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ON THE SYNTHESIS AND APPLICATION OF SOME MONO- AND DIS-AZO ACID DYES

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ABSTRACT

The present paper describes the synthesis of two novel mono azo dyes of a yellow colour and four novel dis-azo dyes of orange and red colours. The dyes are obtained by the commonly accepted procedure - diazotization and coupling reactions. The compounds are isolated and characterized by TLC (Rf values), UV/Vis and IR spectra and conformed by proton NMR spectroscopy. The dyeing performance of the dyes obtained is evaluated on wool fabrics where their fastness properties of washing, rubbing and perspiration are determined in view of their exhaustion and fixation. The results obtained show good to excellent fastness properties on wool.

Keywords: *acid mono- and dis-azo dyes, UV-visible spectroscopy, fastness properties on wool.*

INTRODUCTION

Azo dyes are the largest and the most varied group of synthetic organic colorants in use today. They have characteristically good tinctorial strength as well as stability, whereas their preparation procedures, by the classic diazotization and coupling reactions, are very simple and of low cost. Hence, in addition to their conventional application as colorants for dye protein fibers such as wool, angora, cashmere, and silk, as well as the milk protein fiber called Silk Latte, the soy protein fiber called Soy Silk, and the synthetic polyamide fiber nylon [1 - 9], prints, inks, and toners, dyes for food [10] and cosmetics, azo compounds have also found their way into high-technology areas, such as colorants for liquid-crystalline materials and as photoconductors for photoreceptors in copiers and laser printers [11].

While phenols and naphthols are well established intermediates for the synthesis of various commercial dyes [1, 2, 12 - 15], they are marketed in the form of azo-acid dyes, etc. All of these dyes have phenolic or naphthoic motif, containing hydroxyl group as auxochrome group.

H-acid (1-amino-8-naphtol-3,6-disulfonic acid), I-acid (6-amino-1-naphtol-3-sulfonic acid) and o-aminophenol are one of the most important dye intermediates containing a hydroxyl group. They are widely used in chemical industry for the synthesis of direct, acid, reactive and azoic dyes [4 - 7, 10, 16 - 21]. Recently we have synthesized some new azo-reactive dyes, derivatives of H-acid and I-acid. They may polymerize with different monomers which provides their application to polymer industry [22 - 27].

With this in mind, it was of interest (i) to study the synthesis of some mono- and dis-azo acid dyes, which are o-aminophenol, H-acid and I-acid derivatives; and (ii) to investigate their application and fastness properties on wool.

EXPERIMENTAL

Materials, equipment and analysis

H-acid (75 %), I-acid (85 %), o-aminophenol and sulfanilic acid (4-aminobenzenesulfonic acid) used were Fluka products. Infrared (IR) spectra were recorded on a Specord 71 IR Spectrophotometer (Carl Zeiss, Germany) using potassium bromide (KBr) pellets. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Hewlett Packard 8452A UV/ Vis spectrophotometer (Germany) in a water solution (8×10^{-5} mol l^{-1} for mono-azo dyes and 2×10^{-5} mol l^{-1} for dis-azo dyes). Thin-layer chromatography (TLC) measurements were performed on ready-to-use plates (20 x 20 mm) pre-coated with 0.2 mm silica gel 60F254. 100 % wool fabrics of a mass per unit area of 195±10 g m^{-2} and of a linear density corresponding to warp tex 20 x 2 and weft tex 20 x 2 were used.

Synthesis of the compounds

Synthesis of compounds 1 and 2

Sulphanilic acid (0.1mol) was diazotized using a procedure previously described [10]. The reaction was completed within an hour at the temperature 0 - 5ºC.

0.1 mol (10.9 g) o-aminophenol was dissolved at a room temperature in 75 ml of water to which 15 ml of hydrochloric acid was added. The diazonium salt which was prepared in advance was slowly poured under continuous stirring. The reaction was performed at 10ºC - 15ºC and pH 8.0 - 8.5 (kept in presence of 15 g of sodium carbonate). The process was monitored by TLC on silica gel plates using chloroform–toluene–acetone (of a weight ratio of 4:1:2) eluent system. The process was completed within 7 h. Then dye **1** was isolated using NaCl (15 %) and filtered off. The compound was dried at 40ºC under vacuum.

