

# SYNTHESIS, WASH AND LIGHT FASTNESS OF AZO DYES DERIVED FROM *N, N*-DIETHYLANILINES

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## ABSTRACT

A series of monoazo dyes was prepared by coupling carbocyclic and heterocyclic diazo components to four compounds of the *N, N*-dialkylaniline type. The dyes were characterised by spectroscopic methods, elemental analysis or mass spectrometry. Dispersions of the dyes were applied by conventional techniques to polyester and polyamide, or by reactive dyeing to wool and polyamide, when a CO<sub>2</sub>H group was present. Wash and light fastness ratings of coloured samples are presented.

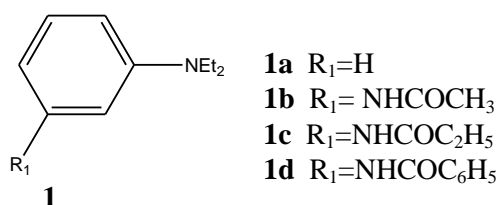
**Keywords:** azo dyes, disperse dyes, *N,N*-diethylanilines, wash fastness, light fastness

## INTRODUCTION

Heterocycles are extensively used in disperse dye chemistry either for textile or non-textile uses. Non-textile applications of heterocyclic dyes include their use in reprography, functional dye and non-linear optical systems, photodynamic therapy and lasers [1].

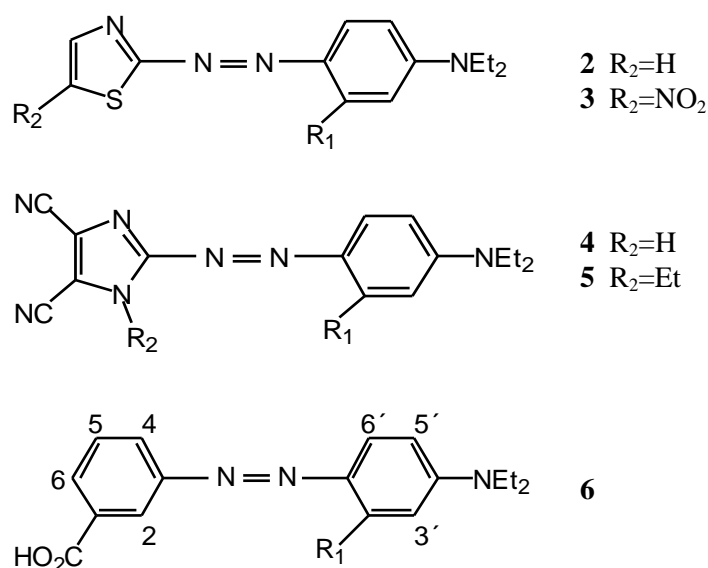
Azo dyes containing heterocyclic rings lead to brighter and often deeper shades than their carbocyclic analogues [2]. Heterocyclic dyes may be good candidates for printing and photographic-like applications on account of their brightness and tinctorial strength [3]. Another essential requirement for this type of application is high light fastness. The introduction of additional acylamino groups on dyes of the *N, N*-dialkylaniline type produces a bathochromic shift and increases the dye light fastness [4].

The objective of this work was to study the influence of three acylamino groups (RCONH-, R = Me, Et, Ph) on the properties of azo dyes of the above type. Amides (**1b-d**) (Figure 1) were prepared and used as coupling components.



**Figure 1** Structures of coupling components

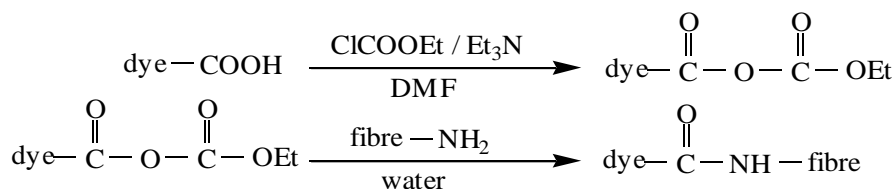
Diazotisation of 2-aminothiazole, 2-amino-5-nitrothiazole and 2-amino-4,5-dicyanoimidazole and coupling to *N,N*-diethylaniline (**1a**) and to the amides (**1b-1d**) gave the dyes **2-6**. (Figure 2).



