

# Synthesis, characterisation and colorimetric study of new azo-stilbene dyes

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## ABSTRACT

Using 4,4'-diaminostilbene-2,2'-disulphonic acid an well known eco-friendly middle component and 2-chlorosalicylanilide and 2-bromosalicylanilide as coupling components, two new symmetrical disazo direct dyes were synthesized. The dyes were analyzed by TLC, VIS, FT/IR, <sup>13</sup>C-NMR spectroscopy, and HPLC technique. The colour assessment of the two new 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 (natural day light), A (tungsten light), F2 (fluorescent light) and the standard 10° observer respectively. The colour differences ( $\Delta E_{ab}^*$ ,  $\Delta E_{CMC}$ ) calculated against an white standard, namely Pigment White 6 (C.I. 77 891) reveal a good colouring power of the new azo-stilbene dyes.

**Keywords:** 4,4'-diaminostilbene-2,2'-disulphonic acid, CIE (or CIELab) colour space

## Introduction

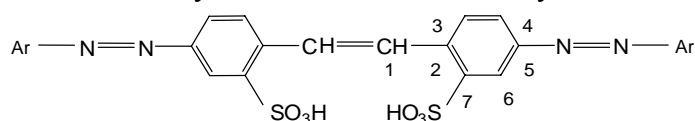
The numerous studies concerning the replacement of carcinogenic benzidine dyes with other structures underline the importance of azo dyes derivatives of 4,4'-diaminostilbene-2,2'-disulphonic acid.<sup>1</sup> The presence of the extended conjugation of the two aromatic remains of the azo group due the stilbenic chromogen leads to some interesting application properties for the synthesized dyes, fact that had oriented us toward the study of such compounds

The 1976 CIELAB color space is a second attempt at providing a perceptually uniform color space, the distance between two points also approximately tells how different the colors are in lightness (L\*), chroma (C\*) and hue (h°), calculated from the tristimulus values XYZ. CIELAB is the worldwide standard for color measurement and allows for easy communication concerning colors because it is based on numerical values, which takes the guess work out of color correction.<sup>2</sup>

In this work, the synthesis, the characterisation and the colorimetric study of two new disazo direct dyes with symmetrical structure derived from 4,4'-diaminostilbene-2,2'-disulphonic acid, an accessible, eco-friendly component<sup>3,4</sup> are presented.

## Results and discussion

The synthesis of the dyes with structure shown in Scheme 1 involved the bis-diazotization of 4,4'-diaminostilbene-2,2'-disulphonic acid and the coupling reactions of the resultant bis-diazonium salt with 2-chlorosalicylanilide and 2-bromosalicylanilide as coupling components.



where the couplings components Ar for the azo-stilbene dyes are; 1 (for dye **I**); 2 (for dye **II**):



**Scheme 1.** Structure of the azo-stilbene dyes **I** and **II** (the atoms position for  $^{13}\text{C}$ -NMR spectrum)

The bis-diazotization of 4,4'-diaminostilbene-2,2'-disulphonic acid was carried out by the direct method, in a HCl aqueous solution and the resulting bis-diazonium salt was separated by filtration for the complete removal of the salts.

The azo coupling reactions were performed in an alkaline aqueous medium (in presence of  $\text{Na}_2\text{CO}_3$ ) at pH around 8 and temperature around  $10^\circ\text{C}$  for the dye **I** and at pH around 8.5 and temperature around  $8^\circ\text{C}$  for the dye **II**. An excess of 3% of the above amides of the salicylic acid was used. The alkaline solutions of the coupling components were added to the acid suspension of the bis-diazonium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid. The reaction time was about 2.5 h. The dyes were purified by recrystallization from dioxane:pyridine 90:10 (v:v) mixture.

The synthesized disazo dyes were obtained in 80% yield and were characterized by means of TLC, VIS, FT/IR,  $^{13}\text{C}$ -NMR, spectroscopy and HPLC technique.

The obtaining of the coupled compounds was examined by means of TLC, using an eluent according generally to the direct dyes (*iso*-propanol:methyl-ethyl ketone:ammonia 25%).

The VIS absorption spectra of dyes **I** and **II** present absorbance values (458-470nm), according to their related chemical structures.

The chromatographic study was carried out in different elution conditions: absolute methanol, methanol-water 90%; 85% (v/v) and flow rate ranging from 0.75-1 of mL/min revealing a single dominant product for each of the two synthesized dyes (**I** and **II**)

The FT/IR and  $^{13}\text{C}$ -NMR spectroscopy data agree well with the dyes' s chemical structures.

