

Disazo symmetrical stilbene dyes. Synthesis and colour evaluation.

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The synthesis of two new symmetrical disazo direct dyes containing 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 3-chlorosalicylanilide and 4-chlorosalicylanilide as coupling components are presented. The synthesized dyes were analyzed by thin layer chromatography (TLC), electronic spectra (VIS) and HPLC technique. Their structures were elucidated by FT/IR and ¹³C-NMR spectroscopy. The CIELAB (1976) colour space was used in all the colour measurements for the two disazo stilbene dyes under the CIE recommended illuminants: D65 (natural day light), A (tungsten light), F2 (fluorescent light) and the standard 10° observer respectively. The colour difference (ΔE_{ab}^) was calculated against one standard.*

Keywords: Azo-stilbene dyes, CIELAB uniform colour space

Introduction

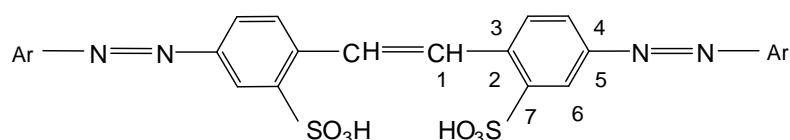
Azo dyestuffs are considered to be one of the largest chemical groups of dyes presently in existence and their success is due to simple synthetic procedures involved, the great structural diversity of available compounds, generally high molar extinction coefficients and medium to high fastness properties with respect to both light and wetness.¹

There are several ways for describing in scientific terms the characteristics of a particular colour. When colour is assessed on the basis of reflectance measurements, it is common to consider the three relevant attributes of perception of colour as hue, chroma and lightness. Nowadays, the mathematical approaches which make use of the concept of colour space for colour measurement and specification are well known. In one of the most important of these approaches, the CIELAB equation for the measurement of colour differences makes use of the visually uniform LAB space.^{2,3}

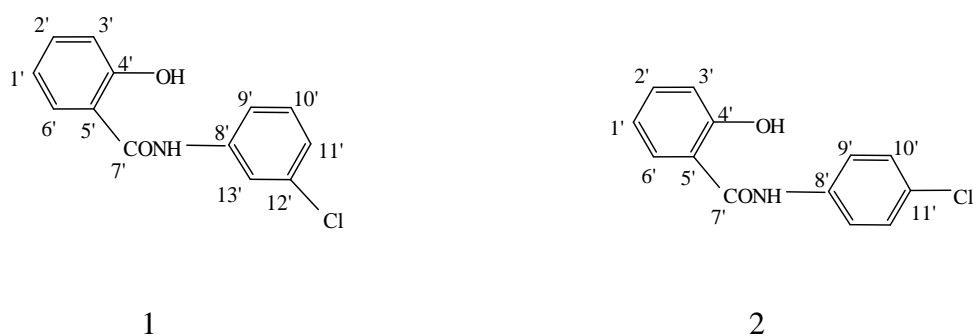
In this work, the synthesis, the physicochemical properties and the colorimetric evaluation of two new disazo direct dyes with symmetrical structure derived from 4,4'-diaminostilbene-2,2'-disulphonic acid, an accessible, non-carcinogenic middle component^{4,7} are presented.

Results and discussion

The synthesis of the dye with structures 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 3-chlorosalicylanilide and 4-chlorosalicylanilide as coupling components in a 1:2 molar ratio.



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 ¹³C-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, unlike the well known method.⁹ In the azo coupling reaction, the diazonium ions formed during diazotization give rise to azo compounds in an electrophilic aromatic substitution. As diazonium ions are relatively weak electrophilic reagents, the phenolate ion (Ar-O⁻) and the free amine (Ar-NH₂) react more easily as coupling components than free phenol (Ar-OH) and the ammonium ion (Ar-NH₃⁺).¹⁰ In

this regard the coupling reactions were performed in an alkaline aqueous medium (pH around 8), in presence of Na_2CO_3 at a temperature around 10°C . It was found that the direct adding of the alkaline solutions coupling components (3-chlorosalicylanilide and 4-chlorosalicylanilide) to the acid suspension of the bis-diazonium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid was optimum for the dye's I and II synthesis. In the coupling step with the above mentioned amides of the salicylic acid, a 3% excess of them was used. The reaction time was about 2.5 h. The progress of the coupling reactions was monitored in the usual way and by TLC, when the formation of the coupled compounds was examined. The dyes were purified by recrystallization from dioxane:pyridine 90:10 (v:v). This mixture was selected according to the lower solubility of the basic dominant product in dioxane as compared to the higher one in pyridine, at high temperatures.

