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Dyes and Pigments 69 (2006) 79–92

DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis and spectroscopic studies of some naphthalimide based disperse azo dyestuffs for the dyeing of polyester fibres

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Received 28 October 2004; received in revised form 11 December 2004; accepted 11 February 2005

Abstract

A series of monoazo disperse dyestuffs derived from some naphthalimide derivatives were prepared. 4-Amino-*N*-methyl (alternatively *N*-ethyl, *N*-propyl, *N*-butyl) derivatives of naphthalimide were used as the diazo components and β-naphthol, *N*,*N*-diethyl-*m*-toluidine and *p*-aminoacetophenone constituted the coupling components.

The various 4-aminonaphthalimide derivatives mentioned above were all prepared by standard reactions from acenaphthene as the starting material. The reaction conditions were varied in order to obtain optimal yields for each stage of the preparation to obtain the corresponding 4-aminonaphthalimide derivative as the diazo component which was subsequently purified. The coupling components were purchased and were of analytical grade. Diazotisation and coupling reactions were carried out in order to obtain the final dyestuffs. Again maximal yields were sought after and the reaction conditions were varied accordingly.

The final dyestuffs were recrystallised in order to be attained in a purified form. The obtained dyestuffs and their corresponding intermediates were characterized by the use of elemental analysis, DSC, FTIR, H NMR, and UV–visible spectroscopic techniques.

Spectrophotometric investigations of the prepared dyestuffs in different solvents were carried out in order to obtain their absorption maxima, halochromic effects and various intensities. The dyestuffs were finally dyed on polyester fibres in order to investigate their dyeing properties and the obtainable colour gamut.

Keywords: Acenaphthene; 4-Aminonaphthalimide derivatives; Synthesis; Characterization; Disperse dyestuffs; Dyeing

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1. Introduction

Pioneering work on naphthalimides and their derivatives has been researched to assess their role as intermediates for dyestuff preparation [1–5].

Other related compounds have also been investigated such as heterocyclic derivatives of naphthalimides, phenylazophthalimides and 1,8-naphthalic anhydrides [6,7]. These compounds have been considered for the preparation of disperse dyestuffs, dyestuffs for other polymer fibres, acid dyestuffs, dyestuffs for polymeric materials and dyestuffs capable of copolymerization.

Naphthalimides have been investigated in a number of ways to examine their use as intermediates for dyes to be applied on both synthetic and natural fibres as well as on other polymeric materials. Derivatives of *N*-methylnaphthalimidoazobenzene have been utilized to produce a series of disperse dyestuffs in order to compare them with the analogous derivatives of phenylazobenzene by means of UV–visible absorption spectra in DMF [8]. Detailed investigation of the structure and properties of naphthalimide dyestuffs derived from pyrazolone have been carried out. The investigation examined the

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0143-7208/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2005.02.007

consequences of using the *N*-methyl and sulpho derivatives of aminonaphthalenes, 3- and 4-aminonaphthalimides as diazo components and derivatives of 1-phenyl-3-methylpyrazol-5-one as coupling components [9]. The fluorescent properties of naphthalic derivatives and their anhydrides have been discussed [10].

Aminonaphthalimides are known to produce yellow dyestuffs for synthetic polymer fibres [11]. The earliest industrial use of such compounds was Celliton Brilliant yellow FFACF (C.I. Disperse yellow 11, C.I. 56200), viz *N*-2,4-dimethylphenyl-4-amino-1,8-naphthalimide. Deficiencies in fastness properties, of these dyestuffs especially on polyester fibres, lead to the development of more satisfactory dyestuffs, e.g. derivatives of 7*H*-benzimidazo-[2,1-*a*]-benz-[*d*,*e*]-isoquinolin-7-one [11], naphthalene-1,4,5,8-tetra carboxylic acid [11], benzo-[*k*,*l*]-thioxanthene-3,4-dicarboxylic acid [11].

Phenylazo derivatives of 1,8-naphthalimides giving scarlet to bluish-red hues on synthetic polymer fibres can be obtained [6] by coupling 4-hydroxy-1,8-naphthalimides with diazotised arylamines. Diazotisation of 4-amino-1,8-naphthalimides, optionally substituted in the 3-position by nitro or halogeno groups, and coupling to arylamines will give red to blue disperse dyestuffs [6] and similar coupling to 2,6-dihydroxy-3-cyano-4-methylpyridine affords yellow pigments.

It has been reported [8] that benzeneazonaphthalimide dyestuffs prepared from 4-aminonaphthalimide have a very intense colour due to the polar forms which occur under normal conditions. The proportion of the different forms of the dyestuff structure depends on the type of dialkylamino group in the coupling component. Polyester fibres can be dyed with these dyestuffs to give reddish-blue shades, while the 3-isomers give orange hues.

It has been shown in the last decade investigations [9] that the use of diazo components such as 4-aminonaphthalimides have advantageous effects on the dyeing properties of the derived disperse azo dyestuffs. The presence of the naphthalimide system also leads to a deep and intense colour.

In general, the relationship between the colour and the structure of azo dyestuffs [12] is dependent on the polarization of the molecule, this being the result of the interaction between electron-acceptor and -donor groups at opposite ends of the conjugated bond system.

In the present study a series of the monoazo disperse dyestuffs have been obtained utilizing 4-amino-*N*-methyl (or alternatively, *N*-ethyl, *N*-propyl, *N*-butyl) naphthalimide as the diazo components and β-naphthol, *N*,*N*-diethyl-*m*-toluidine and *p*-aminoacetophenone as the coupling components. To this end, acenaphthene (as the starting material) was nitrated and further reacted by various unit processes such as oxidation, amination, reduction, diazotisation and coupling to obtain synthesized monoazo disperse dyestuffs. The dyestuffs were then purified and characterized together with their corresponding intermediates. The spectrophotometric properties of the prepared disperse dyestuffs in various solvents were examined. The absorption maxima of these dyestuffs, their halochromic effects, and their intensities have also been obtained.

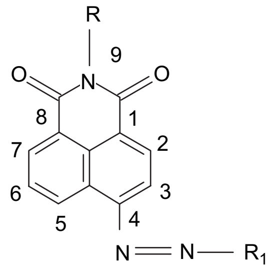


Fig. 1. General formula of the prepared mono azo disperse dyestuff, where R = CH_3, C_2H_5, C_3H_7, C_4H_9; R_1 = β-naphthol, *N*,*N*-diethyl-*m*-toluidine, *p*-aminoacetophenone.

The prepared dyestuffs were subsequently dyed on polyester fibres and finally their optical and dyeing properties; light fastnesses, wash fastnesses and sublimation fastnesses were determined.

General formula of the prepared monoazo disperse dyestuffs is given in Fig. 1.

2. Experimental

2.1. Materials

All compounds used in this study were of analytical grade unless otherwise stated.

2.2. Procedures

(i) Preparation of 5-nitroacenaphthene was carried out by the use of a modified method of Okazaki et al. [13].
(ii) Preparation of 4-nitro-1,8-naphthalic anhydride was carried out according to the method of Okazaki et al. [14].
(iii) Preparation of 4-nitro-*N*-methyl (or alternatively *N*-ethyl, *N*-propyl, or *N*-butyl)-1,8-naphthalimide and the subsequent reduction of the nitro group to an amino group was carried out according to a modified method of Dongwu and Alexiou [15,16].
(iv) The diazotisation of the prepared diazo components (i.e. 4-amino-*N*-methyl, or the alternative *N*-ethyl, *N*-propyl and *N*-butyl derivatives) were carried out by the nitrosylsulphuric acid procedure, and the coupling reaction with β-naphthol, *N*,*N*-dimethyl-*m*-toluidine and aminoacetophenone were carried out according to Peters and Wojciechowski [6,17].

2.3. Instrumentation

The purified dyestuffs and their corresponding intermediates were characterized by the following instruments:

1. FTIR measurements were carried out on a Bomene, Canda instrument (by the KBr method).
2. H NMR measurements were carried out on a 500 MHz Joel instrument.
3. DSC thermal analyses were carried out on a Dupont 2000 DSC instrument.
4. UV–visible spectrophotometry was carried out on a Cecil double beam transmission spectrophotometer.