For **I**: TLC (silicagel plates 60F-254; *iso*-propanol:methyl-ethyl ketone:ammonia 25%=4:3:5 (v:v:v)) ( $R_f$ : 0.72); VIS (50% aqueous MeOH) ( $\lambda_{\text{max}}/\text{nm}$ ;  $\lg\epsilon_{\text{max}}$ : 458; 4.36); IR (KBr) ( $\text{v}/\text{cm}^{-1}$ : 3416, 1319, (OH), 1635, 1543, 1228 (CONH), 1188, 1075 ( $\text{SO}_3\text{H}$ ));  $^{13}\text{C}$ -NMR (100MHz,  $(\text{CD}_3)_2\text{SO}$ ) ( $\delta/\text{ppm}$ : 125.16( $\text{C}_1$ ), 135.34( $\text{C}_2$ ), 127.80( $\text{C}_3$ ;  $\text{C}_{10}$ ), 123.51( $\text{C}_4$ ), 122.87( $\text{C}_6$ ), 146.00( $\text{C}_{1'}$ ), 117.13( $\text{C}_{3'}$ ), 156.78( $\text{C}_{4'}$ ), 119.65( $\text{C}_6$ ), 164.10( $\text{C}_7$ ), 133.81( $\text{C}_8$ ), 129.34( $\text{C}_{12}$ ), 130.66( $\text{C}_{13}$ )); HPLC (C18, 83% aqueous MeOH, isocratic elution, flow rate:0.9mL/min) ( $\lambda/\text{nm}$ ;  $t_R/\text{min}$ : 458; 1.43)

For **II**: TLC (silicagel plates 60F-254, *iso*-propanol:methyl-ethyl ketone:ammonia 25%=4:3:6 (v:v:v)) ( $R_f$ : 0.74); VIS (50% aqueous MeOH) ( $\lambda_{\text{max}}/\text{nm}$ , ( $\lg\epsilon_{\text{max}}$ : 470; 4.59); IR (KBr) ( $\text{v}/\text{cm}^{-1}$ : 3393, 1314 (OH), 1636, 1536, 1231(CONH), 1187, 1072 ( $\text{SO}_3\text{H}$ ));  $^{13}\text{C}$ -NMR (100MHz,  $(\text{CD}_3)_2\text{SO}$ ) ( $\delta/\text{ppm}$ ): 125.87( $\text{C}_1$ ), 136.59( $\text{C}_2$ ), 127.28( $\text{C}_3$ ), 123.70( $\text{C}_4$ ), 150.31( $\text{C}_5$ ), 120.07( $\text{C}_6$ ), 136.93( $\text{C}_7$ ), 146.70( $\text{C}_{1'}$ ), 126.85 ( $\text{C}_2$ ), 117.15( $\text{C}_{3'}$ ), 156.98( $\text{C}_{4'}$ ), 119.07( $\text{C}_5$ ), 119.59( $\text{C}_6$ ), 164.33( $\text{C}_7$ ), 133.85( $\text{C}_8$ ), 123.93( $\text{C}_9$ ), 128.31( $\text{C}_{10}$ ); 130.59( $\text{C}_{12}$ ); HPLC (C18, 83% aqueous MeOH, isocratic elution; flow rate:0.9mL/min) ( $\lambda/\text{nm}$ ;  $t_R/\text{min}$ : 468; 1.36)

A "color space" is a useful conceptual tool for understanding the color capabilities of a particular device or digital file. When trying to reproduce color on another device, color spaces can show whether you will be able to retain shadow/highlight detail, color saturation, and by how much either will be compromised.

**CIE xyz** is based on a direct graph of the signals from each of the three types of color sensors in the human eye. These are also referred to as the X, Y and Z (tristimulus function that were created in 1931). However, this representation allocates too much area to the greens — confining most of the apparent color variation to a small area.<sup>5</sup>

**CIE L\*a\*b\*** remaps the visible colors so that they extend equally on two axes — conveniently filling a square. Each axis in the L\*a\*b\* color space also represents an easily recognizable property of color, such as the red-green and blue-yellow shifts.

Colour-difference evaluation is a complex problem a lot of various solution has been proposed. As in other scientific disciplines, the development of improved colour-difference formulas must proceed as a joint effort of data gathering, theory and statistical model building.<sup>6</sup>

$\Delta E_{ab}^*$  is based on  $L^*$ ,  $a^*$ ,  $b^*$  colour difference and was intended to be a single number metric for pass/fail decision.  $\Delta E_{CMC}$  is a single number measurement that defines an elliptical color difference space around the product standard.

