

## SYNTHESIS AND COLOUR ASSESSMENT OF SOME NEW STILBENE AZO DYES

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The synthesis of two new disazo symmetrical dyes suitable for cellulosic substrates and derived from 4,4'-diaminostilbene-2,2'-disulphonic acid is described. 1,3-dihydroxybenzene and 1-hydroxy-naphthalene-2-carboxylic acid were used as coupling components. Characterisation of the dyes was carried out by thin layer chromatography (TLC), electronic spectra (VIS), infrared spectra (IR) and by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. The colour assessment of the synthesized dyes was made by means of the tri-stimulus colour characteristics lightness (L\*), redness (a\*), yellowness (b\*), chroma (C\*) and hue angle (h°) relative to the standard illuminants: D65 (day light) and the standard 10° observer respectively. The colour difference ( $\Delta E^*_{ab}$ ) was calculated against two standards.

### INTRODUCTION

The wide spreading of the azo dyes is due to the simplicity of their synthesis which generally involves the diazotization and azo coupling reactions, to the many possibilities presented by the variation of the diazo compounds and coupling components as well as to the good light and wet fastness properties and to the colour variety.<sup>1</sup>

The scientific description of colour, or colorimetry, involves the specification of all relevant properties of a colour either objectively or subjectively. In an objective system for colour description, the corresponding properties are the dominant wavelength, the purity, and the luminance. The subjective description gives the hue, the saturation, and the lightness of a colour. A subjective color notation system (the CIE L\*a\*b\* and the CIE L\* C\* h\* systems based on

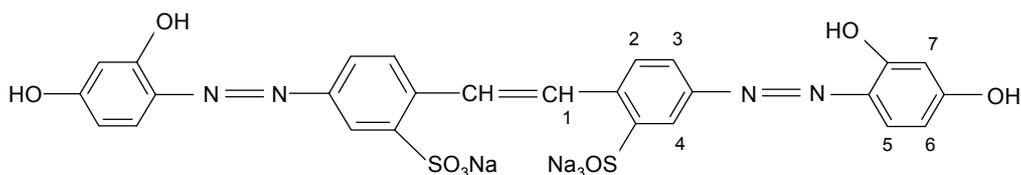
CIELAB 1976 L\*a\* b\* colorimetric system) provides comparison samples of colors rated according to these three properties.<sup>2-7</sup>

The azo-stilbene dyes represent an important class of the azo dyes and 4,4'-diaminostilbene - 2,2'-disulphonic acid was used as diazo compound in some of these dyes synthesis.<sup>8-13</sup>

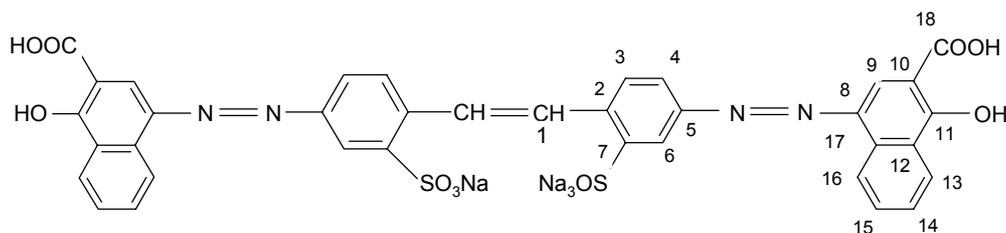
In the present paper the synthesis, the characterisation and the colour assessment of two new disazo symmetrical dyes derived from 4, 4'-diaminostilbene-2,2'-disulphonic acid is reported.

### RESULTS

In the present study, optimal reaction conditions for the synthesis of two new disazo symmetrical dyes (**1a**) and (**1b**) were established.



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Structure of dye **1b** (the atoms position for  $^{13}\text{C}$ -NMR spectrum)

The synthesis of the dyes with structure **1a** and **1b** involved two steps: the bis-diazotisation of 4,4'-diaminostilbene-2,2'-disulphonic acid by direct method, the isolation of the bis-diazonium salt and the coupling reaction of the resultant bis-diazonium salt with the coupling components: 1,3-

dihydroxybenzene (dye **1a**) and 1-hydroxy-naphthalene-2-carboxylic acid (dye **1b**).

The yields and the physicochemical characteristics of the synthesized dyes **1a** and **1b** are presented in Table 1.