λ_{max}, ε, halochromic and solvatochromic effects were also determined.

2.4. Application and properties

The prepared dyestuffs were applied to polyester fibre samples and the following properties were determined.

1. *Optical properties*: The reflectances of the dyed samples were measured on a Macbeth 7000 A color eye reflection spectrophotometer from which the colour coordinates and the Kubelka–Munk constants were calculated.
2. *Light fastness and wash fastness properties*: The light fastness, wash fastness and sublimation fastness of each dyestuff was determined according to ISO 105/B, ISO 105/C and ISO 105 PO1 standards, respectively.

3. Results and discussion

3.1. Synthesis of 5-nitroacenaphthene

The most convenient starting material for the preparation of naphthalic anhydride is acenaphthene, which is readily available as a by-product of processes in the coal industry.

5-Nitroacenaphthene is the main product when acenaphthene reacts with nitric acid in acetic acid at room temperature [13], because of the meta-directing effect of the carbonyl group in naphthalic acid or anhydride only 3-substituted naphthalic anhydrides can be prepared directly by electrophilic substitution [18].

The 2- and 4-substituted naphthalic anhydrides are prepared by the substitution of acenaphthene in which the $-CH_2$ groups direct electrophilic substituents into the *ortho*- or *para*-positions depending on the chosen reaction conditions. Direct nitration of acenaphthene gave yellow needles of 5-nitroacenaphthene with a melting point of 101–102.2 °C after being recrystallised from ethanol with an overall yield of 88.6%. The measured melting point was in accordance with the reported melting points [15,16].

The FTIR, H NMR spectra and elemental analysis (EA) of this compound are shown in Table 1.

3.2. Synthesis of 4-nitronaphthalic anhydride

5-Nitroacenaphthene was oxidized according to a method proposed by Okasaki et al. [14], in which sodium or potassium dichromate was used as the oxidizing agent in hot glacial acetic acid as the solvent. The precipitate was recrystallised from nitric acid giving a m.p. of 229–230 °C.

The yield of the pale yellow needles of 4-nitronaphthalic anhydride was 45–55%. The FTIR, H NMR spectra and elemental analysis of 4-nitronaphthalic anhydride are also shown in Table 1.

3.3. Synthesis of the derivatives of naphthalimides

The imidation of aromatic cyclic anhydrides is a nucleophilic displacement reaction in which the reaction of the attacking amine is carried out in an alcoholic medium under a reflux condition. For preparing 4-nitro-*N*-methyl (or ethyl, propyl, butyl)-1,8-naphthalimide, 4-nitro-1,8-naphthalic anhydride was reacted with the corresponding amine and the reaction was followed to completion by the aid of TLC on silica gel 60.

The yields (*Y*%) of products derived from 4-nitro-*N*-substituted 1,8-naphthalimides, their melting points, the solvents used for the recrystallisation and the form of crystals obtained are given in Table 2. The FTIR, H NMR spectra and EA of 4-nitro-*N*-substituted 1,8-naphthalimides are given in Table 1.

3.4. Synthesis of 4-amino derivatives of naphthalimides

Preparation of 4-amino-1,8-naphthalimide as an intermediate plays a very important role in the naphthalimide dyestuff series. The naphthalimides having an amino group in the 4-position tend also to be fluorescent. However, the improved water-solubility of the 4-amino compounds compared with the 4-alkylamino derivatives is advantageous when used as fluorescent probes and labels in biological and medical examinations [15]. In early works [1–5], some amino-naphthalimide dyestuffs were prepared by the nucleophilic attack of ammonia on various naphthalic anhydrides or imides. However, 4-amino-*N*-substituted 1,8-naphthalimides were obtained by the reaction of 4-nitro-*N*-substituted 1,8-naphthalimides with tin(II) chloride as the reducing agent and hydrochloric acid as the

Table 1
The FTIR, H NMR spectra and EA of 4-nitro-*N*-substituted naphthalimide derivatives

Compounds	FTIR (cm^{-1})	H NMR (δ)	EA found (%)			Required (%)		
			C	H	N	C	H	N
5-Nitroacenaphthene	C–H str. Ar. 3070; C–H str. Aliphatic 2947.68; C=C str. 1620.07, 1596.16; NO_2 str. 1326.33, 1508.96	3.43–3.49(4H, $CH_2{-}CH_2$); 7.31–7.33(1H, 8-H); 7.43–7.47(1H, 3-H); 7.66–7.73(1H, 7-H); 8.47–8.49(1H, 6-H); 8.52–8.56(1H, 4-H)	72	4.4	6.6	72.36	4.52	7.04
4-Nitro-1,8-naphthalic anhydride	C–H str. Ar.3079.86; C=O str., 1756.88, 1787.32; C=C str., 1583.96; NO_2 str.,1302.91, 1526.76	8.06–8.1 (1H, 6-H); 8.46–8.48(1H, 5-H); 8.74–8.76(1H, 7-H); 8.79–8.80(1H, 2-H); 8.94–8.96(1H, 3-H)	59.5	2.4	5.6	59.26	2.06	5.76
4-Nitro-*N*-methylnaphthalimide	C–H str. Ar.3079.24; C=O str. 1671.6, 1707; C=C str. 1583.86; NO_2 str. 1351.55,1524.99	3.58(3H, NCH_3); 7.98(1H, 6-H); 8.40(1H, 5-H); 8.69(1H, 7-H); 8.73 (1H, 2-H); 8.83(1H, 3-H)	61	3.3	10.8	60.94	3.13	10.93
4-Nitro-*N*-ethylnaphthalimide	C–H str. Ar. 3077.61; C=O str. 1660.95, 1691.89; C=C 1614.67; NO_2 str. 1331.19, 1527.14	1.32–1.37(3H, $\mathrm{NCH_2C}H_3$); 4.21–4.25(2H, $\mathrm{N{-}C}H_2\mathrm{CH_3}$); 7.94–8(1H, 6-H); 8.37–8.42(1H, 5-H); 8.65–8.68(1H, 7-H); 8.69–8.75(1H, 2-H); 8.77–8.80(1H, 3-H)	62.1	3.9	10.4	62.2	3.7	10.37
4-Nitro-*N*-*n*-propylnaphthalimide	C–H str. Ar. 2962.02; C=O str. 1660.47, 1707.62; C=C str. 1582.94; NO_2 str. 1345.37, 1525.62	1.01–1.04(3H, $\mathrm{NCH_2CH_2C}H_3$); 1.75–1.81(2H, $\mathrm{NCH_2C}H_2\mathrm{CH_3}$); 4.14–4.17(2H, $\mathrm{NC}H_2\mathrm{CH_2CH_3}$); 7.96–8(1H, 6-H); 8.39–8.41(1H, 5-H); 8.67–8.69(1H, 7-H); 8.72–8.74(1H, 2-H); 8.82–8.84(1H, 3-H)	63.3	4.4	9.8	63.38	4.24	9.85
4-Nitro-*N*-*n*-butylnaphthalimide	C–H str. Ar. 2965; C–H str. Aliphatic 2864; C=O str. 1659, 1704; NO_2 str. 1346, 1533	0.99(3H, $\mathrm{NCH_2CH_2CH_2C}H3$); 1.45–1.46(2H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$); 1.57–1.72(2H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$); 4.19(2H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$); 7.98–8(1H, 6-H); 8.39–8.41(1H, 5-H); 8.68–8.69(1H, 7-H); 8.73–8.74(1H, 2-H); 8.82–8.84(1H, 3-H)	64.8	4.8	9.2	64.43	4.7	9.4

solvent [17], giving a facile and economical product. The yields of products derived from 4-amino-*N*-substituted 1,8-naphthalimides, their melting points, the solvents used for recrystallisation and the form of crystals obtained are illustrated in Table 3. The FTIR, H NMR spectra and EA of 4-amino-*N*-substituted 1,8-napthalimides are given in Table 4.