**Figure 2** Structures of prepared dyes **2-6** (**a**:  $R_1=H$  **b**:  $R_1=NHCOCH_3$  **c**:  $R_1=NHCOCH_2CH_3$  **d**:  $R_1=NHCOCH_2C_6H_5$ )

Since it is known [5] that dyes from dicyanoimidazole have poor light fastness if they are not alkylated, dyes **5** were obtained from dyes **4**. Although several dyes of type **3** [6]. and **5** [5] are known their properties have not been fully reported.

Fibre reactive dyes have been a major topic for industrial dye research over many years. When there is a carboxylic acid group in the dye molecule, an amide bond can be formed with amino group containing fibres, such as wool and polyamide. In previous work this was achieved by activation of the  $CO_2H$  group with ethyl chloroformate [7], and the intermediate mixed anhydride, in dimethyl formamide solution (DMF), was added to the fabric in water (Figure 3).



**Figure 3** Reactive dyeing with a carboxylic dye

Thus, carboxylic dyes **6** were also synthesised in this work with the purpose of relating their fastness properties to the dyeing method - acid or reactive. An increase on wash fastness was expected as a consequence of the reactive dyeing. However, it was suspected that an improvement on light fastness could also be obtained due to the formation of amide bonds.

## EXPERIMENTAL

### Equipment

The infrared and visible absorption spectra were recorded on a Perkin Elmer FTIR-1600 and on a Hitachi U-2000 spectrometers. A Varian Unity Plus Spectrometer at 300 MHz was used to obtain the  $^1\text{H}$  RMN spectra. Electron impact mass spectra were recorded on a Unicam GC/MS 120 by direct insertion, and high resolution mass spectra were run on a VG Ultima HRMS. Light fastness tests were performed on a Xenotest 150 S (Heraeus).

### Starting materials

The coupling components, acylaminodialkylanilides **1b-1d**, were prepared in 22-55% overall yields by acylation of 3-nitroaniline with acetic anhydride, propionic anhydride or benzoyl chloride, respectively, under Schotten-Baumann conditions [8], followed by reduction of the nitro group (EtOH,  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}$ , Pd/C) [9] and alkylation (DMF,  $\text{K}_2\text{CO}_3$ , EtI) [8].

The compounds showed melting points according to literature values: m.p. (**1b**) 69-70 °C (lit. 70-72 °C [10], 77-79 °C [11]); (**1c**) 77-78 °C (lit. 77-79 °C [11]); (**1d**) 89-90 °C (lit. 83-85°C [11]).

### General procedures for the synthesis of dyes

#### Method A [12]

The aminothiazole (20 mmol) was mixed with 2-propanol (10 ml) and trichloroacetic acid (4 g), then the coupling component (20 mmol) was added and the reaction mixture was slightly heated to increase solubility. The solution was cooled (external cooling bath at 5 °C) and isoamyl nitrite (27 mmol) was dropped into the suspension. The temperature was allowed to rise to 20 °C in one hour and the mixture was kept stirring at room temperature overnight. The suspension was poured into water (100 ml) and the precipitated dye was filtered off and washed thoroughly with water.

### **Method B**

Sodium nitrite (0.17 g; 2.46 mmol) was added to concentrated H<sub>2</sub>SO<sub>4</sub> with external cooling (5 °C), the suspension was stirred for 10 minutes and a mixture of propionic-acetic acids 1:5 (3 ml) was added. 2-Aminothiazole (0.24 g; 2.43 mmol) was added in portions and the mixture was left stirring for 1 hour, with external cooling (5-10 °C).

