

Synthesis of Some Monoazo Acid Dyes Based on Naphthalimides

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A series of novel monoazo acid dyes derived from naphthalimide were prepared. 4-Amino-N-methyl (alternatively N-butyl) derivatives of naphthalimide, aniline and *p*-nitroaniline were used as the diazo components and schaeffer's acid and H-acid constituted the coupling components. 4-Aminonaphthalimide derivatives mentioned above were 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. Diazotization and coupling reactions were carried out in order to obtain the final acid dyes. Again maximal yields were sought after and the reaction conditions were varied accordingly. All intermediates and dyes were recrystallized in order to be attained in a purified form. The obtained dyes and their corresponding intermediates were characterized by the use of elemental analysis, DSC, FTIR, ¹H NMR and UV-visible spectroscopic techniques. Spectrophotometric investigations of the prepared dyes in different solvents were carried out in order to obtain their absorption maxima, solvatochromic effects and various intensities. The acid dyes were finally dyed on polyamide fibres in order to investigate their dyeing properties and the obtainable colour gamut.

Key Words: 4-Aminonaphthalimide derivatives, Acid dyes, Polyamide fibres, Synthesis, Monoazo dyes, Dyeing.

INTRODUCTION

Pioneering work on naphthalimides and their derivatives has been researched to assess their role as intermediates for dyes preparation¹⁻³. Other related compounds have also been investigated such as heterocyclic derivatives of naphthalimides, phenylazophthalimides and 1,8-naphthalic anhydrides⁴. These compounds have been considered for the preparation of dyes for textile fibers, dyes for polymeric materials and dyes capable of copolymerization⁵. Derivatives of N-methyl-1,8-naphthalimide-3-sulphonic acid have been synthesized to produce a series of monoazo acid dyes.

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The solvatochromism and fluorescent properties of these dyes were discussed⁶. 4-Amino-1,8-naphthalic acid-imide-3-sulphonic acid compounds have been utilized to produce acid dyes. In these acid dyes the derivatives of aliphatic, cycloaliphatic, aromatic or heterocyclic radical have been used⁷. Some of acid dyes suitable for dyeing wool and polyamide fibers were synthesized, using derivatives of aryl sulphonanilides prepared from *o*-nitrotoluene or chloronitro-toluene. As coupling compounds, derivatives of 1-phenyl-3-methyl pyrazolone and 2-naphthol were used. Fastness and colour properties of the prepared dyes were determined⁸. A series of monoazo acid dyes has been obtained using 4-amino-1,8-naphthalimide and their 3-sulpho derivatives as diazo components. Derivatives of 1- and 2-naphthol were used as coupling components. These acid dyes have been applied on wool and polyamide fiber and their solubility and fastness properties have been determined^{9,10}.

In this study, we reported the synthesis and characterization of some novel monoazo acid dyes derived from naphthalimides as the diazo components and naphthene-based as coupling components (Fig. 1). The dyeing properties of dyes were also compared with analogous azobenzene derivatives. The spectrophotometric properties of the prepared dyes in various solvents were examined. The absorption maxima of these dyes and their intensities have also been obtained. Finally, the synthesized dyes were applied on polyamide fibres and fastness properties were estimated.

EXPERIMENTAL

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

Procedures

Preparation of 5-nitroacenaphthene and 4-nitro-1,8-naphthalic anhydride were carried out by the use of modified method of Okazaki *et al.*¹¹.

Preparation of 4-nitro-N-methyl (or alternatively 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^{12,13}.

The general method of diazotization was as follows: 3.5 mL 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-1,8-naphthalimide was added gradually over a 0.5 h period. Temperature being kept below 10 °C. This was followed by the addition of 1 mL 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.

A solution of 2 mmol aniline and 2.5 mL hydrochloric acid 2 M was cooled to 5 °C and 2 mL sodium nitrite 1 M was added slowly to the solution at 0.5 h and temperature being kept below 10 °C. The reaction mixture was stirred for 1 h at below 10 °C.

A solution of 2 mL of water, 3 mL hydrochloric acid and 2 mmol of the powder of *para*-nitroaniline was dissolved with stirring and heating. Then the solution was cooled and 0.13 g (2 mmol) of sodium nitrite was added quickly to the solution. The reaction mixture was stirred for 1 h at below 10 °C.