3.5. Preparation of monoazo disperse dyes

Diazotisation of naphthalimides were carried out with the aid of nitrosylsulphuric acid [6], the procedure being the dissolution of sodium nitrite in concentrated sulphuric acid followed by slow addition of the given amine to the prepared nitrosylsulphuric acid at below

Table 2
Preparation of 4-nitro-*N*(9)-substituted 1,8-naphthalimides

Reaction conditions				Product					
Series No.	Amine	Solvent	*t* (min)	R	M.p. (°C)	*Y* (%)	Solvent of recrystallisation	Form of crystals	Colour of crystals
I	NH_2CH_3	Ethanol	75	CH_3	211.02	85	Acetic acid and ethanol	Needles	Yellow
II	$NH_2C_2H_5$	Ethanol	75	C_2H_5	193.53	82	Acetic acid	Needles	Yellow
III	$NH_2C_3H_7$	Ethanol	75	C_3H_7	138.18	73.3	Ethanol	Needles	Pale yellow
IV	$NH_2C_4H_9$	Ethanol	75	C_4H_9	105.25	72.5	Ethanol	Needles	Faun

Table 3
Preparation of 4-amino-*N*-substituted 1,8-naphthalimides

Reaction conditions				Product					
Series No.	Amine	Solvent	*t* (h)	R	M.p. (°C)	*Y* (%)	Solvent of recrystallisation	Form of crystals	Colour of crystals
I	NH_2CH_3	Methanol	1.15	CH_3	359.82	93	Nitrobenzene	Needles	Orange–brown
II	$NH_2C_2H_5$	Methanol	1.45	C_2H_5	289.21	99	Acetic acid	Needles	Orange
III	$NH_2C_3H_7$	Ethanol	2.15	C_3H_7	258.46	97.9	Ethanol	Needles	Orange–reddish yellow
IV	$NH_2C_4H_9$	Ethanol	2.15	C_4H_9	180.97	70	Ethanol	Needles	Orange

10 °C until the diazonium salt was formed (note: at higher temperatures the diazonium salt of the series will decompose and nitrogen gas will be evolved) [19,20]. Solutions of the coupling components namely β-naphthol, *N*,*N*-diethyl-*m*-toluidine and *p*-aminoacetophenone were prepared to which the prepared diazonium salts were added gradually to yield different dyestuffs.

3.5.1. Diazotisation

The general method of diazotisation was as follows: 1.5 mol sulphuric acid (98%) was cooled to below 10 °C and 0.13 g (2 mmol) sodium nitrite was added with stirring in a 20 min period, and the stirring continued for a further 10 min, after which the temperature was gradually increased to 65 °C, until all the sodium nitrite was dissolved. The solution was then cooled to below 10 °C and 2 mmol 4-amino-*N*-substituted naphthalimide was added gradually over a 35 min period, the temperature being kept below 10 °C, this was followed by the addition of 1 cc glacial acetic acid over a 10 min period to the reaction mixture. The mixture was stirred for a further 3 h at below 10 °C and the final precipitate was filtered and dried.

3.5.2. Coupling

Two millimoles of β-naphthol was dissolved in 8.5 mol ethanol to which the diazonium salt was added gradually over a 25 min period, the temperature being

Table 4
The FTIR, H NMR spectra and EA of 4-amino-*N*(9)-substituted naphthalimide derivatives

Compounds	FTIR (cm^{-1})	H NMR (*δ*)	EA found (%)			Required (%)		
			C	H	N	C	H	N
4-Amino-*N*-methylnaphthalimide	N–H str. 3429.55, 3354.02; C–H str. Ar. 2925.68; C=O str. 1676.09, 1645.83	3.54(3H, $NC\mathit{H}_3$); 5.30–5.37(2H, NH_2); 6.91(1H, 3-H); 7.72(1H, 6-H); 8.11–8.15(1H, 2-H); 8.52–8.56(1H, 5-H); 8.62–8.71(1H, 7-H)	68.6	4.3	12.3	69.03	4.42	12.39
4-Amino-*N*-ethylnaphthalimide	N–H str. 3456.3, 3346.91; C–H str. Ar. 2980; C=O str. 1672.52, 1654.73	1.25–1.33(3H, $NCH_2C\mathit{H}_3$); 4.22–4.23(2H, $NC\mathit{H}_2CH_3$); 4.95(2H, NH_2); 6.88–6.9(1H, 3-H); 7.64–7.69(1H, 6-H); 8.09–8.11(1H, 2-H); 8.41–8.43(1H,5-H); 8.60–8.66(1H, 7-H)	69.6	5.2	11.3	70	5	11.67
4-Amino-*N*-*n*-propylnaphthalimide	N–H str. 3435.34, 3356.81; C–H str. Ar. 2928.96; C=O str. 1675.9, 1637.66	0.99–1.02(3H, $NCH_2CH_2C\mathit{H}_3$); 1.73–1.79(2H, $NCH_2C\mathit{H}_2CH_3$); 4.10–4.14(2H, $NC\mathit{H}_2\ CH_2CH_3$); 4.94(2H, NH_2); 6.88–6.90(1H, 3-H); 7.64–7.67(1H, 6-H); 8.1–8.11(1H, 2-H); 8.41–8.43(1H, 5-H); 8.60–8.61(1H, 7-H)	70.65	5.6	11	70.87	5.51	11.02
4-Amino-*N*-*n*-butylnaphthalimide	N–H str. 3437.98, 3359.16; C–H str. Ar. 2956.23; C=O str. 1674.93, 1639.93	0.95–1(3H, $NCH_2CH_2CH_2C\mathit{H}3$); 1.42–1.47(2H, $NCH_2CH_2C\mathit{H}_2CH_3$); 1.68–1.74(2H, $NCH_2C\mathit{H}_2CH_2CH_3$); 4.14 – 4.18(2H, $NC\mathit{H}_2CH_2CH_2CH_3$); 4.88–5.18(2H, NH_2); 6.87–6.88(1H, 3-H); 7.62–7.65(1H, 6-H); 8.09–8.11(1H, 2-H); 8.39–8.43(1H, 5-H); 8.57–8.63(1H, 7-H)GGGG	71.2	6.1	10.3	71.64	5.97	10.45

kept below 10 °C. The mixture was stirred for 3 h and was filtered followed by washing with hot water and drying.

The second coupler was *N*,*N*-diethyl-*m*-toluidine 2 mmol of which was dissolved in 8 cc of water and 0.4 cc of hydrochloric acid (30%) and the temperature reduced to under 5 °C and the diazonium salt was added to the coupler. Then saturated sodium acetate solution was added to the mixture until a pH of 4–5 was reached. Then the precipitate was filtered and washed with hot water and dried.

The third coupler was *p*-aminoacetophenone 2 mmol of which was dissolved in 10 cc of water and 0.5 cc of hydrochloric acid (30%) and the temperature reduced to under 5 °C and the diazonium salt was added to the coupler. Then saturated sodium acetate solution was added to the mixture until a pH of 4–5 was reached. The mixture was stirred for 3 h then the precipitate was filtered and washed with hot water and dried.

The corresponding diazo and coupling components, their respective yields and the measured melting points of each synthesized dye are given in Table 5. The FTIR, H NMR spectra and EA of the synthesized dyestuffs are shown in Table 6.

3.6. Spectral characteristics of the dyestuffs

A series of dyestuffs of the general formula (1), having different R,R_1 substituents were synthesized. The dyestuffs had various hues e.g. yellow, red and violet as given in Table 5.

The role of the nature of the *N*-substitutions and the different coupling components in the preparation of monoazo disperse dyestuffs derived from naphthalimides are described in the literature [6,8,9,11,12,17,21], as having pronounced effects on the colour of the dyestuffs, i.e. position of absorption maximum (λ_{max}), and brightness of shade.

The range of prepared dyestuffs containing naphthalimide residues had yields ranging from 67% to 95% (Table 5), after recrystallisation. Table 7 shows the corresponding λ_{max} of the each dyestuff dissolved in various solvents.

The λ_{max} values show the position of the most intense absorption band, which depends on the possibility of the dye existing in the azo or the hydrazone forms.