The coupling component (2.43 mmol) was dissolved in the mixture of propionic-acetic acids 1:5 (3 ml) and to this was added the diazonium solution slowly, keeping external cooling at 10 °C. A saturated solution of ammonium acetate was added until the mixture was neutral to Congo Red paper and it was left standing in the cold for one hour. Then it was poured into water (50 ml) and an oil separated out. The aqueous solution was decanted, the dark red oil was dissolved in chloroform and this solution was washed with water and evaporated to give a sticky solid that later solidified completely. The dye showed only a slight contamination on tlc and gave a clean NMR spectrum.

### **Method C [4b, 5]- Synthesis of dyes 4**

2-Amino-4,5-dicyanoimidazole (0.269 g; 2 mmol) was suspended in water (7 ml) and concentrated HCl (0.64 ml) at 0-5 °C, a 5 N sodium nitrite solution (0.37 ml) was added drop wise and a positive nitrite test (iodine-starch paper) was maintained for 30 minutes. Excess nitrite was destroyed with sulfamic acid. This suspension was used directly in the coupling step.

A solution of the coupling component (2 mmol) in methanol (1.6 ml) and acetic acid (1.6 ml) was added dropwise over 15 minutes at 0-5 °C to the diazonium zwitterion suspension. The reaction was

allowed to warm to room temperature over four hours, the solids collected by filtration, washed acid free with water and dried.

#### **Method D [4b, 5]- Synthesis of dyes 5**

The above dried product (1 mmol) was suspended in acetone (6 ml). A solution of potassium carbonate (0.38 g; 2.75 mmol) in water (6 ml) was added and the reaction mixture stirred for 5 minutes until solution was complete. Diethylsulfate (0.65 ml; 5 mmol) was added and the reaction mixture stirred at 25-30 °C for six hours. The solids were filtered, washed with water and dried. Recrystallisation from 2-propanol provided an analytically pure sample.

#### **Method E- Synthesis of dyes 6**

To a cold solution of the *m*-aminobenzoic acid (4.25 mmol) in a mixture of water (20 ml) and HCl 36 % (1.8 g), was added sodium nitrite (4.25 mmol) and the mixture was kept stirring at low temperature (0-5 °C) for 20 minutes.

To a solution of the coupling component (4.25 mmol) in a mixture of glacial acetic acid (0.7 g) and water (20 ml) the diazonium salt was added at low temperature (0-5 °C) and the mixture was kept stirring for 4 h. A solution of sodium acetate 2 M was then added until pH 5. The dye was filtered off.

#### **Method F [13]- Displacement coupling**

2-Amino-5-nitrothiazole (1.4 g; 10 mmol) was mixed with 2-propanol (2 ml) and trichloroacetic acid (6 g) 4-*N*, *N*-diethylaminobenzoic acid (10 mmol) was added and the mixture was cooled (0-5 °C) before isoamylnitrite (13.5 mmol) was added. The beaker was removed from the ice bath and vigorously stirred (while CO<sub>2</sub> is liberated) for 15 minutes and then poured into water (300 ml). The dye was filtered off and washed with plenty of water. The crude dye was suspended in water (300 ml) and heated to 60 °C. After cooling the dye was filtered off and dried.

#### **General procedure for dyeing of wool and polyamide**

##### **With activation of the carboxylic acid group (reactive dyeing)**

To a cooled solution of the dye (1 mmol) in DMF (1 ml), triethylamine (3 mmol) and the ethyl chloroformate (3 mmol) were added and the solution was kept stirring for 30 minutes. The triethylamine hydrochloride was filtered off and after adding water (200 ml) and the fibre (1.5 g) (the concentration of the dye in the bath was 2 % relatively to the mass of the fibre with liquor ratio 67:1) the mixture was stirred for 30 minutes at 100 °C. The fibre was removed, washed and boiled for 15 minutes in water with Levapon TH soap (2 g/l) and, after drying, it was submitted to the ISO 105 C03 test (wash fastness) and ISO 105 B02 (light fastness).

