ H ₅ | H | H | N(CH ₂ CH ₃) ₂ |
| 4 | CH ₂ COOC ₂ H ₅ | CH ₃ | H | N(CH ₂ CH ₃) ₂ |
| 5 | CH ₂ COOC ₂ H ₅ | NHCOCH ₃ | H | N(CH ₂ CH ₃) ₂ |
| 6 | CH ₃ | CH ₃ | H | N(CH ₂ CH ₃) ₂ |
| 7 | CH ₂ COOC ₂ H ₅ | NH ₂ | COCH ₃ | H |

Fig. 1. The chemical structure of the synthesized dyes.

clearing process may also offer substantial productivity improvements, water and chemical saving and reduction of effluent loads.

In the present study, a series of novel monoazo disperse dyes have been prepared using 4-amino-*N*-methyl(ethyl)-glycinate-1,8-naphthalimide as diazo component and *N,N*-diethylaniline, *N,N*-diethyl-*m*-toluidine, 3-(*N,N*-diethylamino)acetanilide and *p*-aminoacetophenone as coupling components. The chemical structures of the synthesized dyes are showed in Fig. 1. The dyes were applied to polyester fibres and their technical properties in solution and on the fibre were investigated.

2. Experimental

2.1. Materials and apparatus

Acenaphthene, *N,N*-diethylaniline, *N,N*-diethyl-*m*-toluidine, methylglycinate, ethylglycinate, and 3-(*N,N*-diethylamino)acetanilide were purchased from Aldrich company and used without further purification. Melting points were determined using a differential scanning calorimeter 2010 TA instrument. ¹H NMR spectra were obtained on a Bruker AQS AVANCE 300 MHz spectrometer. FTIR spectra were recorded on a Nicolet 470/670/870 instrument, while UV–VIS absorption spectra were measured on a Cecil 9200 double beam spectrophotometer. The colorimetric data of the dyeings were obtained using a Gretag Macbeth 7000A spectrophotometer (D65 illumination, 10° observer).

2.2. Syntheses of intermediates

5-Nitroacenaphthene and 4-nitronaphthalic anhydride were prepared using the method of Okazaki and Taniguchi [12]. 4-Nitro-*N*-ethylglycinate-1,8-naphthalimide and 4-nitro-*N*-methylglycinate-1,8-naphthalimide were made according to the modified method of Dangwu [13–15].

2.3. Synthesis of 4-amino-*N*-ethyl(methyl)glycinate naphthalimide

A mixture of 6 g (18 mmol) 4-nitro-*N*-ethyl(methyl)glycinate-1,8-naphthalimide, 20.31 g (90 mmol) stannous chloride and 22.5 ml hydrochloric acid in 90 ml ethanol was refluxed for 1 h. The reaction mixture was poured into 300 ml water and the precipitated solid filtered off. The crude product was purified by column chromatography (silica gel, eluent: acetone/toluene = 2:1).

2.4. Syntheses of dyes

Sodium nitrite (0.37 g; 5.3 mmol) was added slowly to 2.3 ml of magnetically stirred concentrated sulphuric acid at <10 °C. The temperature of reaction was increased to 65 °C and the solution was then cooled to 5 °C; 5.3 mmol of 4-amino-*N*-(methyl)ethylglycinate-1,8-naphthalimide was slowly added over 40 min and reaction continued for 3 h with stirring. The resulting clear diazonium salt solution was used immediately in the coupling reaction with the following coupling components: *N,N*-diethylaniline, *N,N*-diethyl-*m*-toluidine, *p*-aminoacetophenone and 3-(*N,N*-diethylamino)acetanilide. The diazonium salt was added to a solution of 5.3 mmol of the designated coupling components dissolved in 1 ml of acetic acid and stirred for 1 h at <10 °C. The pH was maintained between 4 and 5 by adding aqueous sodium acetate solution. Stirring was continued for 3 h at that temperature and the resulting dye was filtered, washed with hot water and dried. The crude products were purified using preparative TLC on silica gel (solvent: chloroform). The physical and spectral data of the purified dyes are as follows.