Introduction of the phenylazo chromophore into the 4-position of 1,8-naphthalimides results in a large bathochromic shift in the absorption maxima in chlorobenzene (Table 7) compared with the usual yellow colour of 4-nitro-*N*-substituted 1,8-naphthalimides (Table 2) and the usual orange colour of 4-amino-*N*-substituted 1,8-naphthalimides (Table 3).

The dyestuffs **2**, **4**, **6** and **8** (Table 7) in PhCl absorb between 532.8 nm and 535.2 nm, but the *p*-aminoacetophenone (**9**) in Table 7 as a coupler shows an expected large hypsochromic effect to 108.9 nm as compared to the corresponding *N*,*N* diethyl-*m*-toluidine derivative, because the electron withdrawing effect of the carbonyl end group of the compound (**9**) decreases the basicity of $-NH_2$ group and therefore this coupler is not fully able to act as a donor group to the chromogenic system as a whole.

The colour of the dyestuffs **2**, **4**, **6** and **8** is relatable to the typical electron delocalisations in the conjugated donor–acceptor azo chromogens, as can be observed in structure I. Whilst the nature of the imide residue R is not very significant in the context of colour change, the colour of the dyestuffs is influenced by the introduction of additional donor groups into the coupling component and/or acceptor groups ortho to the azo link in the naphthalene residue [6].

In dyestuffs **2**, **4**, **6** and **8**, the influence of naphthyl residue in the diazo component and of the two carbonyl substituents, which in addition to structure I, can result in a delocalisation structure II, as shown below.

Analogously substituted 4-aminoazobenzenes, e.g. III (R = 4′-NO_2 and R = 4′-CN), having λ_{max} at 490 nm and 466 nm, respectively [22] are still 45.2 nm and 69.2 nm more hypsochcromic compared to dyestuffs **2**, **4**, **6** and **8**.

Table 5
Dyestuffs derived from various diazo and coupling components

Dye	Diazo component	Coupling component	M.p. (°C)	*Y* (%)	Colour of crystals
1	4-Amino-*N*-methylnaphthalimide	β-Naphthol	230.70	74[a]	Red
2	4-Amino-*N*-methylnaphthalimide	*N*,*N*-Diethyl-*m*-toluidine	195.70	81	Bluish red
3	4-Amino-*N*-ethylnaphthalimide	β-Naphthol	283.04	73	Red
4	4-Amino-*N*-ethylnaphthalimide	*N*,*N*-Diethyl-*m*-toluidine	174.52	72	Bluish red
5[b]	4-Amino-*N*-(*n*-propyl)naphthalimide	β-Naphthol	279.43	95	Red
6	4-Amino-*N*-(*n*-propyl)naphthalimide	*N*,*N*-Diethyl-*m*-toluidine	160.40	78	Bluish red
7	4-Amino-*N*-(*n*-butyl)naphthalimide	β-Naphthol	260.00	77	Red
8	4-Amino-*N*-(*n*-butyl)naphthalimide	*N*,*N*-Diethyl-*m*-toluidine	142.47	67	Bluish red
9	4-Amino-*N*-(*n*-propyl)naphthalimide	*p*-Aminoacetophenone	228	86	Yellowish cream

[a] Percentage yield being more than reported by wojciechowski (i.e. 51.2%) [17].

[b] Synthesis and spectroscopic studies of this dye was presented as a paper in the World Textile Conference, 4th Autex Conference 2004 in France [26].

Table 6
The FTIR, H NMR spectra and EA of dyestuffs

Series No.	FTIR (cm^{-1})	H NMR (δ)	EA found (%)			Required (%)		
			C	H	N	C	H	N
1	N=N 1591.88; C–N str. 1366.21, 1140.77; C=O str. 1702.28, 1662.13; O–H str. 3416.65.	3.36–3.78(3H, NCH_3); 6.70–6.72(1H, OH); 7.17(1H, 3′-H); 7.39–7.46(1H, 8′-H); 7.49–7.51(1H, 6′-H); 7.66–7.72(1H, 7′-H); 7.87–7.91(2H, 4′,5′-H); 8.23–8.26(1H, 6-H); 8.31–8.33(1H, 5-H); 8.62–8.67(2H, 2,7-H); 8.74–8.78(1H, 3-H)	71.85	4.2	10.55	72.44	3.94	11.02
2	N=N 1588.25; C–N str. 1355.35, 1184.04; C=O str. 1693.46, 1656.6	1.26–1.29(6H, 4′-N $(CH_2C\mathit{H}_3)_2$); 2.75(3H, CH_3*m*-toluidine); 3.48–3.51(4H, 4′-N$(C\mathit{H}_2CH_3)_2$); 3.55(3H, N–$C\mathit{H}_3$); 6.61(2H, 3′-H, 5′-H); 7.77–7.80(1H, 6-H); 7.86–7.88(1H, 5-H); 7.91–7.93(1H, 6′-H); 8.57–8.59(1H, 7-H); 8.61–8.62(1H, 2-H); 9.20–9.21(1H, 3-H)	71.5	5.8	13.5	72	6	14
3	N=N 1582.68; C–N str. 1339.98, 1066.06; C=O str. 1693.89, 1654.74; O–H str. 3423.98	1.33–1.34(3H, $NCH_2C\mathit{H}_3$); 4.16–4.17(2H, $NC\mathit{H}_2CH_3$); 6.6–6.62(1H, 3′-H); 7.38–7.39(1H, 8′-H); 7.43–7.44(1H, –OH); 7.45–7.47(1H, 7′-H); 7.57–7.59(1H, 5′-H); 7.70–7.73(2H, 6,6′-H); 8.10–8.12(1H, 4′-H); 8.19–8.24(1H, 5-H); 8.31–8.33(1H, 7-H); 8.49–8.52(2H, 2,3-H)	73	4.5	10.2	72.91	4.3	10.63
4	N=N 1593.42; C–N str. 1344.69, 1068.45; C=O str. 1691.87, 1654.5	1.26–1.29(6H, 4′-N$(CH_2C\mathit{H}_3)_2$); 1.34–1.37(3H, N–$CH_2C\mathit{H}_3$); 2.77(3H, 2′-CH_3); 3.47–3.51(4H, 4′-N$(C\mathit{H}_2CH_3)_2$); 4.24–4.28(2H, N–$C\mathit{H}_2$); 6.62(2H, 3′-H, 5′-H); 7.79–7.82(1H, 6-H); 7.91–7.92(1H, 5-H); 7.95–7.97(1H, 6′-H); 8.61–8.62(1H, 7-H); 8.63–8.64(1H, 2-H); 9.24–9.25(1H, 3-H)	71.9	6.3	13.1	72.46	6.28	13.53
5	N=N 1578.85; C–N str. 1066.78, 1343.17; C=O str. 1651.43, 1696.57; O–H str. 3437.02	0.87–1.02(3H, $NCH_2CH_2C\mathit{H}_3$); 1.77(2H, $NCH_2C\mathit{H}_2CH_3$); 4.12(2H, $NC\mathit{H}_2CH_2CH_3$); 6.72–6.73(1H, 3′-H); 7.37–7.44(1H, 8′-H); 7.54–7.56(2H, 7′-H,1H,OH); 7.69–7.74(1H, 5′-H); 7.78–7.82(2H, 6,6′-H); 8.28–8.30(1H, 4′-H); 8.45–8.48(2H, 5, 7-H); 8.62(2H, 2, 3-H)	73.5	4.8	10.2	73.35	4.65	10.26

(*continued on next page*)

Table 6 (*continued*)