The synthesized disazo dyes were obtained in 80-82% yield and were characterized by means of TLC, VIS, FT/IR, ^{13}C -NMR, spectroscopy and HPLC technique.

As shown in the experimental part, the FT/IR and ^{13}C -NMR spectroscopy data agree well with dyes' s chemical structures.

The VIS absorption spectra of dyes **I** and **II** present quite similar 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. As presented in experimental part, the chromatographic separation reveals the presence of a single dominant product for the three synthesized dyes (**I** and **II**). The obtained results by means of two distinct analysis methods (spectroscopic and chromatographic), show insignificant differences.

Dye (**I**):

TLC (silicagel plates 60F254, *iso*-propanol:methyl-ethyl ketone:ammonia 25%=4:3:5.5 (v:v:v)) (R_f): 0.74;

VIS (50% aqueous MeOH) ($\lambda_{\text{max}}/\text{nm}$, ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 466 (26750);

IR (KBr, cm^{-1}): 3412 (stretching of -OH group), 1639(C=O stretching of -CO-NHgroup), 1539(**II** amide band), 1231(**III** amide band), 679(-NH deformatng of secondary amide), 1188(SO_2 asym. stretching of - SO_3H group), 1072(SO_2 sym. stretching of - SO_3H group), 1300(-OH deformatng of -OH group), 912,832,776,747(CH-deformatng of aromatic ring), 554,449 (skeletal deformatng of aromatic ring);

^{13}C -NMR (100MHz, $(\text{CD}_3)_2\text{SO}$, δ/ppm): 124.45(C_1), 137.25(C_2), 126.74(C_3), 123.74(C_4), 150.18(C_5), 120.41(C_6), 139.64(C_7), 146.82($\text{C}_{1'}$), 126.31($\text{C}_{2'}$), 117.21($\text{C}_{3'}$), 158.09($\text{C}_{4'}$), 119.34($\text{C}_{5'}$), 119.82($\text{C}_{6'}$), 166.22($\text{C}_{7'}$), 133.71(C_8), 120.21(C_9), 130.40 (C_{10}), 124.01(C_{11}), 133.06 (C_{12});

HPLC (C18, 83% aqueous MeOH, isocratic elution, flow rate: 0.9mL/min) (λ/nm , (t_{R}/min)):466 (1.40)

Dye (II):

TLC (silicagel plates 60F254, *iso*-propanol:methyl-ethyl ketone:ammonia 25%=4:3:4.5 (v:v:v)) (Rf): 0.62;

VIS (50% aqueous MeOH) ($\lambda_{\text{max}}/\text{nm}$, ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$)): 470 (31231);

IR (KBr, cm^{-1}): 3432 (stretching of -OH group), 1635(C=O stretching of -CO-NHgroup), 1550(II amide band), 1240(III amide band), 700(-NH deforming of secondary amide), 1180(SO_2 asym. stretching of - SO_3H group), 1076(SO_2 sym. stretching of - SO_3H group), 1336(-OH deforming of -OH group), 824(CH-deforming of aromatic ring), 520,485,476 (skeletal deforming of aromatic ring)

^{13}C -NMR (100MHz, $(\text{CD}_3)_2\text{SO}$, δ/ppm): 125.20(C_1), 136.96(C_2), 127.79(C_3), 123.21(C_4), 150.73(C_5), 121.38(C_6), 138.11(C_7), 145.99($\text{C}_{1'}$), 126.57($\text{C}_{2'}$), 117.11($\text{C}_{3'}$), 158.02($\text{C}_{4'}$), 119.11($\text{C}_{5'}$), 119.66($\text{C}_{6'}$), 166.13($\text{C}_{7'}$), 133.71(C_8), 122.32(C_9), 128.57(C_{10}), 129.12(C_{11});
HPLC (C18, 83% aqueous MeOH, isocratic elution; flow rate: 1mL/min) (λ/nm , t_{R}/min):471 (1.55)

CIE 1976 (L^* , a^* , b^*) or CIELAB colour space provides a three-dimensional representation for the perception of colour stimuli.^{11,12} Because the human retina has three types of colour photoreceptor, three numerical components are necessary and sufficient to describe a colour, providing that appropriate spectral weighting functions are used.