The spectrophotometric data are shown in table I for dye I, and in table II for the dye II

Table I The spectrophotometric data of the direct dye (I) obtained by using D65, A and F2 illuminants and 10° observer

Illuminant		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
D65	L*	95.20	82.70	76.73	76.02	68.50
	a*	0.12	13.57	18.19	19.87	24.39
	b*	4.02	20.16	29.33	30.66	34.57
	X	83.59	64.16	55.36	54.81	44.52
	Y	88.10	61.59	51.09	49.93	38.65
	Z	88.71	45.27	29.85	28.13	18.40
	C*	4.02	24.30	34.51	36.53	42.31
	h*	1.54	0.98	1.02	1.00	0.96
	$\Delta E_{ab}^*/\Delta E_{CMC}$		24.25/24.51	36.17/36.08	38.31/38.45	47.28/45.50
A	L*	95.50	85.37	80.30	80.26	72.71
	a*	1.23	15.39	21.13	22.19	26.44
	b*	4.03	24.77	35.58	37.37	42.12
	X	99.47	82.29	73.81	74.24	60.75
	Y	88.82	66.74	57.22	57.14	44.73
	Z	29.34	14.85	9.77	9.36	5.99
	C*	4.21	29.16	41.39	43.46	49.73
	h*	1.28	1.01	1.03	1.03	1.01
	$\Delta E_{ab}^*/\Delta E_{CMC}$		27.08/28.45	40.29/42.20	42.23/44.51	51.05/51.87
F2	L*	95.42	84.70	79.28	79.05	71.33
	a*	0.13	9.08	11.96	13.16	16.42
	b*	4.27	23.48	33.85	35.76	40.12
	X	91.59	71.90	62.38	62.47	50.09
	Y	88.61	65.43	55.41	55.01	42.67
	Z	57.17	29.21	19.14	18.14	11.62
	C*	4.27	25.17	35.91	38.10	43.35
	h*	1.54	1.20	1.23	1.22	1.18
	$\Delta E_{ab}^*/\Delta E_{CMC}$		23.74/24.07	35.71/36.09	37.81/38.56	46.16/44.85

The lightness ( $L^*$ ) values of the dyes in the white pigment mixture show an indirect proportionality to the dyes's concentrations. The increased values of  $a^*$  and  $b^*$  reflect a colour simultaneous shifting of the dyes both to red and to yellow. At the same time, the hue angle values ( $h^\circ$ ), indicate a redder colour for the dye **II** (obtained using 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 2-bromosalicylanilide as coupling component) compared to dye **I** (obtained using 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 2-chlorosalicylanilide as coupling component).

The results shown in tables **I** and **II** indicate different colour characteristics under the influence of daylight (D65), tungsten light (A), and fluorescent light (F2) illuminants (metamerism).

The colour differences ( $\Delta E_{ab^*}$ ) and ( $\Delta E_{CMC}$ ) were calculated against one standard, revealing a high colouring power for the two new studied dyes.

**Table II** The spectrophotometric data of the direct dye (**II**) obtained by using D65, A and F2 illuminants and 10° observer

Illuminant		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
D65	L*	95.20	77.07	71.89	69.31	60.57
	a*	0.12	17.36	21.87	24.45	25.83
	b*	4.02	22.58	31.24	35.36	35.73
	X	83.59	55.61	48.80	45.74	34.19
	Y	88.10	51.65	43.39	39.77	28.76
	Z	88.71	35.16	23.35	18.70	15.27
	C*	4.02	28.48	38.13	42.99	44.08
	h*	1.54	0.92	0.96	0.97	0.95
	$\Delta E_{ab^*}/\Delta E_{CMC}$			31.15/29.75	41.92/40.62	47.38/46.16
A	L*	95.50	80.60	76.01	74.11	65.12
	a*	1.23	18.66	24.41	27.00	27.82
	b*	4.03	27.94	38.34	43.00	43.35
	X	99.47	73.20	66.36	63.75	47.82
	Y	88.82	57.74	49.91	46.88	34.20
	Z	29.34	11.72	7.66	6.24	5.01
	C*	4.21	33.59	45.46	50.78	51.50
	h*	1.28	0.98	1.00	1.01	1.00
	$\Delta E_{ab^*}/\Delta E_{CMC}$			33.13/33.66	45.77/46.98	51.39/52.96
F2	L*	95.42	79.58	74.86	72.03	63
	a*	0.13	11.33	14.52	16.56	17.52
	b*	4.27	26.28	36.24	40.97	41.15
	X	91.59	62.68	55.36	51.31	37.92
	Y	88.61	55.94	48.06	43.71	31.59