#### **Without activation of the carboxylic acid group (acid dyeing)**

To a solution of the dye (1 mmol) in DMF (1 ml), water (200 ml) and the fibre (1.5 g) (the concentration of the dye in the bath was 2 % relatively to the mass of the fibre; liquor ratio 67:1) were added. The mixture was stirred for 30 minutes at 100 °C. The fibre was removed, washed and boiled for 15 minutes in water with Levapon TH soap (2g/L) and, after drying, it was submitted to the ISO 105 C03 test (wash fastness) and ISO 105 B02 (light fastness).

#### **General procedure for dyeing of polyester and polyamide (disperse dyeing)**

The wet fabric was introduced in the bath, the temperature was raised to 60 °C and the dispersing agent "Albegal Set", formic acid and ammonium sulphate were added. The carrier "Levegal DTE" and the required amount of the dye were added in two successive 10 minutes periods. The temperature was raised to 98 °C and the dyeing proceeded for 90 min, followed by washing with a solution of standard soap (5 g/l) and sodium carbonate (2 g/l) at 60 °C for 10 min. The fabric was then rinsed in running water and dried at room temperature.

The wash fastness and light fastness of the dyeing were determined by standard procedures (ISO 105 C03 and ISO 105 B02).

## **RESULTS AND DISCUSSION**

The dyes **2-6** were prepared by different methods as shown on table 1. Lower yields were observed for dyes derived from 2-amino-5-nitrothiazole and isoamyl nitrite [12] was found to be superior to

sodium nitrite for the diazotisation process. Displacement coupling is also convenient for dyes derived from aminonitrothiazole, giving rise to chromatographically pure dyes and it was used to prepare dye **3a**.

**Table 1** Yields, purification details and physical properties of dyes **2-6**

Dye	Preparation Method	Crude yield (%)	Purification Method	Pure Yield (%)	Appearance	m.p. (°C)
<b>2 a</b>	A	52	---	52	Red solid	163.0-168.0 [14]
<b>2 b</b>	B	92	V	50	Red solid	51.4-53.4
<b>2 c</b>	B	99	V	53	Red solid	91.2-92.8
<b>2 d</b>	B	98	V	64	Red solid	151.5-152.7
<b>3 a</b>	F	---	Z	47	Dark blue crystals	195.0-200.0 [15] <sup>a</sup>
<b>3 b</b>	A	---	V	16	Shinny blue-green solid	189.0-191.1
<b>3 c</b>	A	42	Z	32	Shinny blue-green solid	190.0-192.2
<b>3 d</b>	A	---	Z	48	Dark blue solid	164.0-165.4
<b>4 a</b>	C	46	---	46	Dark red solid	205.3-206.2 [4b]
<b>4 b</b>	C	69	---	69	Brown red solid	221.3-223.6 [5] <sup>a</sup>
<b>4 c</b>	C	62	---	62	Dark red solid	149.6-151.8 [5] <sup>a</sup>
<b>4 d</b>	C	54	---	54	Bright red solid	236.5-237.0
<b>5 a</b>	D	94	X	31 (Y)	Bright shinny red crystals	208.0-209.0
<b>5 b</b>	D	100	X	50 (Y)	Dark red crystals	206.3-207.4 [5] <sup>a</sup>
<b>5 c</b>	D	79	X	40 (Y)	Orange red crystals	198.8-200.6 [5] <sup>a</sup>
<b>5 d</b>	D	77	X	39 (Y)	Shinny maroon crystals	226.0-228.9
<b>6 a</b>	E	100	---	100	Orange solid	168.8-171.2
<b>6 b</b>	E	---	W	53	Dark red solid	192.2-194.3
<b>6 c</b>	E	88	---	88	Red solid	184.0-186.0
<b>6 d</b>	E	---	W	80	Orange solid	188.0-191.0

V- plc W- Recrystallisation from acetone/diethyl ether X- Recrystallisation from isopropanol

Y- The reaction is clean. The crude solids are in a pure state. The pure yield accounts for the first crop obtained, only.