2.4.1. Dye 1

¹H NMR (CDCl₃): 1.27–1.34 (6H, CH₂CH₃), 3.50–3.57 (4H, CH₂CH₃), 3.81 (3H, COOCH₃), 4.98–5.00 (2H, NCH₂), 6.78–6.81 (2H, 3'-H, 5'-H), 7.83–7.88 (1H, 6-H), 7.97–8.06 (3H, 2'-H, 6'-H, 5-H), 8.66–8.70 (2H, 2-H, 7-H), 9.28–9.30 (1H, 3-H); FTIR (KBr): ν 2978.17 cm⁻¹ (C–H str. Ar.), 2929.34 cm⁻¹ (C–H str. CH₂), 1738.74 cm⁻¹ (C=O str. ester), 1688.96 cm⁻¹, 1652.05 cm⁻¹ (C=O str.), 1585.44 cm⁻¹ (N=N str.); Anal. Calcd for C₂₅H₂₄N₄O₄: C, 69.77%; H, 5.58%; N, 9.77%; Found: C, 69.26%; H, 5.69%; N, 9.81%. m.p. = 206.29 °C.

2.4.2. Dye 2

¹H NMR (CDCl₃): 1.27–1.35 (6H, CH₃), 2.79 (3H, Ph-CH₃), 3.48–3.56 (4H, N (CH₂CH₃)₂), 3.82 (3H, COOCH₃), 4.98 (2H, NCH₂), 6.69–6.78 (2H, 3'-H, 5'-H), 7.83–7.89 (1H, 6-H), 7.97–8.05 (2H, 6'-H, 5-H), 8.65–8.70 (2H, 2-H, 7-H), 9.27–9.31 (1H, 3-H); FTIR (KBr): ν 2970.25 cm⁻¹ (C–H str. Ar.), 2928.32 cm⁻¹ (C–H str. CH₂), 1748.91 cm⁻¹ (C=O str. ester), 1693.74, 1649.56 cm⁻¹ (C=O str.), 1589.74 cm⁻¹ (N=N str.); Anal. Calcd for C₂₆H₂₆N₄O₄: C, 70.27%; H, 5.86%; N, 9.46%; Found: C, 70.51%; H, 6.11%; N, 9.4%. m.p. = 193.6 °C.

2.4.3. Dye 3

^1H NMR (CDCl_3): 1.27–1.34 (9H, CH_2CH_3), 3.50–3.57 (4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 4.24–4.31 (2H, $\text{COOCH}_2\text{CH}_3$), 4.98 (2H, $\text{N}-\text{CH}_2$), 6.79–6.82 (2H, 3'-H, 5'-H), 7.83–7.89 (1H, 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, 3-H); FTIR (KBr): ν 2960.77 cm^{-1} (C–H str. Ar.), 2924.95 cm^{-1} (C–H str. CH_2), 1748.4 cm^{-1} (C=O str. ester), 1698.61 cm^{-1} , 1662.05 cm^{-1} (C=O str.), 1596.4 cm^{-1} (N=N str.); Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_4$: C, 68.12%; H, 5.68%; N, 12.2%; Found: C, 68.1%; H, 5.6%; N, 12.2%. m.p. = 201.27 °C.

2.4.4. Dye 4

^1H NMR (CDCl_3): 1.27–1.34 (9H, CH_3), 2.79 (3H, $\text{Ph}-\text{CH}_3$), 3.48–3.55 (4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 4.24–4.31 (2H, $\text{COOCH}_2\text{CH}_3$), 4.98 (2H, NCH_2), 6.60–6.65 (2H, 3'-H, 5'-H), 7.82–7.87 (1H, 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, 3-H); FTIR (KBr): ν 2972.25 cm^{-1} (C–H str. Ar.), 2932.22 cm^{-1} (C–H str. CH_2), 1752.02 cm^{-1} (C=O str. ester), 1695.59, 1659.37 cm^{-1} (C=O str.), 1588.21 cm^{-1} (N=N str.); Anal. Calcd for $\text{C}_{27}\text{H}_{28}\text{N}_4\text{O}_4$: C, 68.64%; H, 5.93%; N, 11.86%; Found: C, 68.8%; H, 6%; N, 11.8%. m.p. = 202.38 °C.