Series No.	FTIR ($\mathrm{cm^{-1}}$)	H NMR (δ)	EA found (%)			Required (%)		
			C	H	N	C	H	N
6	N=N 1588.76; C–N str. 1326.74, 1075.04; C=O str. 1691.89, 1655.92	1.01–1.04(3H, $\mathrm{NCH_2CH_2C}H_3$); 1.25–1.28(6H, 4′-$\mathrm{N(CH_2C}H_3)_2$); 1.76–1.80(2H, $\mathrm{NCH_2C}H_2\mathrm{CH_3}$); 2.75(3H, 2′-C$H_3$); 3.47–3.51(4H, 4′-N (C$H_2$–$\mathrm{CH_3})_2$); 4.13–4.16(2H, $\mathrm{NCH_2}$); 6.61(2H, 3′-H, 5′-H); 7.77–7.80(1H, 6-H); 7.85–7.88(1H, 5-H); 7.93–7.95(1H, 6′-H); 8.57–8.59(1H, 7-H); 8.60–8.62(1H, 2-H); 9.21–9.22(1H, 3-H)	72.7	6.4	12.6	72.9	6.54	13.08
7	N=N 1584.64; C–N str. 1353.2, 1075.38; C=O str. 1693.34, 1656.46; O–H str. 3417.67	0.93–1.01(3H, $\mathrm{NCH_2CH_2CH_2C}H_3$); 1.26–1.37(2H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$; 1.65–1.74(2H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$); 4.12–4.19(2H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$); 6.75–6.79(1H, 3′-H); 7.46–7.47(1H, 8′-H); 7.55–7.60(2H, 7′-H, 1H, OH); 7.72–7.76(1H, 5′-H); 7.84–7.90(2H, 6,6′-H); 8.31–8.35(1H, 4′-H); 8.50–8.54(2H, 5,7-H); 8.63–8.68(2H, 2,3-H)	73.3	5.2	9.5	73.76	4.96	9.93
8	N=N 1577.23; C–N str. 1354.13, 1078.31; C=O str. 1696.41, 1651.6	0.98–1.01(3H, $\mathrm{NCH_2CH_2CH_2C}H_3$); 1.26–1.29(6H, 4′-N $\mathrm{(CH_2C}H_3)_2$); 1.45–1.51(2H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$); 1.71–1.77(2H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$); 2.77(3H, 2′-$\mathrm{CH_3}$); 3.49–3.50(4H, 4′-N(C$H_2\mathrm{CH_3})_2$); 4.18–4.21(2H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$); 6.63(2H, 3′-H,5′-H); 7.80–7.83(1H, 6-H); 7.87–7.93(1H, 5-H); 7.96–7.98(1H, 6′-H); 8.59–8.62(1H, 7-H); 8.63–8.64(1H, 2-H); 9.24–9.26(1H, 3-H)	72.85	6.7	12.2	73.3	6.79	12.67
9	N=N, 1576.28; C–N str. 1347.12, 1163.94; C=O str. 1693.35, 1660.07; N–H overtone bend 3205.26; C=O str. Ketone acetophenone 1739.08	1.04(3H, $\mathrm{NCH_2CH_2C}H_3$); 1.78(2H, $\mathrm{NCH_2C}H_2\mathrm{CH_3}$); 2.59–2.66(3H, $\mathrm{COC}H_3$); 4.15(2H, $\mathrm{NC}H_2\mathrm{CH_2CH_3}$); 7.50–7.52(1H, 3′-H); 7.70–7.73(1H, 6-H); 7.90–7.92(2H, $\mathrm{NH_2}$); 8.01–8.02(1H, 5-H); 8.06–8.08(1H, 7-H); 8.58–8.63(2H, 2,3-H); 9.03–9.07(2H, 4′, 6′-H)	69.0	5.0	14.1	69.0	5.0	14.0

Table 7
UV–visble electronic spectral data of dyestuffs (**1**–**9**)

Dye	R	R_1	MeOH		1 M-H_2SO_4		10 M-H_2SO_4		PhCl	
			λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
1	CH_3	β-Naphthol	335.3		335.0		350.3			
			509.6	[a]	519.5	[a]	572.0	[a]	526.5	4.175
2	CH_3	*N*,*N*-Diethyl-*m*-toluidine	356.0	3.36	383.6	4.23	375.8	3.94		
			538.1	4.04	534.2	4.02	542.6	4.57	535.2	4.52
3	C_2H_5	β-Naphthol	350.4		334.5		358.8			
			519.9	[a]	517.2	[a]	571.2	[a]	527.0	4.417
4	C_2H_5	*N*,*N*-Diethyl-*m*-toluidine	356.3	3.85	383.3	4.12	368.9	3.91		
			539.6	4.6	531.2	3.96	543.5	4.54		
									532.8	4.55
5	*n*-C_3H_7	β-Naphthol	350.0		330.3		356.1			
			520.8	[a]	520.8	[a]	572.4	[a]	525.3	4.49
6	*n*-C_3H_7	*N*,*N*-Diethyl-*m*-toluidine	347.0	3.79	347.3	4.079	370.7	4.036		
			541.4	4.45	534.5	3.79	543.5	4.58		
									534.3	4.50
7	*n*-C_4H_9	β-Naphthol	381.3		370.2		370.5			
			539.7	[a]	543.3	[a]	572.4	[a]	526.1	4.44
			600.0		600.0					
8	*n*-C_4H_9	*N*,*N*-Diethyl-*m*-toluidine	383.3	2.92	385.7	4.13	378.5	4.41		
			541.1	3.73	533.9	3.91	542.9	4.92		
									534.9	4.53
9	*n*-C_3H_7	*p*-Aminoaceto-phenone	329.4	3.32	344.1	4.01	346.5	3.98		
			429.3	3.71	374.4	3.79	380.0	3.18	425.4	4.59
					435.0	3.59				

[a] Some dyestuffs were not completely soluble in some of the solvents, therefore the molar extinction coefficients could not be calculated correctly and so were ommited from the table.

The effect of the naphthyl residue and the carbonyl groups are, therefore, apparent and the dyestuffs **2**, **4**, **6** and **8** are bathochromic with respect to the analogous aminoazobenzenes III. The effect of $-CH_3$ group in the coupling component at ortho-position to the azo link in the synthesized dyestuffs is more bathochromic (≈ 8 nm) compared to when the $-CH_3$ group is not present as mentioned in Wojciechowski works [21,23].

The performance properties of disperse dyes based on 4-aminoazobenzene III are considerably influenced by the nature of the substituents at the 4- and 4′-positions. The visible absorption maxima of several donor-substituted azobenzenes were considered [22], and it is clear that for a monosubstituted dye, the bathochromic shift depends in the expected manner on the electron donating strength of the substituent. Since the electronic transition in these compounds involves a general migration of electron density from the donor group towards the azo group, it is not surprising that electron withdrawing groups in the second benzene ring exert a bathochromic effect. The largest shift is observed for the para nitro group, and the smallest shifts for halogen atoms. It is found that the bathochromic shift in these series of disperse dyes is related roughly to the Hammett σ-constant for the electron withdrawing group [22].

Similar investigations have been carried out on naphthalimide series of disperse dyes [23], and the effect of the *N*,*N*-dialkylamino residue on the colour properties of some 4-aminonaphthalimide and *N*-methyl-4-aminonaphthalimide dyestuffs has been quantitatively determined by means of spectrophotometric measurements, in conjugation with PPP-MO calculations of electronic structure of the molecules.

In the present study as illustrated in structure I, the *N*,*N*-diethylamino residue acts as a donor group and the two carbonyl groups of naphthalimide residue act as acceptor groups, and following the same lines of reasoning, the mentioned dyestuffs **2**, **4**, **6** and **8** give a bathochromic shift effect whilst the *p*-aminoacetophenone derivative (**9**) in Table 7 has a hypsochromic shift effect.

The λ_{max} shifts of the prepared dyestuffs in various solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvent (Table 7) [23].

Of the readily available solvents with low dielectric constants ($\varepsilon = 5.6$), [23] chlorobenzene was used. This solvent slightly solvates the molecules of the compounds dissolved in it.

The substituent in the imide group ($R = CH_3$, C_2H_5, C_3H_7, C_4H_9) in general formula (1) only slightly affects the λ_{max} values (Table 7), on the basis that the imide nitrogen atom does not participate in the redistribution of electron density in the excited state of the dyestuffs.

The dyestuffs based on β-naphthol as a coupler (**1**, **3**, **5**, **7**) in PhCl in Table 7 absorb between 525.3 nm and 527.0 nm.

The colour of the dyestuffs **1**, **3**, **5** and **7** is related to azo–hydrazone tautomerism, since the two tautomeric forms will, in general, have different spectroscopic properties. It is found experimentally that the hydrazones always absorb at longer wavelengths than their azo tautomers. These two forms are shown in structures IV and V.