Table 1

Reaction yields and the physicochemical characteristics of the disazo dyes **1a** and **1b**

Dye	Yield [%]	$\lambda_{\text{max}}^*$ [nm]	$\epsilon_{1\text{cm}}^{1\text{g/L}}$	$R_f^{**}$
<b>1a</b>	75	478	51.52	0.79
<b>1b</b>	78	454	37.73	0.77

\*from dye solutions in 50% MeOH aqueous solution;

\*\*Silica gel, eluent methyl-ethyl-ketone: $\text{NH}_3$  25%:methanol=3:2:3 (v:v:v) (dye **1a**)  
2:2:1(v:v:v) (dye **1b**)

The dye **1a** was investigated by means of infrared spectroscopy (IR) and  $^1\text{H}$ -NMR spectroscopy. The dye **1b** was investigated by means of infrared spectroscopy (IR) and  $^{13}\text{C}$ -NMR spectroscopy.

**Dye 1a; IR (KBr tablet,  $\text{cm}^{-1}$ ):** 3432(OH); 1610( $\text{C}=\text{C}_{\text{cis}}$ ); 1540, 1484 ( $\text{C}=\text{C}_{\text{feni}}$ ); 1188(C-O); 1024 ( $\gamma\text{CH}$  trans), 1078( $\text{SO}_2\text{sym}$ ), 928, 836 (phenyl, 1,2,4-trisubst), 638 ( $\gamma\text{CH}$  cis).

**Dye 1b; IR (KBr tablet,  $\text{cm}^{-1}$ ):** 3448(OH); 1640(C=O); 1608( $\text{C}=\text{C}_{\text{cis}}$ ); 1580, 1406 ( $\text{C}=\text{C}_{\text{feni}}$ ); 1228 (C-O); 1070( $\text{SO}_2\text{asym}$ ), 912, 860 (phenyl, 1,2,4-trisubst), 750(phenyl, 1,2-disubst) 630 ( $\gamma\text{CH}$  cis).

**Dye 1a;  $^1\text{H}$ -NMR (400MHz,  $(\text{CD}_3)_2\text{SO}$ , ppm):** 7.26(d, H1); 7.71(d, H2); 8.00(d, H3); 8.17(s, H4); 7.56(d, H5); 6.19(d, H6); 5.75(s, H7).

**Dye 1b;  $^{13}\text{C}$ -NMR (400MHz,  $\text{CDCl}_3$ , ppm):** 124.81(C1); 136.75(C2); 127.71(C3); 128.81(C4); 137.20(C7); 146.93(C8); 118.45(C9); 105.99(C10); 160.27(C11); 124.02(C12); 123.08(C13); 126.07(C14); 129.53(C15); 126.80(C16); 130.77(C17); 172.98(C18).

The colour of the synthesized dyes, **1a** and **1b** was evaluated by spectrophotometric method in terms of CIELAB parameters ( $L^*$ ), redness ( $a^*$ ), yellowness ( $b^*$ ) for the CIE D65 (day light)/ $10^\circ$ , illuminant observer conditions. The chroma ( $C^*$ ) and hue angle ( $h^\circ$ ) were derived from these values. The colour difference ( $\Delta E^*_{ab}$ ) was calculated against two standards (white and black). The spectrophotometric result are shown in Table 2 for dye **1a** and in Table 3 for dye **1b**.

Table 2

The spectrophotometric data of the azo-stilbene dye (**1a**) obtained using a D65 illuminant and a  $10^\circ$  observer

	W Stand	W <sub>1</sub> 2%dye	W <sub>2</sub> 5%dye	W <sub>3</sub> 8%dye	W <sub>4</sub> 15%dye	Bk Stand	Bk <sub>1</sub> 92%dye	Bk <sub>2</sub> 96%dye	Bk <sub>3</sub> 97%dye	Bk <sub>4</sub> 98%dye
$L^*$	95.20	75.24	71.74	52.64	46.10	26.83	31.29	30.67	30.92	30.47
$a^*$	0.12	18.34	22.18	17.51	14.41	0.62	4.60	4.44	4.24	2.72

Table 2 (continued)

b*	4.02	16.06	16.80	12.21	9.80	0.87	5.42	5.27	5.26	3.47
X	83.59	52.90	48.67	23.34	17.02	4.82	6.87	6.59	6.68	6.35
Y	88.10	48.66	43.27	20.72	15.34	5.03	6.78	6.51	6.62	6.43
Z	88.71	37.80	32.62	16.03	12.34	5.21	5.92	5.70	5.80	6.04
C*	4.02	24.37	27.82	21.35	17.42	1.06	7.10	6.89	6.76	4.41
h°	1.54	0.72	0.65	0.61	0.60	0.95	0.87	0.87	0.89	0.91
$\Delta E^*_{ab}$		29.58	34.65	46.71	51.47		7.52	6.98	7.01	4.94