2.4.5. Dye 5

^1H NMR (CDCl_3): 1.27–1.34 (9H, CH_3), 2.35 (3H, NHCOCH_3), 3.52–3.59 (4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 4.24–4.31 (2H, $\text{COOCH}_2\text{CH}_3$), 4.98 (2H, $\text{N}-\text{CH}_2$), 6.54–6.56 (1H, 5'-H), 7.82–7.89 (1H, 6-H), 7.93–7.96 (2H, 6'-H, 5-H), 8.18 (1H, 3'-H), 8.65–8.70 (2H, 2-H, 7-H), 9.12–9.15 (1H, 3-H); FTIR (KBr): ν 2976.64 cm^{-1} (C–H str. Ar.), 2930.82 cm^{-1} (C–H str. CH_2), 1747.05 cm^{-1} (C=O str. ester), 1697.99, 1658.53 cm^{-1} (C=O str.), 1588.77 cm^{-1} (N=N str.); Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{N}_5\text{O}_5$: C, 65.24%; H, 5.63%; N, 13.59%; Found: C, 65.1%; H, 5.8%; N, 13.4%. m.p. = 276.11 °C.

2.4.6. Dye 6

^1H NMR (CDCl_3): 1.26–1.28 (6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 2.76 (3H, $\text{Ph}-\text{CH}_3$), 3.47–3.50 (4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 3.54 (3H, $\text{N}-\text{CH}_3$), 6.61–6.63 (2H, 3'-H, 5'-H), 7.78–7.80 (1H, 6-H), 7.86–7.88 (1H, 5-H), 7.90–7.93 (1H, 6'-H), 8.56–8.57 (1H, 7-H), 8.61–8.62 (1H, 2-H), 9.21–9.23 (1H, 3-H); FTIR (KBr): ν 2973.43 cm^{-1} (C–H str. Ar.), 2931.09 cm^{-1} (C–H str. CH_2), 1693.71, 1653.97 cm^{-1} (C=O str.), 1583.18 cm^{-1} (N=N str.); Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4$: C, 72%; H, 6%; N, 14%; Found: C, 71.4%; H, 5.5%; N, 13.7%. m.p. = 195.70 °C.

2.4.7. Dye 7

^1H NMR (CDCl_3): 1.27 (3H, CH_2CH_3), 2.65 (3H, PhCOCH_3), 4.25–4.32 (2H, CH_2CH_3), 4.98 (2H, $\text{N}-\text{CH}_2$), 7.28 (2H, NH_2), 7.51–7.54 (1H, 3'-H), 7.82 (1H, 6-H), 7.97–8.0 (1H, 6'-H), 8.06–8.09 (2H, 5-H, 4'-H), 8.64–8.70 (2H, 2-H, 7-H), 8.82–8.85 (1H, 3-H); FTIR (KBr): ν 3221.5 cm^{-1} (N–H str.), 2973.13 cm^{-1} (C–H str. Ar.), 2932.41 cm^{-1} (C–H str. CH_2), 1751.34 cm^{-1} (C=O str. ester), 1738.64 cm^{-1} (C=O str. ketone), 1668.42 cm^{-1} ,

1659.21 cm^{-1} (C=O str.), 1584.15 cm^{-1} (N=N str.); Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_5$: C, 64.86%; H, 4.5%; N, 14.44%; Found: C, 64.1%; H, 4.5%; N, 13.7%. m.p. = 194.1 °C.

2.5. Preparation of dye dispersions

Dye (0.5 g), dispersing agent (1 g) (*Lyoprint EV*, Ciba-Geigy) and water (2 ml) were added to a mortar and milled for 60 min; the ensuing mixture was diluted with 20 ml water, transferred to a ball mill and milled for 20 h. The volume of the dispersion was adjusted to 100 ml and filtered through a 5 μm Micro-Prazisions Sieb Fritsch.