In aqueous solutions of $pH = 7$, the naphthol derivatives usually occur in the azo form. The absorption of the hydrazone form is very strongly shifted bathochromically in acid medium compared to the azo form, by as much as 62 nm depending on the degree of conjugation in the dyestuff (Table 7 azo form in methanol for dye **1**, $R = CH_3$ $\lambda_{max} = 509.6$ nm and in methanolic 10 M-H_2SO_4 $\lambda_{max} = 572.0$ were recorded).

The observations are illustrated in structures VII and VIII. These observations are in accord to the Griffiths [22] and Wojciechowski [23] results.

As noted above, the dyes can occur in two different hydrazone forms, viz, either with the imido system (amido–iminol tautomerism VI) or with the azo system (azo–hydrazone tautomerism V), according to Wojciechowski results [23].

Replacing the neutral methanolic solvent by solutions acidified with H_2SO_4 leads to significant changes in the spectra and to the appearance of new absorption bands in both the UV and the visible range (see Table 7). The dyestuffs studied have different proton-accepting centres, viz, azo, dialkylamino, and the carbonyl groups of a heterocyclic amide system.

In the UV range, there are only the naphthalene bands, characteristic for simple naphthalene derivatives which are ascribed to the absorption of the benzeneazonaphthalene (BAN) chromophore and in the visible range bands characteristic for azo dyestuffs [21]. In view of the insolubility of some dyestuffs, it was possible only to record their spectra in saturated solutions of unknown concentrations. This has no influence however on comparisons of the spectra of the dyestuffs.

Very characteristic changes are observed in the spectra recorded in methanolic solutions of 1 M- and 10 M-H_2SO_4.

All dyes **2**, **4**, **6** and **8** which are 4-substituted, usually show two absorption maxima in methanol which are characteristic for benzeneazonaphthalene derivatives.

In the UV range naphthalene bands are observed which are ascribed to the absorption of the benzeneazonaphthalene (BAN). Chromophore in the 349–370 nm range, and in the visible range the K-band ($\pi \rightarrow \pi^*$ shift) appears in the region 492–573 nm, characteristic for azo dyes. The present considerations are limited to a discussion of bands within 206–572 nm, where the known K and R bands ($n \rightarrow \pi^*$ shifts) appear and which show characteristic changes depending on the solvent used [21].

The equilibria existing in neutral and acidic solutions are illustrated in Scheme 1. A general pattern can be observed, resulting from the use of the coupling components containing the diethylamino group, which results in a bathochromic shift in the visible range (see Table 7), because of the formation of structures derived from $A_1 \leftrightarrow A_2$ (Scheme 1).

The azo derivatives of 4-aminonaphthalimide with couplers such as β-naphthol and *p*-aminoacetophenone show quite different physical, chemical and dyeing properties from the coupling component of diethylamino group. The presence of an azo group in the 4-position creates an additional possibility of electron interaction between the cyclic 6-membered amide system and the *N*,*N*-diethylamino group. The acceptor and donor character of these substituents should bring about a considerable bathochromic effect which can be observed in the λ_{max} of the dyestuffs in Table 7. Dyestuffs having different couplers such as *p*-aminoacetophenone, β-naphthol and *N*,*N*-diethylamino group in fact give yellow, red and red-blue dyeings on polyester fibres, respectively.

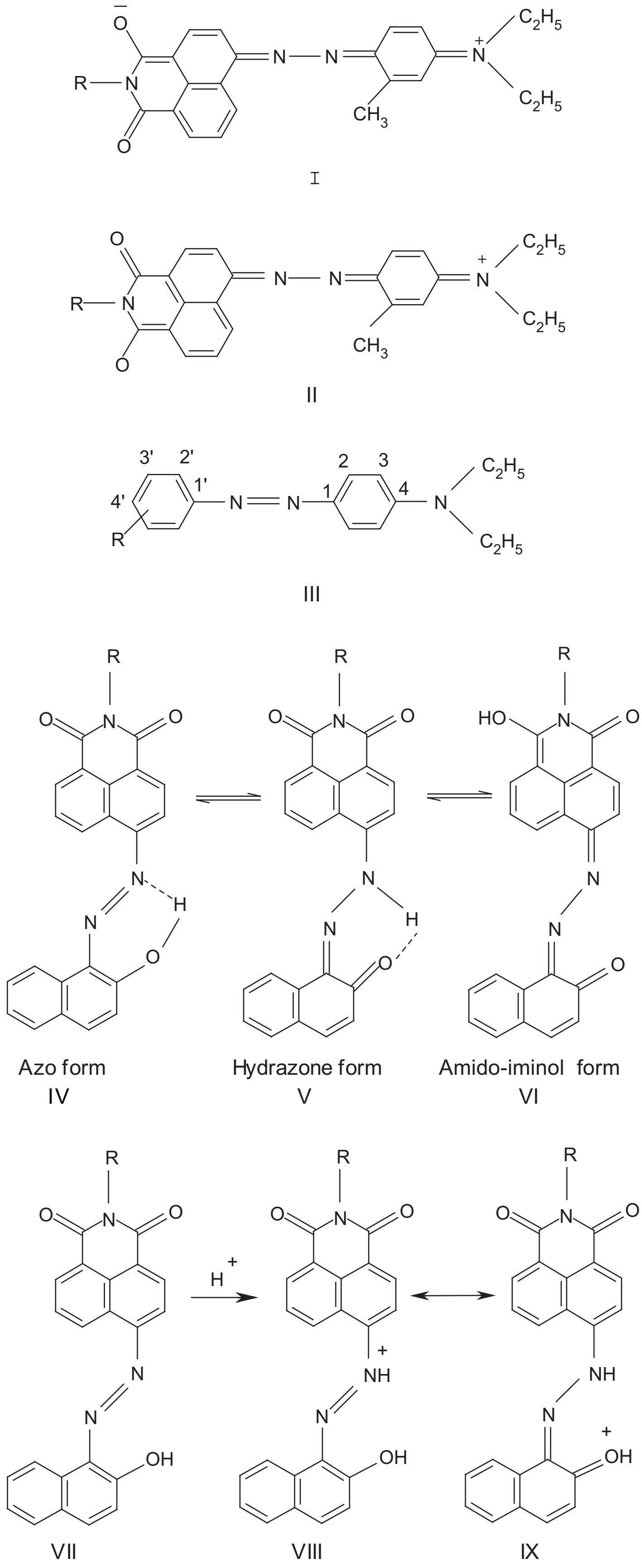
A study of the absorption spectra in neutral and acidic solutions indicates the reasons for these results. The dyes **2**, **4**, **6** and **8** show a double maxima in the visible range, one around 410–459.2 nm and a second in the 509.6–572.0 nm (Table 7), due to their structures ($A_1 \leftrightarrow A_2$).

Due to conjugation, dyestuffs **2**, **4**, **6** and **8** can exist in the neutral (D_1) as well as in the polar forms (D_2) [21]. This effect illustrates that these dyestuffs in neutral solutions are more bathochromic than the dye **1** where the coupler is β-naphthol. This effect i.e. $D_1 \leftrightarrow D_2$ is not present in dye **1**. In the range 347–383 nm, the absorption of the benzeneazonaphthalene chromophore is observed (Table 7). Derivatives of 4-benzeneazonaphthalimides, i.e. the dyes **2**, **4**, **6**, **8**, have basic absorption bands within the range 445.4–459.2 nm in 1 M methanolic acid solutions (Table 7).