Table 3

The spectrophotometric data of the azo-stilbene dye (**1b**) obtained using a D65 illuminant and a 10° observer

	W Stand	W <sub>1</sub> 2%dye	W <sub>2</sub> 5%dye	W <sub>3</sub> 8%dye	W <sub>4</sub> 15%dye	Bk Stand	Bk <sub>1</sub> 92%dye	Bk <sub>2</sub> 96%dye	Bk <sub>3</sub> 97%dye	Bk <sub>4</sub> 98%dye
L*	95.20	68.58	56.87	52.93	44.97	26.83	23.89	24.15	23.53	23.89
a*	0.12	22.46	25.48	21.06	12.57	0.62	2.45	0.53	0.31	0.23
b*	4.02	8.31	13.92	12.82	8.36	0.87	0.80	-0.09	-0.12	-0.35
X	83.59	43.98	29.70	24.43	15.84	4.82	4.02	3.97	3.77	3.87
Y	88.10	38.77	24.79	20.99	14.52	5.03	4.07	4.15	3.96	4.07
Z	88.71	34.88	18.70	15.99	12.15	5.21	4.21	4.47	4.27	4.43
C*	4.02	23.95	29.04	24.65	15.10	1.06	2.57	0.54	0.33	0.42
h°	1.54	0.35	0.50	0.55	0.59	0.95	0.31	6.11	5.92	5.30
$\Delta E^*_{ab}$		35.02	47.02	47.99	51.94		3.46	2.84	3.46	3.20

## DISCUSSION

The bis-diazotization of 4,4'-diaminostilbene-2,2'-disulphonic acid was performed by the direct method, in a HCl aqueous solution and the resulting bis-diazonium salt was separated by filtration unlike the conventional manner.<sup>14</sup>

It is well known that in aqueous medium the coupling reactions occurred at different pH values depending on whether coupling is performed with a phenol (naphtol), or with an aromatic amine. In the present work the used coupling components are aromatic hydroxy derivatives, therefore a low alkaline pH value of the reaction medium was required. In this regard the coupling reactions were carried out in an alkaline aqueous medium, in Na<sub>2</sub>CO<sub>3</sub>, at a temperature around 8°C. 1,3 dihydroxy benzene is an important and reactive coupling component with 3 possible coupling positions (2,4, or 6). In order to obtain a dye without by-products a stronger alkalinity of the reaction

medium was avoided. It was also established that the direct adding of the 4,4'-diaminostilbene-2,2'-disulphonic acid suspension to the alkaline solution of coupling component method was optimum for the dye's **1a** synthesis. In the case of the dye **1b** synthesis the coupling component was added to the disazonium salt suspension.

Infrared, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy data agree well with the dyes' structures.

CIELAB allows the specification of color perceptions in terms of a three dimensional space.

CIE XYZ tristimulus values can be calculated by integration of the reflectance values R(λ), the relative spectral energy distributions of the illuminant E(λ), and the standard observer functions x(λ), y(λ), and z(λ). The quantities L\*, a\*, and b\* are obtained from the tristimulus values according to the CIE 1976 equations. The L\* axis is known as the lightness and extends from 0 (black) to 100 (white). The other two coordinates a\* and b\* represent redness-greenness and yellowness-blueness respectively.

The polar parameters  $C^*$ ,  $h^\circ$  derived from the  $a^*$  and  $b^*$  values<sup>15</sup> are alternatively used.  $C^*$  (chroma) represents the colour saturation and  $h^\circ$  (hue angle) express the hue colour and lead to a more intuitive representation of a colour.

One measure of the difference in colour between two stimuli is the Euclidian distance ( $\Delta E^*_{ab}$ ), between the two points in the CIELAB three-dimensional space. The lightness ( $L^*$ ) values of the dye **1a** shown in table 2 range from 30.47 to 31.29 in the case of mixture with the black pigment (P.Bk 7) and from 46.10 to 75.24 in the case of the white pigment (P.W.6) respectively. The lightness ( $L^*$ ) lower values of dye **1b** shown in table 3 indicate a reduced light reflexion capacity of this compound.