For the synthesis of dye **2**, the diazonium salt and the coupling component were prepared in a manner similar to that used for dye **1**. The coupling component solution was slowly poured under continuous stirring to the diazo-derivative solution which was prepared in advance. The reaction was performed at 10 - 15ºC and pH 4.0 - 4.5 (in presence of 5 g of sodium acetate). The process was monitored by TLC on silica gel plates using eluent system n-propanol–ethanol (of a weight ratio of 2:1) eluent system. The process was completed within 5 h and 15.9 g of sodium carbonate were added until to the mixture to reach pH of 8.0 - 8.5. Dye **2** was isolated using 15 % of NaCl, filtered off and dried at 40ºC under vacuum.

Mono-azo dyes **1** and **2** were characterized by TLC (R_f values) and UV spectra (Table 1) and identified by IR and ^1H NMR spectra.

Dye 1: IR (KBr), cm^{-1}: 3462 (OH), 3375 and 3304 (NH_2), 3051 and 2958 (C-H from ArH), 1603 (NH_2), 1575 (N=N), 1470 (C-H from ArH), 1402 and 1216 (OH), 1141 and 1084 (S-O), 1031 (N=N), 896 and 812 (C-H from ArH); ^1H NMR (DMSO - d_6), ppm: 8.95 (s, 1H, -SO_3H), 6.66-6.37 (m, 7H, ArH), 4.53 (s, 1H, OH), 2.51 (s, 2H, NH_2).

Dye 2: IR (KBr), cm^{-1}: 3467 (OH), 3370 and 3302 (NH_2), 3031 and 2958 (C-H from ArH), 1601 (NH_2), 1570 (N=N), 1465 (C-H from ArH), 1210 (OH), 1042 and 1083 (S-O), 1031 (N=N), 894 and 844 (C-H from ArH); 1H NMR (DMSO - d6), ppm: 8.97 (s, 1H, -SO_3H), 6.67-6.36 (m, 7H, ArH), 4.48 (s, 1H, OH), 2.51 (s, 2H, NH_2).

Synthesis of compounds 1.1 and 2.2

Diazotation of dyes **1** and **2**: 0.003 mol (1 g) of mono-azo dye **1** or **2** were dissolved in a solution containing 0.002 mol (0.214 g) of sodium carbonate in 3.5 ml of water. Then 0.003 mol (0.207 g) of sodium nitrite as 30 % w/w solution was added to the mixture. The latter was further poured slowly under continuous stirring over a mixture of 22.6 ml of hydrochloric acid and 100 g ice. The temperature was kept 0ºC - 5ºC. The reactions were completed in an hour.

Coupling reaction: 0.003 mol (0.84 g) of I acid or 0.003 mol (1.28 g) of H acid were dissolved at room temperature in 15 ml of water by adding 2 ml 20 mass % solution of sodium carbonate. The corresponding diazonium salt prepared in advance was slowly poured to these solutions under continuous stirring. The reactions were performed at 10 ºC-15ºC and pH 8-8.5 (in presence of 1 g of sodium carbonate for **1.1** and **2.2**, whereas 1.5 g of sodium carbonate for **1.2** and **2.1**). The processes were monitored by TLC on silica gel plates using chloroform-toluene-acetone (of a mass ratio of 4:1:2) eluent system. The processes were completed within 7 h (for the dyes **1.1, 1.2** and **2.2**) and 5 h (for the dye **2.1**). All dyes were isolated using 15 % of NaCl, filtered off and dried at 40ºC under vacuum. The synthesized compounds were characterized by TLC (Rf values) and UV spectra. They were identified by IR and ^{1}H NMR spectra. The data obtained is listed in Table 1.

Dye 1.1: IR (KBr), cm^{-1}: 3461 (OH), 3435 and 3375 (NH_2), 3042 and 2955 (C-H from ArH), 1592 (NH_2), 1572 (N=N), 1484 (C-H from ArH), 1404 and 1218 (OH), 1204, 1142 and 1083 (S-O), 1033 (N=N), 876 and 814 (C-H from ArH); ^{1}H NMR (DMSO - d_6), ppm: 7.94-6.37 (m, 11H, ArH), 6.34 (s, 1H, OH), 6.18 (s, 1H, OH), 2.51 (s, 2H, NH_2).