Schaeffer's acid and H-acid have been utilized as coupling components:

2 mmol of each coupling components was dissolved in 5 mL NaOH 30 %. Then the clear diazonium salt of each sample was added gradually to these solutions during 0.5 h. Then the pH of the solution was maintained at almost 9 by adding the NaOH solution (30 %). Stirring was continued for 3 h at less than 10 °C. The dyes were filtered off, washed with NaCl solution and dried. The crude products were purified by the aid of TLC on silica gel 60.

The purified acid dyes and their corresponding intermediates were characterized by the following instruments: (1) FTIR measurements were carried out on an Nicolet 470/670/870. (2) ¹H NMR measurements were carried out on an Avance 500 MHz Bruker instrument. (3) UV-visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer. ϵ_{\max} and solvatochromic effects were also determined. (4) Elemental analysis was carried out on a CHNO-Rapid Heraeus instrument.

The prepared acid dyes were applied to polyamide fibres samples and the following properties were determined.

Optical properties: The λ_{\max} , L*, a*, b*, C* and h° of the dyed samples were measured on a Macbeth 7000 A colour eye reflection spectrophotometer

RESULTS AND DISCUSSION

Synthesis of intermediates

Preparation of 5-nitroacenaphthene and 4-nitro-1,8-naphthalic anhydride were carried out by the use of modified method of Okazaki *et al.*¹¹. These compounds were obtained with the melting points of 101-102 °C and 231-232 °C with the yield of 88.6 and 45.66 %, respectively.

The imidation of aromatic cyclic anhydrides is a nucleophilic substitution reaction, in which the reaction of the attacking amine is carried out in an alcoholic medium under a reflux condition¹². 4-Nitro-N-methyl (or alternatively N-butyl)-1,8-naphthalimide were prepared with the melting points of 211 and 104 °C with the yield of 85 and 80 %, respectively.

Preparation of 4-amino-N-substituted-1,8-naphthalimide as an intermediate plays a important role in the synthesis of naphthalimide dyes. The naphthalimides with an amino group at the 4-position are also fluorescent. 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 solvent¹⁰. The products were prepared with the melting points of 359.82 and 180.97 °C with the yield of 93 and 70 %, respectively.

Preparation of monoazo acid dyes: Diazotization of naphthalimides were carried out with the aid of nitrosylsulphuric acid⁵, 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 10 °C until the diazonium salt was formed. The reaction was completed in 3 h. Aniline and *p*-nitroaniline were diazotized with different method and present reactions were completed in 1 h^{14,15}. Then diazonium salts were reacted with various coupling component such as Schaeffer's acid and H-acid in alkaline media (pH ~ 9) (Fig. 1).