In the white pigment mixture, dye **1b** is redder (increased values of  $a^*$ ) compared to the dye **1a**. In the black pigment mixture, dye **1a** is redder (increased values of  $a^*$ ) compared to the dye **1b** and a colour shifting to blue (negative values of  $b^*$ ) to the later is recorded. The colour hue modification can be easier observed from the hue angle values ( $h^\circ$ ) presented in Table 2 for dye **1a** and in Table 3 for dye **1b**.

Saturation refers to the richness of a hue as compared to a gray of the same lightness. The chroma ( $C^*$ ) very low values of dye **1b**, in the black pigment mixture reveal an impure colour.

A comparison between the colour difference ( $\Delta E^*_{ab}$ ), values presented in table 2 for dye **1a** and in table 3 for dye **1b** suggests a good colouring power of the dye **1a** in the white pigment mixture and the black pigment mixture respectively.

## EXPERIMENTAL

The chemical used in this work were obtained from Chimopar București, Merck, AcrOs Organic, Monicolor, S. C. Azur S.A.

The thin layer chromatographic (TLC) data were taken from silica gel plates (Merck 60-F254). Electronic spectra (VIS) were recorded on a Perkin Elmer  $\lambda$ 12 spectrophotometer for dye **1a** and on a CECIL CE 7200 spectrophotometer for dye **1b**. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a BRUKER Avance DRX-400 spectrometer. The infrared (IR) spectra were recorded on a Shimadzu FT/IR 8900 spectrometer.

### Synthesis of dye 1a and 1b

1. Bis-diazotization of 4,4'-diaminostilbene-2,2'-disulphonic acid

2.1 g 4,4'-diaminostilbene-2,2'-disulphonic acid (0,005 mol) were suspended in 10 mL distilled water. After 5 minutes of stirring 1.1 mL 30% NaOH aqueous solution were added. The reaction mixture was cooled to 5°C and treated

with 3 mL (0.03 mol) 32% HCl. The bis-diazotisation reaction was carried out by the adding of 0.75 g (0.01 mol) NaNO<sub>2</sub> solid to the 4,4'-diaminostilbene-2,2'-disulphonic acid suspension. The pH value of the mixture was kept around 1. After the NaNO<sub>2</sub> addition the mixture was stirred for another 20 minutes and the excess of the nitrous acid was decomposed by urea. Finally the obtained bis-diazonium salt was filtered out and the precipitate was washed with distilled water.

### 2. Bis-azo coupling reactions

A quantity corresponding to 0.011 mol of coupling components (e.g. 1,3-dihydroxybenzene and 1-hydroxy-naphthalene-2-carboxylic acid) was dissolved in 10% NaOH aqueous solution. The bis-diazonium salt obtained in step 1 was suspended in 20 mL distilled water and was added to the alkaline solution of 1,3-dihydroxybenzene. In the case of dye **1b** coupling reaction the bis-diazonium salt suspension was treated with the alkaline solution of 1-hydroxy-naphthalene-2-carboxylic acid. The reaction mixture was stirred another 3 hours at 8°C and the pH was maintained in the range of 7-8 by periodic addition of 10% Na<sub>2</sub>CO<sub>3</sub> aqueous solution. The coupling reaction was controlled by the drop reaction. The dye **1a** precipitated after 15 hours at pH=8, and was separated by filtration and washed with methanol. The dye **1b** was separated by precipitation of the dye from the acid solution (pH=5.5) obtained by addition of 10% HCl solution. The precipitate was washed with anhydrous ethyl ether. Finally the crude dyes were purified by crystallization from ethanol. The obtained compounds were characterised by thin layer chromatography (TLC), infrared spectra (IR), electronic spectra (VIS) and by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy.

### Colour analysis of dye 1a and 1b

The colour spectrophotometric study of the new synthesized azo-stilbene dyes was performed on a Minolta 3200d spectrophotometer. The samples differentiated by the dye concentration, the white pigment (P.W.6) and black pigment (P.Bk.7) respectively and were layed on a cellulosic substrate (wood). Further details on the general procedure may be found in references.<sup>16</sup> Using a D65 illuminant and a 10° observer, the CIELAB coordinates, the hue angle ( $h^\circ$ ), and the chroma ( $C^*$ ) were determined for each sample partly. The colour difference ( $\Delta E^*_{ab}$ ) was calculated confronted by two standards.

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