Dye 1.2: IR (KBr), cm^{-1}: 3463 (OH), 3439 and 3374 (NH_2), 3058 and 2885 (C-H from ArH), 1596 (NH_2), 1585 (N=N), 1508 (C-H from ArH), 1404 and 1216 (OH), 1210, 1042 and 1083 (S-O), 1033 (N=N), 893 and 815 (C-H from ArH); ^{1}H NMR (DMSO - d_6), ppm: 7.78-6.84 (m, 10H, ArH), 6.37 (s, 1H, OH), 6.18 (s, 1H, OH), 2.51 (s, 2H, NH_2).

Dye 2.1: IR (KBr), cm^{-1}: 3460 (OH), 3442 and 3376 (NH_2), 3062 and 2881 (C-H from ArH), 1600 (NH_2), 1596 (N=N), 1506 (C-H from ArH), 1214 (OH), 1202 (S-O), 1044 (N=N), 980 and 848 (C-H from ArH); ^{1}H NMR (DMSO - d_6), ppm: 7.98-6.68 (m, 11H, ArH), 6.34 (s, 1H, OH), 6.18 (s, 1H, OH), 2.51 (s, 2H, NH_2).

Dye 2.2: IR (KBr), cm^{-1}: 3463 (OH), 3442 and 3374 (NH_2), 3060 and 2886 (C-H from ArH), 1588 (NH_2), 1584 (N=N), 1499 (C-H from ArH), 1404 and 1216 (OH), 1213 (S-O), 1044 (N=N), 980 and 845 (C-H from ArH); ^{1}H NMR (DMSO - d_6), ppm: 7.78-6.84 (m, 10H, ArH), 6.41 (s, 1H, OH), 6.18 (s, 1H, OH), 2.51 (s, 2H, NH_2).

Dyeing procedure

Wool fabrics were dyed with the dyes at 2 % depth o.w.f. according to a standard procedure [16]. Materials with an intense colour were obtained. After dyeing the wool samples were withdrawn and washed at 40ºC and dried.

Measurements and analyses

Dye exhaustion

The uptake of the acid azo-dyes by the blend fabric was measured by sampling the dye bath prior to and after the dyeing. The concentration (g l^{-1}) of the dye bath was measured on HP8452A UV/visible spectrophotometer at λ_{max} of the corresponding dye. The percentage of the individual dye exhaustion on wool (% E) was calculated using eq. (1) [28]:

$$\%E = \frac{C_1 - C_2}{C_1} \cdot 100 \qquad (1)$$

where E was the extent of the bath dye exhaustion in percent, C_1 and C_2 were the concentrations of the dye prior to and after dyeing, respectively.

The data obtained is presented in Table 2.

Dye fixation

The dye fixation ratio (% F), i.e. the percentage of the exhausted dye chemically bound to the blend fabric, was measured by refluxing the dyed samples in water for 15 min to extract the unfixed dye. This procedure was repeated until the extract was clear. The concentration of the extracts was then measured spectrophotometrically at λ_{max} of the corresponding dye and the value of F was calculated using eq. (2) [20]:

$$\%F = \frac{C_1 - C_2 - C_3}{C_1 - C_2} \cdot 100 \qquad (2)$$

The data obtained is listed in Table 2.

The total dye fixation (T/%), i.e. the percentage of the dye chemically bound referred to the total amount of the dye used, was calculated on the ground of the values of E and F using eq. (3) [20]:

$$T = \frac{E.F}{100} \qquad (3)$$

The data obtained is presented in Table 2.

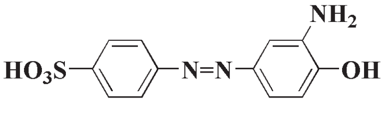
Fastness testing

The dyed samples were tested after washing-off using 2 g l^{-1} non-ionic detergent for 15 min at 40ºC in accordance with ISO standard methods. The specific tests were: BDS EN ISO 105-X12 (2004) - colour fastness to rubbing; BDS EN ISO 105-C06/A1S (2010) - colour fastness to washing; and BDS EN ISO 105-E04 (2013) - colour fastness to perspiration.