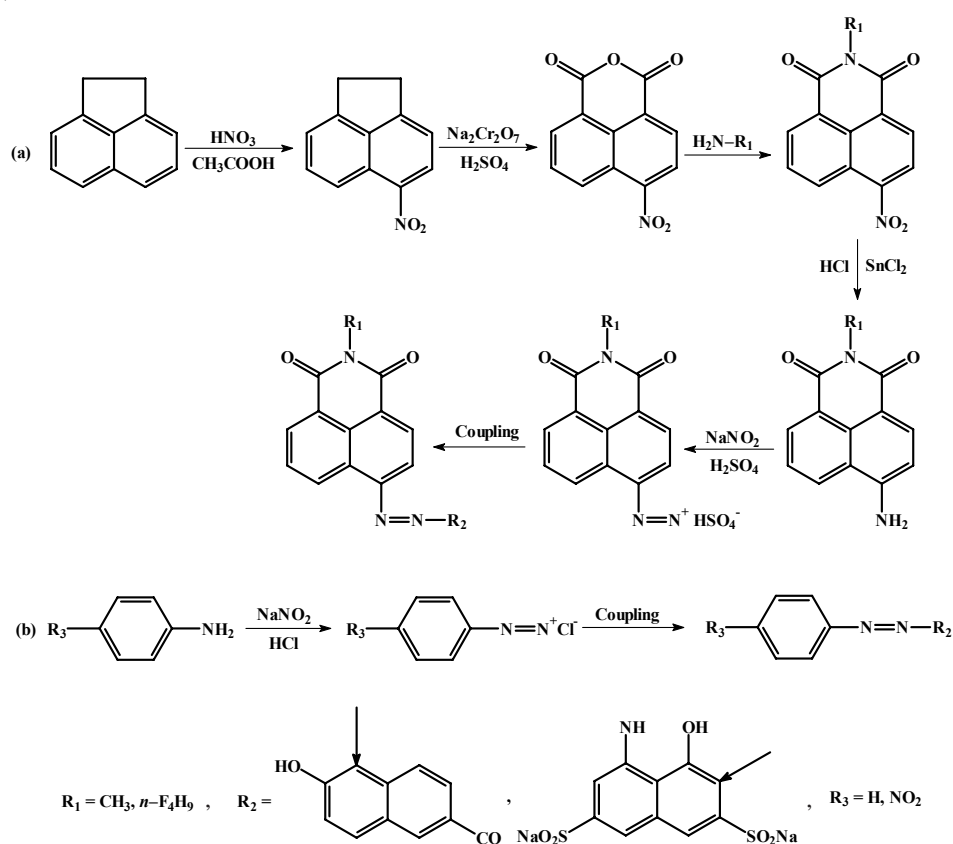


Fig. 1. Synthesis of acid dyes from 4-amino-*N*-alkyl-1,8-naphthalimide, aniline and *p*-nitroaniline

The coupling reactions were carried out with Schaeffer's acid and H-acid at pH 9. The corresponding diazo and coupling components, their respective yields and colour of each synthesized dyes are given in Table-1.

The FTIR and ¹H NMR spectra are given in Tables 2 and 3 and elemental analysis data of synthesized dyes are shown in Table-4.

TABLE-1
ACID DYES DERIVED FROM VARIOUS DIAZO AND COUPLING COMPONENTS

Dye	Dazo component	Coupling component	Yield (%)	Colour
1	4-Amino-N-methyl naphthalimide	Schaeffer's acid	87.0	Red
2	4-Amino-N-butyl naphthalimide	Schaeffer's acid	85.0	Red
3	4-Amino-N-methyl naphthalimide	H-acid	87.5	Violet
4	4-Amino-N-butyl naphthalimide	H-acid	89.0	Violet
5	Aniline	Schaeffer's acid	91.0	Yellow
6	Aniline	H-acid	92.5	Red
7	<i>p</i> -Nitroaniline	Schaeffer's acid	90.0	Orange
8	<i>p</i> -Nitroaniline	H-acid	91.4	Violet