2.6. Dyeing

Polyester fibre (1 g) was pretreated with 5 g/l nonionic detergent (*Lotensol*, Hansa) at 80 °C for 20 min using a liquor ratio of 50:1 after which, the substrate was rinsed and dried. Dyeing was carried out in a Rotadyer (Nasaj Sanat Yazd) using a liquor ratio of 50:1, pH 4–5 (acetic acid) at 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2 and 4% o.m.f. (Fig. 2). At the end of dyeing, excess dye was removed by subjecting the dyeings to both conventional reduction clearing and alkali clearing. Reduction clearing was performed at a liquor ratio of 50:1 using 2 g l^{-1} sodium hydrosulphite, 1 g l^{-1} sodium hydroxide and 1 g l^{-1} nonionic detergent for 20 min at 50 °C. Alkali clearing was undertaken using a 50:1 liquor ratio, 2.5 g l^{-1} sodium hydroxide and 1 g l^{-1} detergent for 30 min at 80 °C. The reduction cleared and alkali cleared samples were rinsed and allowed to dry.

3. Results and discussion

3.1. Spectral properties

Correlation between colour and constitution is a highly interesting aspect of dye development and commercialization; in this context, the λ_{max} , molar extinction coefficients (ϵ_{max}) and half-band widths ($\Delta\lambda_{1/2}$) are important parameters for dyes. A higher extinction coefficient and a broader half-band width relate to a stronger chromophore, which makes the product more cost effective [16].

The UV–visible absorption data for dyes 1–7 were determined in chloroform, toluene and DMF (Table 1). The results showed that the nature of the imide residue R was not significant in terms of the hue of the dye. The magnitude of the difference in λ_{max} for dyes 1 and 3, dyes 2 and 4 was small

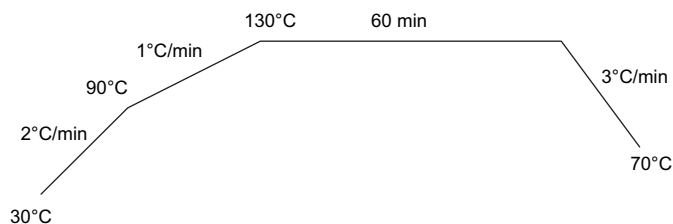


Fig. 2. Dyeing profile of the synthesized dyestuffs.

Table 1
Spectral data of synthesized dyestuffs in solution

| Dye | Chloroform | | | Toluene λ_{\max} (nm) | DMF λ_{\max} (nm) | $\Delta\lambda_{\max}$ (nm) | Dyed polyester λ_{\max} (nm) |
|-----|-----------------------|--|----------------------------|-------------------------------|---------------------------|-----------------------------|--------------------------------------|
| | λ_{\max} (nm) | ϵ (l mol ⁻¹ cm ⁻¹) | $\Delta\lambda_{1/2}$ (nm) | | | | |
| 1 | 529.7 | 37,637 | 120 | 515.1 | 542.9 | 24.6 | 540 |
| 2 | 536.6 | 38,233 | 123 | 524.1 | 549 | 24.9 | 560 |
| 3 | 528.5 | 36,983 | 120 | 514.8 | 547 | 32.2 | 540 |
| 4 | 538.7 | 33,196 | 129 | 523.6 | 554.7 | 31.1 | 560 |
| 5 | 554.6 | 49,080 | 113 | 544.5 | 563.4 | 18.9 | 570 |
| 6 | 538.7 | 40,833 | 121 | 523.2 | 548.7 | 25.5 | 550 |
| 7 | 425.9 ^a | 25,863 ^a | 85 ^a | 420.8 | 425.9 | 5.1 | 430 |

^a Measured in DMF.

($\Delta\lambda_{\max} \leq 2.1$ nm, $\Delta\lambda_{\max} \leq 0.5$ nm and $\Delta\lambda_{\max} \leq 5.7$ for chloroform, toluene and DMF, respectively). In contrast, dyes possessing the same imide substituent with various arylazo coupling components showed significant differences in maximum absorption; similar results were reported for the analogues of naphthalimide dyes [8,10].