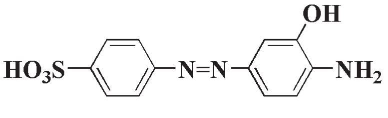
RESULTS AND DISCUSSION

Synthesis of the dyes

The paper presents the synthesis and the description of two mono-azo dyes of structure formulas **1** and **2** and four dis-azo dyes of structure formulas **1.1** and **2.2.**



1



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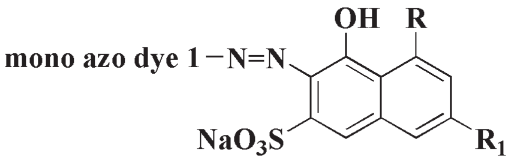
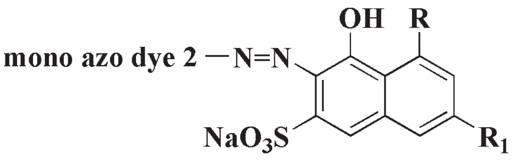


1.1 and 1.2



2.1 and 2.2

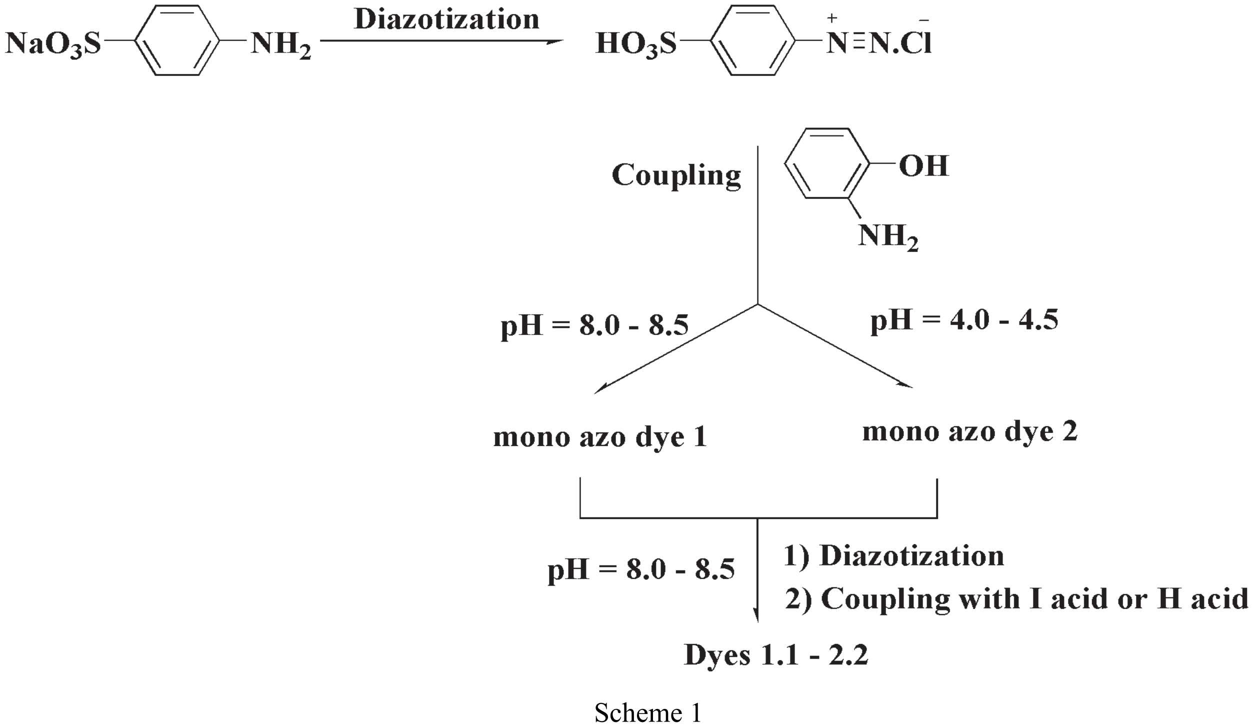
where R = -H and R_1 = $-NH_2$ (for dyes **1.1** and **2.1**), whereas R = $-NH_2$ and R_1 = $-SO_3Na$ (for dyes **1.2** and **2.2**).

The dyes were obtained following Scheme 1.

Spectral investigations

Spectrophotometric investigations are carried out to characterize the compounds synthesized and to determine the influence of the functional group(s) on their spectral properties. The absorption UV-Vis spectra of the compounds dissolved in water are recorded. The data is presented in Table 1.

It is easily seen that all compounds absorb in the visible region between 436 nm and 544 nm. The coupling



Scheme 1

Table 1. Characteristic data for the mono and dis-azo dyes.