TABLE-2
FTIR, ¹H NMR OF THE SYNTHESIZED ACID DYES BASED ON
NAPHTHALIMIDE DERIVATIVES

Dye	FTIR (cm ⁻¹)	¹ H NMR (δ)
1	O-H str. 3446.75; C=O str. 1587.17; C-N str. 1341.23; N=N str. 1508.44	1.33-1.34 (3H, CH ₃); 7.38-7.47 (2H, 8', 3'-H); 7.57-7.59 (1H, 7'-H); 7.72-7.73 (2H, 4', 5'-H); 8.10-8.12 (2H, 6, 5-H); 8.22-8.33 (2H, 2, 7- H); 8.34-8.61 (1H, 3-H); 16.60 (1H, O-H);
2	O-H str.3409.33; C=O str.1621.59; C-N str. 1344.23; N=N str.1508.08;	1.02 (3H, N-CH ₂ CH ₂ CH ₂ CH ₃); 1.56 (2H, N-CH ₂ CH ₂ CH ₂ CH ₃); 1.77 (2H, N-CH ₂ CH ₂ CH ₂ CH ₃); 4.12 (2H, N-CH ₂ CH ₂ CH ₂ CH ₃); 7.25-7.56 (2H, 8,3'-H); 7.69-7.70 (1H, 6-H); 7.77-7.82 (2H, 4', 5'-H); 8.25-8.30 (2H, 7',5-H); 8.45-8.48 (2H, 2,7-H); 8.49-8.62 (1H,3-H); 16.61 (1H,O-H);
3	O-H str.3435.85; C=O str.1591.21; C-N str. 1341.40; N=N str.1506.27;	1.22 (3H, CH ₃); 7.38-7.47 (2H, NH ₂); 7.57-7.59 (1H,6-H); 7.72-7.73 (2H, 4',5'-H); 8.10-8.13 (2H, 7',5-H); 8.22-8.33 (2H, 2,7-H); 8.49- 8.52 (1H,3-H); 16.79 (1H, O-H);
4	O-H str.3443.75; C=O str.1579.73; C-N str. 1381.14; N=N str.1553.75;	0.87 (3H, N-CH ₂ CH ₂ CH ₂ CH ₃); 1.45-1.46 (2H, N-CH ₂ CH ₂ CH ₂ CH ₃); 1.72 (2H, N-CH ₂ CH ₂ CH ₂ CH ₃); 3.49-3.50 (2H, N-CH ₂ CH ₂ CH ₂ CH ₃); 7.49-7.51 (2H, NH ₂); 7.58-7.59 (1H, 5-H); 7.60-7.62 (1H, 7'-H); 7.80- 7.88 (2H, 4',5'-H); 8.11-8.16 (1H,6-H); 8.21-8.29 (2H, 2,7-H); 8.45- 8.62 (1H, 3-H); 16.01 (1H, O-H);

Electronic absorption spectra of the synthesized acid dyes: A series of monoazo acid dyes with different substituents were synthesized which are shown in Fig. 1. The dyes had various hues *e.g.* yellow, red and violet with very good depth as given in Table-1. The dyeing performance of these dyes was assessed on polyamide fibres. The dyed fibres showed moderate light fastness and excellent wash fastness. The wavelength of absorption maximum (λ_{\max}), the molar absorption coefficients (ϵ_{\max}) and half-band widths ($\Delta\lambda_{1/2}$) of the dyes are very important for evaluation of dyeing properties of dyes¹⁶. A higher extinction coefficient and a broader half-band width relate to a stronger chromophore, which makes the product more cost effective¹⁷. The absorption spectra of the dyes were run in benzene,

TABLE-3
FTIR, ¹H NMR OF THE SYNTHESIZED ACID DYES BASED ON
BENZENE DERIVETIVES

Dye	FTIR (cm ⁻¹)	¹ H NMR (δ)
5	O-H str.3416.65; C=O str.1702.28; C-N str. 1366.21; N=N str.1591.88;	6.61-6.62 (2H, 3', 5'-H); 7.26-7.43 (1H, 8'-H); 7.44-7.47 (2H, 3,5-H); 7.56-7.59 (2H, 4, 7'-H); 7.72-7.73 (1H, 6-H); 7.98-7.99 (2H, 2, 4'-H); 15.99 (1H, O-H);
6	O-H str.3423.98; C=O str.1693.89; C-N str. 1339.98; N=N str.1582.68;	7.46-7.49 (1H, 5'-H); 7.51-7.59 (2H, 3,5-H); 7.60-7.62 (2H, 4,7'-H); 7.80-7.88 (2H,NH ₂); 8.10-8.24 (1H, 6-H); 8.31-8.62 (2H, 2,4'-H); 17.12 (1H, O-H);
7	O-H str.3437.02; C=O str.1651.43; C-N str. 1066.78; N=N str.1578.85;	6.63-6.65 (2H, 3', 5'-H); 7.34-7.42 (1H, 8'-H); 7.44-7.49 (2H, 3,5-H); 7.52-7.56 (1H, 7'-H); 7.68-7.76 (1H, 4'-H); 7.95-7.96 (2H, 2, 6-H); 16.01 (1H, O-H);
8	O-H str.3417.67; C=O str.1693.34; C-N str. 1353.2; N=N str.1584.64;	7.38-7.43 (1H, 5'-H); 7.44-7.47 (2H, 3,5-H); 7.57-7.59 (2H, NH ₂); 7.72-7.73 (1H,7'-H); 8.10-8.33 (2H, 2,6-H); 8.49-8.52 (1H, 4'-H); 17.10 (1H, O-H);