Z- Recrystallisation from ethanol/diethyl ether

<sup>a</sup> m.p. not quoted

During the preparation of some of the dyes coloured by-products were also obtained and chromatography was necessary for purification. It is known that the synthesis of heterocyclic dyes is

very sensitive towards the acidity of the medium and the optimum conditions for diazotisation are also responsible for the formation of unidentified by-products [1].

Dyes **4** were synthesised by known methods and their alkylation with diethyl sulphate in acetone/water/K<sub>2</sub>CO<sub>3</sub> gave the pure dyes **5**, in high yields.

In most cases the dyes were purified either by recrystallisation or chromatography.

All the compounds synthesized were characterized by proton <sup>1</sup>H NMR spectroscopy and in table 2 sets of selected data for one dye of each class are presented.

**Table 2** <sup>1</sup>H NMR data for some selected dyes

Dye	Solvent	δ (ppm, 300 MHz)
<b>2 a</b>	Acetone-d <sub>6</sub>	1.25 (6H, t J 7.0 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 3.60 (4H, q J 7.0 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 6.90 <sup>a</sup> (2H, d J 9.0 Hz, 3 and 5-H), 7.52 (1H, d J 3.0 Hz, thiazole 4-H), 7.86 <sup>a</sup> (2H, d J 9.0 Hz, 2 and 6-H) 7.91 (1H, d J 3.0 Hz, thiazole 5-H)
<b>3 d</b>	DMSO-d <sub>6</sub>	1.23 (6H, t J 8.0 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 3.64 (4H, q J 8.0 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 6.94 (1H, dd J 9.9 and 2.7 Hz, 5'-H), 7.56-7.68 (3H, m, COPh), 7.74 (1H, d J 9.9 Hz, 6'-H), 8.04-8.12 (3H, m, 3'-H + COPh), 8.25 (1H, s, thiazole 4-H), 8.74 (1H, s, NH)
<b>4 b</b>	DMSO-d <sub>6</sub>	1.18 (6H, t J 7.0 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 2.24 (3H, s, COCH <sub>3</sub> ), 3.50 (4H, q 7.0Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 6.65 (1H, dd J 9.6 and 2.7 Hz, 5'-H), 7.74 (1H, d J 9.6 Hz, 6'-H), 7.96 (1H, d J 2.7 Hz, 3'-H), 9.82 (1H, br s, NH), NH- imidazole was not observed.
<b>5 b</b>	DMSO-d <sub>6</sub>	1.19 (6H, t J 7.2 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 1.42 (3H, t J 7.5 Hz, imidazole-NCH <sub>2</sub> CH <sub>3</sub> ), 2.18 (3H, s, COCH <sub>3</sub> ), 3.52 (4H, q J 7.2 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 4.40 (2H, q J 7.5 Hz, imidazole-NCH <sub>2</sub> CH <sub>3</sub> ), 6.67 (1H, dd J 9.6 and 2.5 Hz, 5'-H), 7.76 (1H, d J 9.6 Hz, 6'-H), 7.86 (1H, d J 2.5 Hz, 3'-H), 10.10 (1H, br s, NH)
<b>6 b</b>	DMSO-d <sub>6</sub>	1.15 (6H, t J 7.7 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 2.17 (3H, s, COCH <sub>3</sub> ), 3.42 (4H, q J 7.7 Hz, 2x CH <sub>2</sub> CH <sub>3</sub> ), 6.55 (1H, dd J 9.0 and 2 Hz, 6'-H), 7.59 (1H, t J 7.7 Hz, 5-H), 7.69 (1H, d J 9.0 Hz, 5'-H), 7.78 (1H, d J 2.0 Hz, 2'-H), 7.92 (1H, d J 7.7 Hz, 6-H or 4-H), 8.05 (1H, d J 7.7 Hz, 4-H or 6-H), 8.27 (1H, t <sub>ap</sub> J 1.6 Hz, 2-H), 10.61 (1H, exchangeable s, NH)

dap and tap- pseudo doublet and pseudo triplet

<sup>a</sup> These signals described as dap are in fact an AA'XX' system.