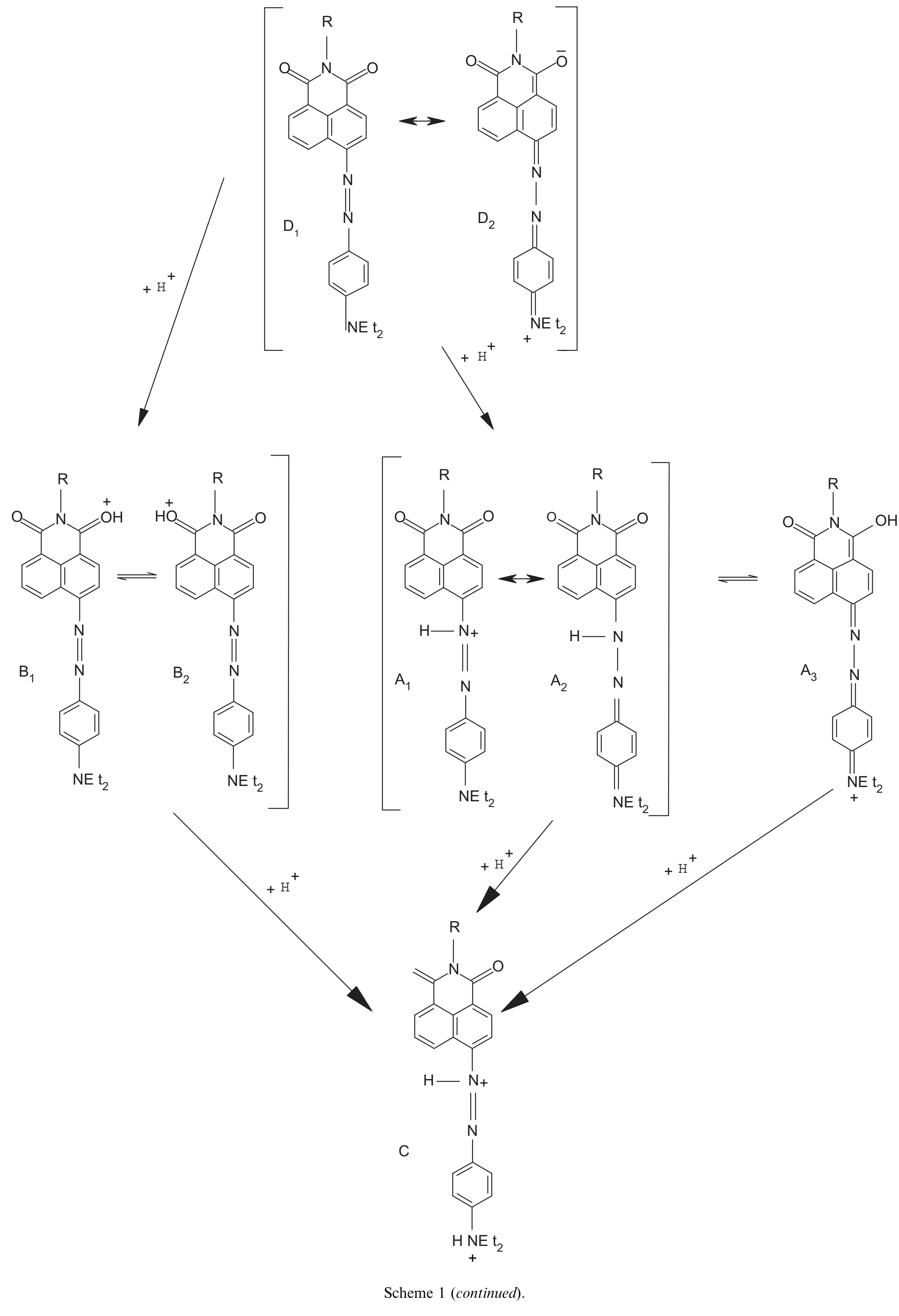
The results obtained show that the colour shifts observed in the 4-substituted naphthalimides are due to the coexistence, even in unacidified solution, of the neutral (D_1) and polar (D_2) forms which results in the bathochromic shift of the long-wavelength absorption bands.

This can be attributed to the presence of an electron-donating substituent (*N*,*N*-diethylamino) and an electron-accepting (cyclic amide) system in positions allowing mutual conjugation. This is not observed for the dye **1** where β-naphthol is the coupler.

The synthesized dyestuffs were applied to polyester fabric at concentrations of 0.1, 0.5 and 2.5% (OWF) with 0.5% (OWF) acetic acid and 1% (OWF) dispersing


I
II
III
Azo form
IV
Hydrazone form
V
Amido-iminol form
VI
VII
VIII
IX

Scheme 1.



Scheme 1 (*continued*).

agent together with a liquor to goods ratio of 50:1 at temperatures of 135 °C.

The exhaustion was complete and there were no dyestuffs left in the dyebath. The leveling properties of the dyestuffs were good for all the dyestuffs. The light fastness, wash fastness, staining, sublimation fastness and initial sublimation point are shown in Table 8. The values of the L^*, a^*, b^*, c^*, h^* and selected K/S of the dyed polyester are shown in Table 9.

Light fastnesses, wash fastnesses and sublimation fastnesses of all dyes were also measured according to ISO 105/B and ISO 105/C and ISO 105 PO1 standards, respectively. The wash fastness of all dyestuffs were 5 and the staining of polyesters were 4–5.

The imides **2**, **4**, **6** and **8** dyed polyester in bright violet (bluish red) hues and **1**, **3**, **5** and **7** dyed polyester in bright red hues and **9** dyed polyester in yellowish cream of generally good build up.

Visual evaluation of the dyeings on polyester fabrics showed that the nature of the alkyl residue in the amine group of the coupling component affects both the intensity of dyeings and their shade. The highest intensity is shown by the dyeing of dyes **2**, **4**, **6** and **8**, which contain *N*,*N*-diethyl groups. These substituents bring about an increase in the nucleophilic character of the tertiary nitrogen atom and of the stability of polar forms [8], especially when there are no substituents in the phenyl rings causing steric effects.

The dyeings were violet or bluish red. The electron acceptor group on the coupling component such as $-COCH_3$ like the dye (**9**) causes considerable hypsochromic effect (yellowish cream). The colour of naphthalimide dyes depends on the delocalisation of electrons through the conjugated azo chromophore and depends on the energy difference between structures D_1 and D_2 in Scheme 1. The lower is this difference, the higher is the bathochromic effect of the basic absorption band [24]. The contribution of the higher energy stabilized dipolar structure D_2 is enhanced by the presence of a conjugated electron acceptor (naphthalimide residue) and electron donor (dialkylamino group), and this results in a considerable bathochromic shift.

Table 8
L.F, W.F, S, S.F and I.S.P

Dyestuff	L.F.	W.F.	S	S.F.		I.S.P. (°C)
				180 °C	210 °C	
1	5–6	5	4–5	4–5	3–4	200
2	5–6	5	4–5	4	3–4	150
3	4–5	5	4–5	4	3–4	200
4	4–5	5	4–5	4	3–4	150
5	5–6	5	4–5	5	4–5	200
6	5–6	5	4–5	5	4–5	150
7	4–5	5	4–5	5	4–5	200
8	4–5	5	4–5	4–5	4–5	150
9	4	5	4–5	4–5	4–5	180

L.F., light fastness; W.F., wash fastness; S, staining; S.F., sublimation fastness and I.S.P., initial sublimation point.

Table 9
The values of the L^*, a^*, b^*, c^*, h^* and $(K/S)_{530}$

Dye	Conc.	L^*	a^*	b^*	c^*	h^*	$K/S_{(530)}$
1	0.1	55.098	42.901	14.919	45.421	19.175	3.525
	0.5	46.358	50.850	9.531	51.735	10.616	7.99
	2.5	39.097	50.035	17.087	52.872	18.855	14.520
2	0.1	41.080	30.317	−10.431	32.061	18.987	5.356
	0.5	28.933	35.079	−12.397	37.205	19.464	14.779
	2.5	17.263	16.834	−1.755	16.925	5.952	27.146
3	0.1	54.179	45.860	13.399	47.777	16.287	3.977
	0.5	42.902	56.452	11.233	57.559	11.254	12.865
	2.5	35.980	53.725	16.831	56.300	17.395	20.912
4	0.1	49.177	27.498	−5.379	28.019	11.068	3.012
	0.5	29.217	35.394	−12.404	37.505	19.313	14.486
	2.5	19.229	23.448	−3.040	23.644	7.387	26.198
5	0.1	56.263	43.640	3.417	43.77	4.477	3.162
	0.5	46.441	54.722	6.681	55.128	6.961	8.934
	2.5	42.341	55.245	15.424	57.358	15.599	13.122
6	0.1	42.304	33.553	−4.725	33.884	8.016	5.420
	0.5	26.287	34.221	−10.163	35.698	16.54	18.296
	2.5	17.802	17.802	−1.176	17.84	3.779	26.391
7	0.1	60.596	37.461	4.429	37.722	6.743	2.035
	0.5	51.413	48.263	4.674	48.489	5.532	4.971
	2.5	42.092	51.117	12.630	52.654	13.879	11.148
8	0.1	44.368	32.869	−3.728	33.107	6.466	4.67
	0.5	29.789	35.349	−10.248	36.804	16.167	14.118
	2.5	26.716	34.426	−6.327	35.003	10.414	18.192
9	0.1	74.803	9.535	30.172	31.64	72.46	1.98[a]
	0.5	63.605	16.400	23.298	28.49	54.86	3.18
	2.5	49.008	31.360	33.871	46.16	47.20	10.26

[a] K/S of dyestuff (**9**) is measured at 400 nm.