The description of colour is based on the interaction of three elements: illuminant, object, and observer. Illuminants are normally specified in terms of the relative energy tabulated for each wavelength or wavelength band. The reflectance spectrum of a coloured sample can be used, in conjunction with the CIE standard observer function and the relative spectral energy distribution of an illuminant, to calculate the CIE XYZ tristimulus values for that sample under that illuminant. It is well known that in the CIELAB colour space each colour has an unique location defined by its cartesian co-ordinates with respect to the axes L^* , a^* , and b^* (obtained from the tristimulus values according to the CIE 1976 equations,

where L^* is the degree of lightness and covered a range from white (100) to black (0) along a grey scale, a^* is the degree of redness and greenness and b^* is the degree of yellowness and blueness). The polar parameters of colour which closely match the visual experience are the chroma (C^*) which represents the saturation of the colour and the hue angle (h°) which express the hue colour. CIELAB colour difference (ΔE_{ab}^*) is based on the Euclidian distance between two colours represented in the CIE 1976 CIELAB uniform colour space¹³ The colour analysis results 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, F2 illuminants and 10° observer

Illuminant		A	A ₁	A ₂	A ₃	A ₄
		Stand.	2%dye	5%dye	8%dye	15%dye
D65	L*	95.20	79.06	73.39	71.10	65.49
	a*	0.12	19.02	24.00	24.42	25.65
	b*	4.02	24.21	33.45	36.88	38.23
	X	83.59	59.78	52.01	48.49	40.60
	Y	88.10	55.03	45.76	42.34	34.66
	Z	88.71	36.56	23.57	19.51	14.34
	C*	4.02	30.78	41.17	44.23	46.04
	h°	1.54	0.90	0.95	0.99	0.98
	ΔE_{ab}^*		32.02	43.73	47.44	52.01
	A	L*	95.50	82.65	77.82	75.67
a*		1.23	20.48	26.31	26.87	28.14
b*		4.03	30.27	41.05	44.20	45.55
X		99.47	78.73	71.04	66.82	56.73
Y		88.82	61.51	52.90	49.35	41.00
Z		29.34	12.03	7.74	6.49	4.81
C*		4.21	36.55	48.75	51.73	53.55
h°		1.28	0.98	1.00	1.02	1.02
ΔE_{ab}^*			34.99	48.09	51.63	55.59
F2		L*	95.42	81.08	75.24	73.74
	a*	0.13	12.71	16.13	16.60	17.25
	b*	4.27	28.12	38.71	42.72	43.52
	X	91.59	66.23	56.69	54.24	45.53
	Y	88.61	58.62	48.66	46.29	38.36
	Z	57.17	23.30	14.39	12.12	9.10
	C*	4.27	30.86	41.93	45.83	46.81
	h°	1.54	1.15	1.18	1.20	1.19
	ΔE_{ab}^*		30.54	43.00	47.11	50.69

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

Illuminant		A	A ₁	A ₂	A ₃	A ₄
		Stand.	2%dye	5%dye	8%dye	15%dye
D65	L*	95.20	77.97	75.95	70.65	66.59
	a*	0.12	15.72	18.88	23.57	24.80
	b*	4.02	22.82	27.13	34.06	35.26
	X	83.59	56.50	54.30	47.48	41.88
	Y	88.10	53.16	49.81	41.67	36.09
	Z	88.71	36.17	30.44	20.57	16.49
	C*	4.02	27.71	33.06	41.43	43.11
	h*	1.54	0.97	0.96	0.97	0.96
	ΔEab*		29.90	35.45	45.34	49.03
	A	L*	95.50	81.09	79.77	75.29
a*		1.23	17.90	20.79	25.55	27.12
b*		4.03	28.47	33.25	41.37	42.81
X		99.47	73.89	72.48	65.43	57.98
Y		88.82	58.63	56.28	48.75	42.31
Z		29.34	11.80	10.09	6.87	5.44
C*		4.21	33.63	39.21	48.63	50.68
h°		1.28	1.01	1.01	1.02	1.01
ΔEab*			32.91	38.52	48.94	52.64
F2		L*	95.42	80.20	78.68	73.76
	a*	0.13	10.36	12.79	15.79	16.77
	b*	4.27	26.88	31.52	39.27	40.45
	X	91.59	63.43	61.60	53.95	47.21
	Y	88.61	57.04	54.38	46.33	40.00
	Z	57.17	23.17	19.72	13.29	10.54
	C*	4.27	28.81	34.02	42.32	43.79
	h°	1.54	1.20	1.19	1.19	1.18
	ΔEab*		29.11	34.39	44.03	47.53

The lightness (L*) values of the dyes in the white pigment mixture show an indirect proportionality to the dyes 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°), which express better the colour hue modifications suggest a redder colour for the dye **I** (obtained using 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 3-chlorosalicylanilide as coupling component) compared to dye **II**. Regarding the dye **I**, increased values of the chroma (C*) and the colour difference (ΔE*) are recorded. 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).