TABLE-4
ELEMENTAL ANALYSIS OF ACID DYES

Dye	Found (%)				Required (%)			
	C	H	N	S	C	H	N	S
1	57.29	2.91	8.40	6.80	57.14	2.90	8.60	6.62
2	59.40	3.72	7.87	6.40	59.42	3.80	8.00	6.10
3	45.76	2.36	9.66	10.56	46.00	2.33	9.33	10.66
4	48.24	3.14	8.54	9.92	48.59	3.11	8.72	9.96
5	54.36	3.12	8.40	9.28	54.85	3.14	8.00	9.14
6	41.04	2.32	9.10	14.08	41.11	2.35	8.99	13.70
7	48.36	2.52	10.43	8.01	48.60	2.53	10.63	8.11
8	37.25	1.93	10.98	12.48	37.50	1.95	10.93	12.50

H₂O and DMF:H₂O with the solvent ratio of 50:50 respectively and they are summarized in Table-5. The λ_{\max} value shows the position of the most intense absorption band, which depends on the possibility of the dyes existing in the azo or hydrazone forms. The colour of dyes 1-4 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 tautomers¹⁸.

In the present study as illustrated in Fig. 1, the naphthol residue acts as donor group and the two carbonyl groups, of naphthalimide residue acts as acceptor groups and following the same lines of reasoning. The mentioned dyes (1-4) give a bathochromic shift effect whilst the phenylazo structure in dyes (5-8) in Table-5 has a hypsochromic shift effect.

TABLE-5
UV-VISIBLE ELECTRONIC SPECTRA DATA OF SYNTHESIZED ACID DYE (1-8)

Dye	DMF:H ₂ O = 50:50		H ₂ O	Benzene	$\Delta\lambda$ (nm)
	λ_{\max} (nm)	ϵ_{\max} (L/mol cm)	λ_{\max} (nm)	λ_{\max} (nm)	
1	530.0	38995	519.0	479.0	40.0
2	530.0	41925	510.5	481.5	29.0
3	563.5	39562	543.5	490.0	53.5
4	554.5	49080	549.5	489.0	60.5
5	482.5	33196	478.0	417.5	60.5
6	529.0	36983	507.0	479.5	27.5
7	509.5	38233	479.0	425.5	53.5
8	549.5	37637	538.5	483.0	55.5

Introduction of the naphthylazo chromophore into the 4-position of 1,8-naphthalimide results in a large bathochromic shift in the absorption maxima in H₂O and H₂O/DMF (Table-5) compared with phenylazo chromophore.

The effect of the naphthyl residue and the carbonyl groups are, therefore, apparent and the acid dyes **1**, **2**, **3** and **4** are bathochromic with respect to the analogous phenyl residue (Table-5). The effect of -NO₂ group in the diazo component at *p*-position to the azo link in the synthesized acid dyes (dyes **7**,**8**) is more bathochromic compared to when the -NO₂ group is not present (dyes **5**,**6**) as mentioned in Table-5.

The λ_{\max} shift of the prepared dyes in various solvents is brought about by the solvatochromic effect. Resulting from changes in the dielectric constant of the solvent¹⁹ (Table-5).

Of the readily available solvents with low dielectric constants ($\mu = 2.28$)¹⁹, benzene was used. This solvent slightly solvates the molecules of the compounds dissolved in it.

Dyeing: Polyamide fibres (1 g) were pretreated with a nonionic detergent (5 g/L) at 50 °C for 0.5 h prior to being used for dyeing. Dyeing was carried out in Rotadyer apparatus by using of a liquor ratio of 40:1 and the pH was adjusted to 4-5 with acetic acid. The dyeing was carried out at 100 °C according to Fig. 2.

Dyes **1-4** gave red to violet dyeings of excellent build up, while dyes **5-8** with phenylazo structures gave yellow to violet hue on polyamide fibres. The bathochromic shift in dyes **1-4** is related to presence of naphthalimide ring in diazo components. The present of electron withdrawing group in diazo component and electron donating in coupling component in monoazo acid dyes were caused to higher absorption maxima wavelength¹⁸. The colour characteristics of all dyes were showed in Table-5.