## Materials and Methods

The chemicals employed in this study as *p.a.* commercial products were provided by Acr̄Os Organic Co, Lachema Co, S. C. Chimopar S. A., Fluka Co. Merck Co., S.C. Azur S.A. and Monicolor S. A. The thin layer chromatography (TLC) data were taken from silica gel (60F-254) plates (Merck). The solvent system employed was: *iso*-propanol:methyl-ethyl ketone:ammonia 25%. Electronic absorption spectra (VIS) of dyes in 50% aqueous MeOH solution were performed on a CECIL CE 7200 spectrophotometer in the range 300–800nm. The HPLC study has been performed on a JASCO ensemble, using a diode-array UV–VIS detector. The dyes's purity was investigated using a C18 (25x0.46mm), 5µm column and an 83% aqueous MeOH solution as mobile phase. The HPLC method consists of an isocratic elution and a flow rate of 0.9-1mL/min. The FT/IR spectra were recorded on a JASCO FT/IR–4200 spectrometer in the range 400-4000cm<sup>-1</sup>. The <sup>13</sup>C-NMR spectra were recorded as solution in DMSO–d<sub>6</sub> using a BRUKER AVANCE DRX-400 spectrometer with tetramethylsilane (TMS) as the internal standard. The colour parameters were measured using a MINOLTA 3200d spectrophotometer.

## Synthesis of the dyes I and II

A mixture of 1.95 g of 95% 4,4'-diaminostilbene- 2,2'-disulphonic acid (0.005 mol), 10 mL distilled water and 30% NaOH aqueous solution was cooled to 5°C. Then, 3 mL (0.03 mol) of 32% HCl were added to the mixture. The resulting suspension was bis-diazotised with 0.71 g of 98% solid NaNO<sub>2</sub> (0.0101 mol) at 5°C and a pH value around 1. The mixture was maintained under stirring for 1 hour for the completion of the diazotation reaction. Finally, the excess of the nitrous acid was destroyed by urea. The obtained bis-diazonium salt was filtered out and the precipitate was washed with distilled water. Thereafter, 2.86g and 3.38 g of 95% coupling components (2-cholrosalicylanilide and 2-bromosalicylanilide), (0.011 mol) were dissolved in 10% NaOH aqueous solution and the previously obtained bis-diazonium salt was suspended in 20 mL distilled water. The coupling reactions were carried out by direct treating of the bis-diazonium salt suspensions with the alkaline solutions of the above mentioned components. The pH of the reaction mixture was maintained around 8 for dye **I** and 8.5 for dye **II** by periodic addition of 10% Na<sub>2</sub>CO<sub>3</sub> aqueous solution. The temperature did not exceed 10°C for dye **I** and 8°C for dye **II**. The coupling reactions were controlled in the conventional method (drop reaction with an alkaline solution of 1-amino-8-naphtol-3,5-disulphonic acid (acid H) and with the diazonium salt of 4-nitroaniline). After the complete addition of the alkaline solutions of the coupling components, the mixtures were maintained under stirring for 2.5 hours for the completion of the coupling reactions. The dyes were separated by precipitation from an acid solution (pH=6-6.5) by addition of 10% HCl solution. The crude dyes were collected by filtration, washed with dimethyl-ketone and methanol for dye **I** and N, N-dimethylformamide and methanol for dye **II** and dried. Thereafter, the dyes were purified by recrystallization from dioxane:pyridine 90:10 (v:v) mixture.

## Colour assessment

The samples were layed on a cellulosic substrate (wood) and were differentiated by the dyes's and the titanium dioxide's concentration (P.W.6; C.I. 77 891). The colour analysis was carried out by measuring the CIELAB parameters for the CIE D65/10°, A/10° and F2/10° illuminant/observer conditions. The hue angle (h°), and the chroma (C\*) were derived from these values. The colour difference (ΔE<sub>ab</sub>\* and ΔE<sub>CMC</sub>) were calculated confronted by the mentioned white standard

## Conclusions

Two new disazo symmetrical direct dyes containing 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 2-chorosalicylanilide and 2-bromosalicylalideni as coupling components were synthesized and characterized. The spectroscopy data (VIS, FT/IR, <sup>13</sup>C-NMR), the chromatographic data (TLC and HPLC) and the colour analysis data (CIELAB) support explicitly the proposed related chemical structures for the synthesized dyes. The colour differences ( $\Delta E_{ab}^*$  and  $\Delta E_{CMC}$ ) calculated against one standard reveal a good colouring power of the dyes **I** and **II** in the white pigment mixture.

## Acknowledgement

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