The λ_{\max} of the synthesized dyes in chloroform ranged between 425.9 and 554.6 nm. The strong hypsochromic effect (425.9 nm, dye 7) was obtained using *p*-aminoacetophenone as a coupling component in comparison with the corresponding *N,N*-diethylaniline derivative (528.5 nm, dye 3). This hypsochromic effect can be attributed to the electron withdrawing effect of the carbonyl group of dye 7 which decreases the basicity of the $-\text{NH}_2$ group as a result of which the coupling component cannot fully act as a donor to the chromogenic system [8].

As expected, dye 5 was characterized by significant bathochromic shifts compared to its *N,N*-diethylaniline analogues ($\Delta\lambda_{\max} = 26.1$ nm) due to the possession of the $-\text{NHCOCH}_3$ group *ortho* to the azo linkage. The colour of the dye is influenced by the introduction of additional donor groups into the coupling component and/or acceptor groups *ortho* to the azo group in the naphthalimide residue [10]. In all cases, the λ_{\max} increased with increasing solvent polarity [14]. By changing toluene to DMF, positive solvatochromism was observed ($\Delta\lambda_{\max}$ of 5.1–31.2 nm). The λ_{\max} of the dyes in toluene varied from 420.8 to 544.5 nm, whereas in the more polar solvent (DMF) they lay between 425.9 and 563.4 nm. Additionally, the molar extinction coefficients (ϵ_{\max}) of this series in chloroform were in the range of 33,196–49,080 l mol⁻¹ cm⁻¹ (except dye 7).

In comparison with aminoazobenzene, all dyes containing the naphthalimide residue showed pronounced bathochromicity due to the delocalization structures **a** and **b** shown in Fig. 3. Therefore, the naphthyl residue and carbonyl groups imparted significant bathochromicity to dyes 1 and 3 with respect to their aminoazobenzene analogous, **c**. In other words, the substituted 4-aminoazobenzene, e.g. **c** (R = NO₂, SO₂F), having λ_{\max} of 490 and 469 nm, respectively [17], were still 40 and 57 nm more hypsochromic than dyes 1 and 3. The visible absorption maximum of several donor-substituted azobenzene has been studied [17,18]. It is clear that for a monosubstituted dye, the bathochromic shift depends on the electron donating strength of the substituted group. The electronic transitions

in these compounds usually involve electron density migration from the donor group towards the azo group.

Incorporating a $-\text{CH}_3$ group on the coupling component *ortho* to the azo linkage imparted a bathochromic effect (≈ 8 nm). The strongest bathochromic effect (≈ 25 nm) was observed for dye 5 in which the $-\text{NHCOCH}_3$ group was present in the coupling component *ortho* to the azo group.

Table 1 reveals that the solvatochromism of the acetilamino derivatives in toluene and DMF was less pronounced than that of the toluidine and *N,N*-diethylaniline based dyes. The solvatochromic effect for dye 5 was not more than 19 nm, whereas the value for other dyes without the acetilamino substituent was >24 nm. This can be attributed to the weaker solvatochromism of the acetilamino derivatives, despite the fact that the acetilamino group of these dyes imparts a bathochromic shift and increased brightness as a result of intramolecular hydrogen bonding [16]; this hydrogen bonding potential is pronounced in the case of dye 7 ($\Delta\lambda_{\max} = 5.1$ nm).

The value of $\Delta\lambda_{1/2}$ is a convenient criterion for the evaluation of the brightness of a dye insofar as dyes with low $\Delta\lambda_{1/2}$