Materials and Methods

The chemicals employed in this study as *p.a.* commercial products were provided by AcrÕs 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 ($c=1.0 \times 10^{-5}$ mol/dm³) were performed on a CECIL CE 7200 spectrophotometer in the range 300-800 nm. 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 200 spectrometer in the range 400 - 4000cm⁻¹.

The ¹³C-NMR spectra were recorded as solution in DMSO-d₆ 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, 3mL (0.03 mol) of 32% HCl were added to the mixture. The resulting suspension was bis-diazotised with 0.71 g of 98% solid NaNO₂ (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, 2.86 g of 95% coupling components (3-chlorosalicylanilide and 4-chlorosalicylanilide), (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

coupling components. The pH of the reaction mixture was maintained around 8 by periodic addition of 10% Na₂CO₃ aqueous solution. The temperature did not exceed 10°C. The coupling reactions were controlled in the conventional method (drop reaction with an alkaline solution of 1-amino-8-naphthol-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 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, methanol and dried. Thereafter, the dyes were purified by recrystallization from dioxane:pyridine 90:10 (v:v).

Colour assessment

The samples were layed on a cellulosic substrate (wood) and were differentiated by the dyes concentration and the titanium dioxide (P.W.6; C.I. 77 891). Further details on the general procedure may be found in reference.⁸ 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_{ab}^*) was calculated confronted by one white standard\

Conclusions

Two new disazo symmetrical direct dyes containing 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 3-chlorosalicylanilide and 4-chlorosalicylanilide as coupling components were synthesized and characterized. The spectroscopy data (VIS, FT/IR, ¹³C-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 (ΔE_{ab}^*) calculated against one standard reveal a good colouring power of the dyes **I** and **II** in the white pigment mixture

References

1. H. Zollinger, *Color Chemistry: Syntheses, properties and applications of organic dyes and pigments*, 3rd ed. Wiley, VCH, 2003, p.166
2. S. Popa, D. Jurcău, C. Jurcău, N. Pleșu, *Pigmenți Organici*, I, Ed. Orizonturi Universitare, Timișoara, 2005, p.91

3. R. M. Christie, *Colour Chemistry*, ed. The Royal Society of Chemistry, Cambridge, 2001, p.21
4. J. Szadowski, Z. Niewiadomski, *Dyes Pigm.* **19** (1992) 41
5. I. Jr. E. Radigan, L. V. Isganitis, W. E. Soldar, K. B. Gundlach, (Xerox Corp.),U.S. 5.360.472 (1994)
6. Y. C. Chao, S. S. Yang, *Dyes Pigm.* **29** (1995) 131
7. M. E. Grad, G. M. Simu, A. X. Lupea, Șt. Tomas, A. Pascariu, *Rev. Roum. Chim.*, **53(2)** (2008) 107
8. M. E. Grad, G. M. Simu, S. G. Muntean, A. X. Lupea, *Proceedings of the 14th Symposium on Analytical and Environmental Problems, (2007), Szeged, Hungary,(2007)*, 344
9. H. Sanielevici, H. Urseanu, *Sinteze de coloranți organici, 2*, Ed. Tehnică, București, 1987, 287
10. L. Floru, F. Urseanu, C. Tărăbășanu, R. Palea, *Chimia si tehnologia intermediarilor aromatici si a coloranților organici*, Ed. Didactică și Pedagogică, București, 1980, 317
11. S. M. Burkinshaw, N. Kumar, *Dyes Pigm.* **76**, (2008) 799
12. S .M. Burkinshaw, D. S. Jeong , *Dyes Pigm.* **77**, (2008) 171
13. J. Schanda, *Colorimetry: Understanding the CIE system*, John Wiley & Sons Inc, Hoboken, 2007, 8.