The electron donor substituents in the ring of the coupling components also considerably affect the colour of the dyeings, especially those in an ortho position to the azo bond such as dyes **1**, **3**, **5** and **7** this phenomenon was described previously in structures VII and VIII.

The naphthalimide derivatives show exceptionally good thermal stability and their dyeings have good fastness properties [6,23]. Generally, the highest initial sublimation points were shown by the dyes containing a naphthalimide group in their structure. They tended to undergo association in the crystalline state, which was confirmed by their IR spectra and high melting points. This propensity for association provides dyes with good thermal stability, as reflected in the sublimation fastness of dyeings and in the high initial sublimation point.

Practical applications of the naphthalimide dyes, despite their undeniable advantages, are limited because of their complicated synthesis and high cost of intermediates. The use of these dyes is further restricted due to their strong tendency to aggregate, making the dye sorption and diffusion in polyester fibre difficult. The synthesis of these dyes in Iran may be economically viable because of the availability of coal tar which can provide acenaphthene, i.e. the primary starting material for naphthalimide dyestuffs.

4-Amino-*N*-methylnaphthalimide is a useful diazo component for the synthesis of azo disperse dyestuffs. Its acceptor "force" is comparable with that of 2,4-dinitroaniline and its use additionally ensures high-performance properties of the dyestuffs [23,25].

4. Conclusion

A series of known naphthalimide derivatives were prepared. The essential intermediate 4-nitro-1,8-naphthalic anhydride was synthesized by nitration and oxidation of acenaphthene. This compound was readily converted into various naphthalimide derivatives by nucleophilic substitution of the anhydride with different amines, and the subsequent reduction of 4-nitro to 4-amino group.

The solvent plays an important role in the nucleophilic substitution reactions in 4-nitro-1,8-naphthalic anhydride. Some naphthalimides with different substituents in the 9-position have been prepared. The naphthalic anhydride is reacted with an amine in a protic solvent such as alcohol or acetic acid to give the corresponding 9-substituted derivative. In a protic solvent the substitution occurs only in the 9-position. 4-Aminonaphthalimides have been synthesized by reduction of the 4-nitro group of the appropriate naphthalic imides.

From the investigations into the use of *N*-substituted naphthalimide as an intermediate for monoazo disperse dyestuffs, it was found that dyestuffs derived from 4-amino-*N*-methyl (alternatively *N*-ethyl, *N*-propyl, *N*-butyl) were suitable for dyeing polyester. The various dyestuffs obtained and their corresponding intermediates were identified by the use of elemental analysis, DSC, FTIR, H NMR, and UV–visible spectroscopic techniques.

The spectrophotometric properties of the prepared monoazo disperse dyestuffs in various solvents were examined. The absorption maxima of these dyestuffs, their halochromic effects, and their intensities have also been obtained.

Finally, the prepared dyestuffs were dyed on polyester fabrics and subsequently their optical and dyeing properties, light fastness, wash fastness and sublimation fastness were determined. All these properties were proved to be reasonably good.

From these investigations, it may be concluded that naphthalimides and related compounds are reasonable monoazo disperse dyestuffs giving good all round properties on polyester fabrics.

References

[1] Rule HG, Thompson SB. Bromo- and nitro-derivatives of naphthalic acid. J Chem Soc 1937;1764–7.

[2] Dashevskii MM, Malevannaya ZP. Structure of dinitro derivatives of acenaphthene. J Org Chem USSR 1965;7:1286–9.

[3] Peters AT. Acenaphthene series part I. J Chem Soc 1942;562–5.

[4] Peters AT. Acenaphthene series part II. J Chem Soc 1947;742–6.

[5] Cason J, Weiss A, Monti SA. Synthesis of four methoxy substituted 1,8-naphthalic anhydrides and of the three monomethyl 1,8-naphthalic anhydrides. J Org Chem 1968;33(9):3404–8.

[6] Peters AT, Bide MJ. Dyes for synthetic polymer fibre. Dyes pigments 1986;7:237–47.

[7] Peters AT, Mak KH. New intermediates and dyes for synthetic polymer fibres. J Soc Dyers Colour 1985;101:398–403.

[8] Wojciechowski K. Spectral properties of disperse dyes, derivatives of *N*-methylnaphthalimidoazobenzene 1990;12:273–86.

[9] Wojciechowski K. Properties and structure of naphthalimide dyes drived from pyrazolones. Dyes Pigments 1993;22:239–54.

[10] Christie RM. Fluorescent brighteners based on naphthalimides. Rev Prog Colouration 1993;22:2–3.

[11] Peters AT, Bide MJ. Amino derivatives of 1,8-naphthalic anhydride and derived dyes for synthetic-polymer fiber. Dyes Pigments 1985;6:349–75.

[12] Wojciechowski K, Szadowski J. Spectrophotometric investigation and PPP-MO calculations of some phenylazophthalimide dyes. Dyes Pigments 1991;6:35–56.

[13] Okazaki M, Tanaka T, Taniguchi S. Synthesis of 5-nitroacenaphthene. Yuki Gosei, Kagaku Kyokai Shi 1956;14:344–6; Chem Abs 1957;51:8050.

[14] Okasaki M, Suhara Y, Fujiyama M. Synthesis of derivatives of 4-aminonaphthalimide. Yuki Gosei, Kagaku Kyokai Shi 1956;14:394–8; Chem Abs 1957;8050.

[15] Dongwu Y. Ph.D Thesis. Leeds University, U.K. 1994;78:185–8, 267–8.

[16] Alexiou M. Ph.D Thesis. Brunel University, U.K. 1983;214–220, 223–230.

[17] Wojciechowski K. Synthesis and properties of naphthalimide acid dyes. Dyes Pigments 1993;22:117–30.

[18] Anselm P, Zuchmayer F. Derivatives of acenaphthene. Ber Dtsch Chem Ges 1899;32:3283.

[19] Anne Fox M, Whitesell JK. Core organic chemistry. Boston: Jones and Bartlett Inc.; 1997. p. 554.

[20] Morrison RT, Boyd RN. Organic chemistry. 5th ed. Boston: Allyn and Bacon Inc.; 1987. p. 973.

[21] Wojciechowski K. Spectrometric characteristics of *N,N*-dialkylamino-3- and 4-phenylazonaphthalimides. Dyes Pigments 1988; 9:401–17.

[22] Griffiths J. Colour and constitution of organic molecules. London: Academic Press; 1976. p. 181–6.

[23] Wojciechowski K. Structure-property relationships in azo disperse dyes derivatives of naphthalimide. Dyes pigments 1997; 33:149–65.

[24] Hallas G. Effect of terminal groups in 4-aminoazobenzene and disperse dyes related thereto. J Soc Dyers Colour 1979;285–94.

[25] Szadowski J, Malinowski W, Wojciechowski K. Synthesis and properties of amide derivatives of 4-*N*-*N*-dialkylaminoazobenzenes. J Soc Dyers Colour 1985;101:105.

[26] A paper entitled as a Synthesis and Characterization of an Azo Dye Based on Naphthalimide Derivatives as a Disperse Dyestuff for Dyeing of Polyester Fabrics, Presented in the world Textile Conference, 4th Autex Conference-June 22–24 2004 Roubaix, France.