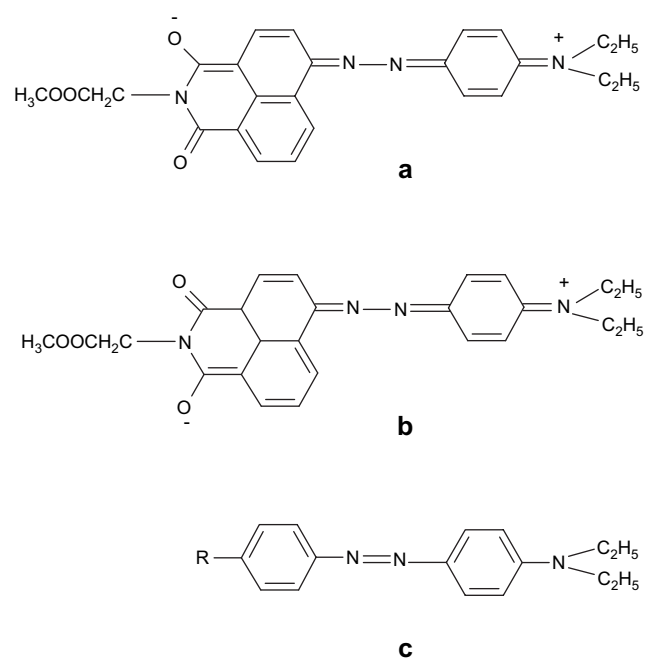


Fig. 3. Delocalization of azonaphthalimide and aminoazobenzene.

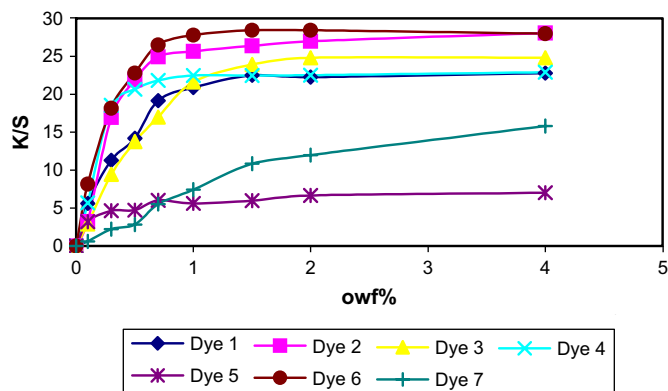


Fig. 4. Build up curves for dyes 1–7.

have bright hues (hyperchromic effect) while those with high values of $\Delta\lambda_{1/2}$ possess dull hues (hypochromic effect) [5]. In the present study, half-widths of the absorption bands in chloroform are given in Table 1. The substituents, X in dyes 1–6, influenced half-width values. In this series, the lowest $\Delta\lambda_{1/2}$ pertained to dye 5 (113 nm), presumably due to intramolecular hydrogen bonding between the azo and acetyl amino groups. The highest $\Delta\lambda_{1/2}$ value belonged to dye 4 (4-amino-*N*-ethylglycinate-1,8-naphthalimide as a diazo component and *N,N*-diethyl-*m*-toluidine as a coupling component).

3.2. Dyeing properties

Fig. 4 illustrates the build up curves of dyes 1–7 from which it is apparent that they generally reached saturation at concentrations <1% o.m.f. The results showed that dyes 5 and 6 displayed the lowest and the highest build up, respectively. The introduction of an acetyl group at the 3-position in dye 5 produced a pronounced bathochromic shift but the dye possessed low uptake.

The absorption maxima of the dyes in solution and on polyester showed good correlation, especially in the case of DMF (Table 1). However, as Hu and co-workers have noted [19], there is no simple relationship between the absorption properties of disperse dyes in solution and the corresponding spectrophotometric data of dyed polyester fibres. The highest value of

Table 2

Spectrophotometric data of dyed polyester with dyes at 1/1 standard depth

| Dye | L^* | a^* | b^* | c | h |
|----------------|--------|--------|---------|--------|---------|
| 1 | 33.24 | 40.856 | −10.684 | 42.23 | 345.345 |
| 2 | 31.012 | 34.019 | −17.153 | 38.10 | 331.124 |
| 3 | 32.716 | 39.421 | −9.83 | 40.60 | 345.41 |
| 4 | 30.812 | 32.136 | −21.596 | 38.718 | 323.53 |
| 5 ^a | 39.833 | 27.45 | −28.519 | 39.583 | 313.906 |
| 6 | 30.861 | 33.698 | −12.051 | 35.79 | 339.38 |
| 7 | 60.037 | 12.905 | 58.64 | 60.043 | 77.589 |

^a Measured in 1% o.m.f.