For dyes **2**, for example, protons 4 and 5 of the thiazole ring are observed as two doublets with J 3 Hz. For dyes **3** the 4-H of the thiazole is a singlet at 8.25 ppm for **3d** (DMSO-d<sub>6</sub>). The signal due to the amide NH is observed as a broad singlet, for dyes **5b** and **6b** at 10.10 and 10.61 ppm respectively.



For dyes **3c** and **3d** two sets of signals in CDCl<sub>3</sub> solution were observed, due to coexistence of two conformations differing by internal rotation around the C<sub>1</sub>-N bond [16, 17]. This is not observed in DMSO-d<sub>6</sub> solutions, which could suggest that, under these conditions, conformer interchange is rapid.

The characterisation also included elemental analysis and/or mass spectra as shown in the table 3. Typical fragments derived from the thiazole ring were observed as well as for the amide, when it was present.

**Table 3** Mass spectra and elemental analysis data for dyes **2-6**

Dye	Mass Spectra m/z (%) (EI)	Elemental Analysis (%)	
		Found	Theory
<b>2 a</b>	260(M <sup>+</sup> , 35) 32(100)	C(59.76), H(6.41), N(21.38), S(12.32)	C(60.00), H(6.15), N(21.54), S(12.30) C <sub>13</sub> H <sub>16</sub> N <sub>4</sub> S
<b>2 b</b>	317(M <sup>+</sup> , 17) 45(9) 43(100)	C(55.19), H(6.09), N(21.25), S(9.75)	C(55.21), H(6.13), N(21.47), S(9.82) C <sub>15</sub> H <sub>19</sub> N <sub>5</sub> OS.½H <sub>2</sub> O
<b>2 c</b>	331(M <sup>+</sup> , 27) 57(100) 45(16)	C(58.11), H(6.52), N(19.86), S(9.09)	C(58.01), H(6.34), N(21.15), S(9.67) C <sub>16</sub> H <sub>21</sub> N <sub>5</sub> OS
<b>2 d</b>	379(M <sup>+</sup> , 25) 77(100) 45(9)	C(59.69), H(6.10), N(16.60), S(7.47)	C(59.11), H(5.91), N(17.24), S(7.88) C <sub>20</sub> H <sub>21</sub> N <sub>5</sub> OS.1½H <sub>2</sub> O
<b>3 a</b>	305(M <sup>+</sup> , 38) 57(100)	---	---
<b>3 b</b>	362((M <sup>+</sup> , 19) 45(5) 43(100)	C(48.92), H(5.17), N(22.18), S(8.56)	C(48.52), H(5.12), N(22.64), S(8.62) C <sub>15</sub> H <sub>18</sub> N <sub>6</sub> O <sub>3</sub> S.½H <sub>2</sub> O
<b>3 c</b>	377(M <sup>+</sup> +1, 24) 376(M <sup>+</sup> , 100) 246(83) 219(70) 45(3)	C(50.70), H(5.50), N(22.20), S(8.57)	C(51.06), H(5.32), N(22.34), S(8.51) C <sub>16</sub> H <sub>20</sub> N <sub>6</sub> O <sub>3</sub> S
<b>3 d</b>	424(M <sup>+</sup> , 43) 105(100) 45(5)	---	---
<b>4 a</b>	294(M <sup>+</sup> +1, 66) 293((M <sup>+</sup> , 11) 278((M <sup>+</sup> -15, 100)	C(61.19), H(5.28), N(33.12)	C(61.43), H(5.12), N(33.45) C <sub>15</sub> H <sub>15</sub> N <sub>7</sub>
<b>4 b</b>	350(M <sup>+</sup> , 54) 206(100)	350.1604 (HRMS)	350.1608 C <sub>17</sub> H <sub>18</sub> N <sub>8</sub> O
<b>4 c</b>	365(M <sup>+</sup> , 6) 53(100)	364.1755 (HRMS)	364.1755 C <sub>18</sub> H <sub>20</sub> N <sub>8</sub> O
<b>4 d</b>	412(M <sup>+</sup> , 12) 105(100)	C(62.79), H(5.15), N(26.90)	C(62.70), H(4.99), N(26.60) C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> O.H <sub>2</sub> O
<b>5 a</b>	321(12) 278(7) 76(100) 69(97) 55(78) 53(78)	C(63.44), H(6.23), N(30.51)	C(63.55), H(5.92), N(30.53) C <sub>17</sub> H <sub>19</sub> N <sub>7</sub>
<b>5 b</b>	378(M <sup>+</sup> , 7) 335(2) 69(100) 55(83)	---	---
<b>5 c</b>	292(M <sup>+</sup> , 7) 335(5) 57(100)	C(61.00), H(6.21), N(28.40)	C(61.22), H(6.12), N(28.57) C <sub>20</sub> H <sub>24</sub> N <sub>8</sub> O
<b>5 d</b>	440(M <sup>+</sup> , 2) 105(27) 77(100) 51(19)	C(64.21), H(5.65), N(24.86)	C(64.14), H(5.57), N(24.94) C <sub>24</sub> H <sub>24</sub> N <sub>8</sub> O
<b>6 a</b>	297(M <sup>+</sup> , 13) 133(100)	C(66.69), H(6.13), N(13.67)	C(66.59), H(6.53), N(13.71) C <sub>17</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> .½H <sub>2</sub> O
<b>6 b</b>	354(M <sup>+</sup> , 25) 205(100)	C(64.40), H(6.19), N(15.90)	C(64.39), H(6.26), N(15.81) C <sub>19</sub> H <sub>22</sub> N <sub>4</sub> O <sub>3</sub>
<b>6 c</b>	369(M <sup>+</sup> +1, 46) 368/(M <sup>+</sup> , 100)	C(64.35), H(6.64), N(14.64)	C(63.66), H(6.63), N(14.85) C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>3</sub> .½H <sub>2</sub> O
<b>6 d</b>	416(M <sup>+</sup> , 20) 77(100)	C(69.19), H(5.82), N(13.11)	C(69.23), H(5.77), N(13.46) C <sub>24</sub> H <sub>24</sub> N <sub>4</sub> O <sub>3</sub>