The spectrophotometric properties of dyeings in terms of the CIE Lab system are shown in Table-6. Depending on the substituents present in coupling component, the dyeings varied in colour from red to violet as indicated in Fig. 2.

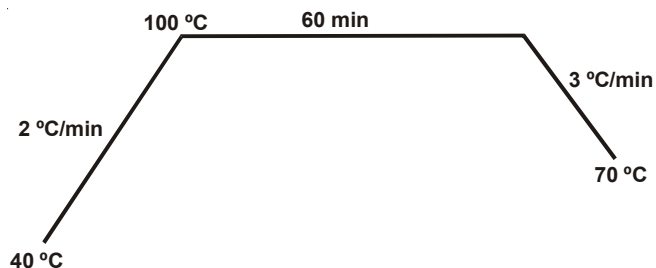


Fig. 2. Dyeing of polyamide fibres with the synthesized dyes

TABLE-6
SPECTROPHOTOMETRIC DATA OF THE SYNTHESIZED
DYES ON POLYAMIDE FIBRES (1.5% omf)

Dye	L*	a*	b*	C*	h°
1	34.098	46.764	-7.255	47.324	351.181
2	40.917	49.102	-6.529	37.859	210.700
3	47.720	8.402	-16.029	18.098	297.663
4	46.992	8.822	-14.426	15.216	17.597

Dyes **3** and **4** were bathochromic on dyed fibres relative to dyes **1** and **2**, respectively. The presence of H-acid as a coupling component due to having two electron donor group relative to Schaeffer's acid which have only a hydroxyl group as an electron donor causes bathochromic effect and thus give blue hues.

Residue in the naphthalimide group is not very significant in the context of colour change, which are shown in Table-1.

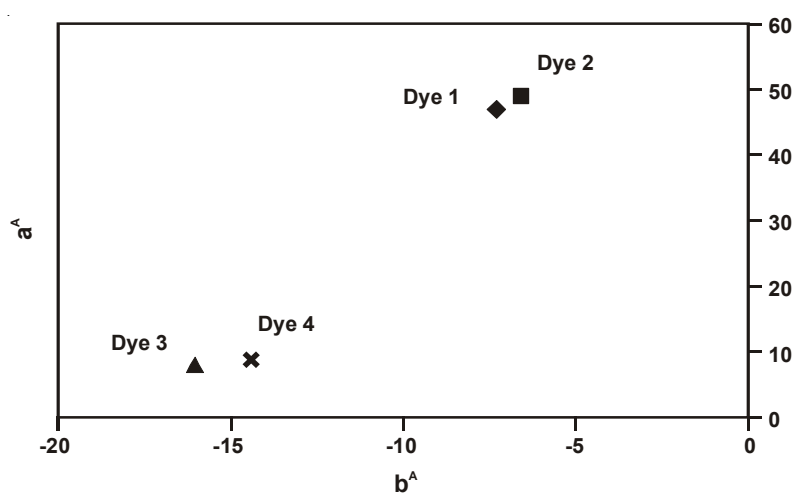


Fig. 3. Chromaticity of the synthesized dyes on polyamide fibres

Conclusion

A series of monoazo acid dyes based on naphthalimides, aniline and *p*-nitroaniline were prepared. In the dyes based on naphthalimides, acenaphthene was used as the primary material and various reactions such as nitration, oxidation, amination, reduction, diazotization and coupling were carried out.

It was found that dyes derived from 4-amino-N-methyl (alternatively N-butyl)-1,8-naphthalimide, aniline and *para*-nitroaniline were suitable for dyeing polyamide. The spectrophotometric properties of the prepared monoazo acid dyes in various solvents were examined. It was found that in these acid dyes there is a positive solvatochromic effect. The absorption maxima of these dyes and their intensities have also been obtained.

Finally, the prepared acid dyes were dyed on polyamide fibres and subsequently their optical and dyeing properties, light fastness and wash fastness were determined. All these properties were proved to be reasonably good.

From these investigations, it may be concluded that naphthalimides acid dyes, aniline and *p*-nitroaniline and related compounds are reasonable monoazo acid dyes giving good all round properties on polyamide fibres.

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