Dye No	Yield, %	R_f	λ_{max}, nm	*log ε*, $l\ mol^{-1}\ cm^{-1}$
1	92	0.53^a	436	3.976
1.1	87	0.70^a	492	4.660
1.2	81	0.60^a	540	4.660
2	91	0.41^b	438	3.973
2.1	89	0.44^b	490	4.658
2.2	82	0.49^b	544	4.659

[a] *TLC on silica gel in a solvent system chloroform : toluene : acetone = 4 : 1 : 2*

[b] *TLC on silica gel in a solvent system n-propanol : ethanol = 2 : 1*

Table 2. Exhaustion (E), fixation (F) and total fixation (T) of acid azo dyes on wool.

Dyes No	E, %	F, %	T, %
1	79	80	63.2
1.1	82	88	72.2
1.2	85	89	75.6
2	74	80	59.2
2.1	77	89	68.5
2.2	76	87	66.1

[a] *TLC on silica gel in a solvent system chloroform : toluene : acetone = 4 : 1 : 2*

[b] *TLC on silica gel in a solvent system n-propanol : ethanol = 2 : 1*

of the yellow mono-azo dyes **1** and **2** with I acid and H acid show bathochromic shift at λ_{max} (the dyes with I acid are orange, while the dyes with H acid are red in colour). The logarithmic values of the molar extinction coefficient (log ε) of all dyes obtained are in the range of 3.973 - 4.660, which is consistent with their high absorption intensity. The change of the position of the second azo-group in respect to the first one does not affect the absorption spectral characteristics.

Dyeing and fastness properties of the dyes

The dyes are applied at 2 % depth on wool fabric and intensively colored samples are obtained. The percentage exhaustion, fixation and total fixation are calculated for all samples dyed by measuring the visible absorbance at the corresponding λ_{max} of the dye solutions prior to and after dyeing. The results are shown in Table 2. The total fixation percentage of the dyes is in the range of 59 to 76.

The results from the fastness tests of washing, rub-

Table 3. Fastness properties of dyed wool fabrics.

Dye No	Washing fastness	Perspiration fastness		Rubbing fastness	
		Acid	Alkaline	Dry	Wet
1	5 / 4 / 5	5 / 4 / 3	5 / 4 / 3	4-5	4
1.1	5 / 3 / 5	5 / 2 / 2	5/ 2 / 2	4	3-4
1.2	5 / 4 / 5	5 / 4 / 3	5 / 3 / 3	4-5	4
2	5 / 4 / 5	5 / 3 / 3	5 / 3 / 3	4-5	4-5
2.1	5 / 3 / 5	5 / 3 / 3	5 / 3 / 3	4-5	4
2.2	5 / 5 / 5	5 / 4 / 4	5 / 3 / 4	4	4

Fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent
Data x / y/ z indicate a change in color / staining wool / staining cotton

Table 4. Fastness properties of dyed wool fabrics with dyes of Bezema AG (Switzerland).

Dye	Washing fastness*	Sweat, alkaline**
Bemacid Yellow E-TL	3-4 / 4-5 / 2	4 / 3 / 2
Bemacid Red E-TL	4 / 3-4 / 3	4-5 / 4 / 3
Bemacid Yellow E-4G	3-4 / 3 / 3	4-5 / 2-3 / 2
Bemacid Yellow E-5R	2-3 / 4 / 2-3	4-5 / 3 / 2-3
Bemacid Red E-KRL	3 / 3-4 / 3	4-5 / 2-3 / 2-3
Bemacid Red E-T2B	4 / 3 / 4-5	5 / 2-3 / 2-3

** Washing fastness 40 °C (WO) DIN EN ISO 105C06/A1S;*
*** Perspiration fastness alkaline DIN EN ISO 105E04*
Fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent
Data x / y/ z indicate a change in color / staining wool / staining cotton

bing and perspiration of samples that had been dyed with the dyes synthesized are given in Table 3.

The fastness of washing and alkaline sweat of the dyed samples is compared to that of dyes of a similar structure (Table 4) used in practice (Bezema AG, Switzerland [29]).

The dyeing shows that dye **2.2** provides excellent washing fastness, while the rest acid azo-dyes synthesized by us show good to very good washing fastness. All newly synthesized dyes exhibit good to excellent fastness to perspiration and rubbing. Only dye **1.1** shows moderate perspiration fastness. The synthesized dyes provide better fastness of washing and alkaline sweat when compared to the commercial one (Table 4).

CONCLUSIONS

The present communication describes the synthesis of six new acid dyes, two mono- and four dis-azo dyes of yellow, orange and red colour. They show good dyeing performance on wool. Their fastness properties of washing, rubbing and perspiration are good to excellent and they can be used for dyeing under industrial conditions.

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