In table 4 the absorption characteristics for the dyes are described. In the IR bands due to NH, CO and CN stretching vibrations are included. As reported by Hutchings [18] a bathochromic shift is observed after introduction of an acylamino group; this effect is almost unnoticed for nitro dyes **3**. In all cases, except for dyes **2**, the propionylamino group produces a smaller bathochromic shift than the acetylamino group. The solvatochromism of compounds **3b** and analogues has been described [18]. In some cases, particularly for the heteroarylazo compounds, the results suggest that two conformers are present [18].

**Table 4** Spectroscopic data for dyes **2-6**

Dye	Uv-Visible <sup>a</sup>		IR <sup>b</sup>
	$\lambda_{\text{max}}$ (nm)	$\epsilon \times 10^{-3}$ (mol <sup>-1</sup> . dm <sup>3</sup> . cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )
<b>2 a</b>	486	43	[14]
<b>2 b</b>	508	37	3379, 1696
<b>2 c</b>	509	42	3373, 1694 <sup>b)</sup>
<b>2 d</b>	512	39	3378, 1679 <sup>b)</sup>
<b>3 a</b>	580	40.5	[15]
<b>3 b</b>	585	30	3446, 1684 <sup>b)</sup>
<b>3 c</b>	582	34	3433, 1676 <sup>b)</sup>
<b>3 d</b>	584	45	3448, 1677
<b>4 a</b>	478	30	2230
<b>4 b</b>	493	43	2223, 1614
<b>4 c</b>	488	31	3320, 2230, 1612
<b>4 d</b>	513	58	2234, 1601
<b>5 a</b>	508	49.4	2235, 2228, 1603
<b>5 b</b>	538	52.2	2242, 2229, 1696, 1608
<b>5 c</b>	532	54.5	2239, 2232, 1681, 1610
<b>5 d</b>	520	47.3	2229, 1678, 1613
<b>6 a</b>	437 <sup>c)</sup>	31	3448, 1685
<b>6 b</b>	465 <sup>c)</sup>	35	3488, 1716, 1652
<b>6 c</b>	460 <sup>c)</sup>	45.7	3464, 1694
<b>6 d</b>	459	33	3405, 1696, 1675