$\Delta\lambda_{\max}$ between absorption maxima of dyes in solution and on polyester fibres belongs to dyes in toluene.

Table 2 shows that the ester groups did not have a significant effect on the colour of dyeings. The light fastness data of the dyes (Table 3) varied from very poor to moderate, with the exception of dyes that possessed a $-\text{NHCOCH}_3$ group, where the heat fastness was good. In terms of wash fastness (Table 3), dyeings which had not been aftercleared possessed poor fastness, as expected. The reduction cleared dyeings displayed high fastness, this being greater than that of the alkali cleared samples (Table 3). It is anticipated that introducing more ester group may result in better washing fastness. However, alkali-clearable dyes offer some potential environmentally friendly advantages such as elimination of the use of sodium hydrosulphite and reduction of the BOD of wastewater. The mechanism of hydrolysis of the synthesized dyes in alkaline media can be represented by Fig. 5.

4. Conclusions

A series of novel monoazo disperse dyes derived from *N*-ester-1,8-naphthalimide were synthesized and their spectral properties were investigated both in solution and on polyester fibre. The presence of an ester group had little influence on the colour of the dyes; in addition, the colour of the dye was influenced by the introduction of additional donor groups into the coupling component. The bathochromic shifts of dyes 3–5 varied in the order: $\text{NHCOCH}_3 > \text{CH}_3 > \text{H}$. The dyes gave yellow to bluish-red shades on polyester and dyeings

Table 3

Colour fastness of dyed polyester fibres with dyes at 1/1 standard depth

| Dye | UC | | | AC | | | RC | | | Light fastness | Heat fastness | | |
|----------------|----------------|----------------|--------|----------------|----------------|--------|----------------|----------------|--------|----------------|---------------|--------|--------|
| | P ^a | N ^a | Change | P ^a | N ^a | Change | P ^a | N ^a | Change | | 150 °C | 180 °C | 210 °C |
| 1 | 4–5 | 4 | 4–5 | 5 | 5 | 5 | 5 | 5 | 5 | 3–4 | 5 | 4–5 | 3–4 |
| 2 | 4–5 | 4 | 4–5 | 5 | 4–5 | 5 | 5 | 5 | 5 | 4 | 4 | 3–4 | 3–4 |
| 3 | 4–5 | 3–4 | 4–5 | 5 | 3–4 | 4–5 | 5 | 4–5 | 5 | 3–4 | 4–5 | 4–5 | 4 |
| 4 | 5 | 4–5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 3–4 | 5 | 4–5 | 4 |
| 5 ^b | 3–4 | 3 | 4–5 | 4–5 | 3–4 | 4 | 4–5 | 4–5 | 5 | 3 | 5 | 5 | 5 |
| 6 | 5 | 4 | 5 | 5 | 4–5 | 5 | 5 | 5 | 5 | 4 | 4–5 | 4–5 | 2–3 |
| 7 | 3 | 1–2 | 3–4 | 3–4 | 4 | 4–5 | 5 | 5 | 4–5 | 2–3 | 4 | 3–4 | 3 |

UC, uncleared; AC, alkali cleared; RC, reduction cleared; P, polyester; N, nylon.

^a Staining.^b Measured in 1% o.m.f.

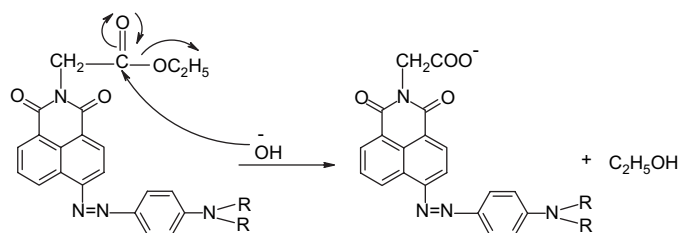


Fig. 5. Hydrolysis of dyes in alkaline media.

displayed low fastness to light and moderate/good wash fastness. The dyes with ester groups proved to have potential alkali-clearable properties.

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