<sup>a</sup> Absorption spectra in the visible region were measured in ethanol except for c) (acetone)

<sup>b</sup> IR spectra were run in KBr pellet except in d) (liquid film)

The results obtained for wash and light fastness for disperse and reactive dyeings are shown in tables 5 and 6 respectively.

**Table 5** Wash and light fastness of disperse dyeings with dyes 2-5

Dye	Wash Fastness <sup>a</sup>		Light Fastness	
	Nylon 6.6	Polyester	Nylon 6.6	Polyester
<b>2 a</b>	2/3	--	2	--
<b>2 b</b>	2/3	4	3	1
<b>2 c</b>	3	4/5	4	1
<b>2 d</b>	3/4	4	3	3
<b>3 a</b>	3/4	5	2	4
<b>3 b</b>	3/4	5	2	3
<b>3 c</b>	--	5	--	3
<b>3 d</b>	4	3/4	1	2
<b>4 a</b>	2 <sup>b</sup>	4/5	3	1/2
<b>4 b</b>	2 <sup>b</sup>	4/5	3	3
<b>4 c</b>	2 <sup>b</sup>	4/5	4	3
<b>4 d</b>	1 <sup>b</sup>	4	3	3/4
<b>5 a</b>	4	5	4	4
<b>5 b</b>	4/5	4/5 <sup>c</sup>	5	5
<b>5 c</b>	4	5	5/6	6
<b>5 d</b>	3/4	5	5/6	6

<sup>a</sup> Change in shade

<sup>b</sup> The colour changes from red to orange after washing

<sup>c</sup> Stained

**Table 6** Wash and light fastness of reactive dyeings with dyes 6

Dye	Wash Fastness <sup>a</sup>				Light Fastness			
	Wool		Nylon 6.6		Wool		Nylon 6.6	
	Without Activation	With Activation	Without Activation	With Activation	Without Activation	With Activation	Without Activation	With Activation
<b>6 a</b>	2	5	3	5	1	3	1	7
<b>6 b</b>	2	4/5	2	5	1	4	1	6/7
<b>6 c</b>	1/2	4/5	2/3	5	1	3	1	7
<b>6 d</b>	4	4	4 <sup>b</sup>	4	4	5	3	6

<sup>a</sup> Change in shade

<sup>b</sup> The colour is much less intense compared with the dyeing with activation

In general, dyes **2-5** presented higher wash fastness ratings on polyester than on polyamide, however dyes **6** gave the highest values when they are applied with activation.

As expected the wash fastness ratings for dyes **6** increase if they are applied by reactive means. Of the range of dyes **2-5**, dyes **5** give the best light fastness performance.

It is noteworthy that the light fastness of dyes **6** improves when they are applied by a reactive dyeing method as compared to acid dyeing (without activation).

Among the twenty dyes presented the highest ratings on polyamide were observed for reactive dyes **6**.

## CONCLUSIONS

From the results obtained it was not possible to observe any influence of the variation of the acylamino group on the wash and light fastness properties of the dyes.

Most of the dyes synthesised showed poor fastness results, with the most promising being **5** and **6**. Since the reactive dyeing resulted in improved light fastness as observed for dyes **6** it could be interesting to investigate the introduction of a carboxylic group on dyes of the type **5b** to **5d**.

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