

Synthesis, properties and trichromatic study of new dyes with stilbenic structure.

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ABSTRACT

Two new symmetrical disazo direct dyes containing 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 3-bromosalicylanilide and 4-bromosalicylanilide as coupling components were synthesized. The dyes were characterised by TLC, VIS, FT/IR, ¹³C-NMR spectroscopy, and HPLC technique. The colour, spectrophotometric study of the two disazo stilbene dyes with symmetrical structure was performed using the CIE 1976 (CIELAB) uniform colour space parameters, under the CIE (Commission Internationale d'Eclairage) recommended illuminants: D65 (natural day light), A (tungsten light), F2 (fluorescent light) and the standard 10° observer respectively. The colour differences (ΔE_{ab}^*) and (ΔE_{CMC}) were calculated against one standard, revealing a high colouring power for the two new studied dyes.

Keywords: 4,4'-diaminostilbene-2,2'-disulphonic acid, CIELAB scale

Introduction

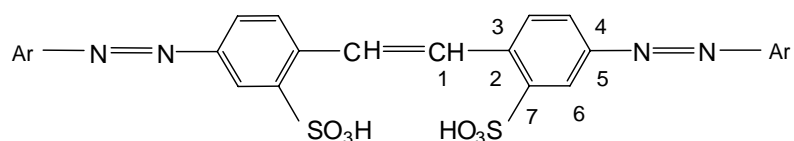
Azo dyes, which contain one or more azo bonds (–N=N–), are a major class of synthetic, colored organic compounds. It is estimated that about half a million tonnes of azo dyes are manufactured each year all over the world and account for nearly 50% of all dyes produced.¹

The two CIE color space versions, 1931 CIE and 1976 CIE (or CIELab), are used for defining human color perception of an object. The 1931 CIE system is limited in that it does not uniformly express differences in lightness, purity and dominant wavelength between colors. However, the CIELab system has improved organization of colors so that numeric differences between colors agrees more consistently with human visual perceptions, and therefore, offers specific advantages over the 1931 CIE system.²

In this work, the synthesis, the physicochemical properties and the colour expression of two new disazo direct dyes with symmetrical structure derived from 4,4'-diaminostilbene-2,2'-disulphonic acid, an accessible, eco-friendly component^{3,4} 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 3-bromosalicylanilide and 4-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}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 (well known as electrophilic aromatic substitutions)⁵ were performed in an alkaline aqueous medium (pH around 8.5), in presence of Na_2CO_3 at a temperature around 8°C . The use of 3% excess of the above amides of the salicylic acid and the direct adding of their alkaline solutions to the acid suspension of the bis-diazonium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid were found to be optimum for the dyes's **I** and **II** synthesis. The reaction time was about 2.5 h. The progress of the coupling reactions was monitored in the usual way by TLC. 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 81-82% yield and were characterized by means of TLC, VIS, FT/IR, ^{13}C -NMR, spectroscopy and HPLC technique.

The FT/IR and ^{13}C -NMR spectroscopy data agree well with the dyes's 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 two synthesized dyes (**I** and **II**).

The VIS absorption spectra of dyes **I** and **II** present quite similar absorbance values (462-468nm), according to their related chemical structures.

Dye I: TLC (silicagel plates 60F-254, *iso*-propanol:methyl-ethyl ketone:ammonia 25%=4:3:6 (v:v:v)) (R_f : 0.78); VIS (50% aqueous MeOH) ($\lambda_{\text{max}}/\text{nm}$, ($\lg\epsilon_{\text{max}}$: 462; 4.61); IR (KBr) (ν/cm^{-1} : 3413, 1330 (OH), 1639, 1534, 1230 (CONH), 1188, 1071 (SO_3H)); ^{13}C -NMR (100MHz, $(\text{CD}_3)_2\text{SO}$) δ/ppm): 124.46(C_1), 137.26(C_2), 126.93(C_3), 123.04(C_4), 150.17(C_5), 121.48(C_6), 139.91(C_7), 146.84($\text{C}_{1'}$), 126.65 ($\text{C}_{2'}$), 117.20($\text{C}_{3'}$), 158.10($\text{C}_{4'}$), 119.55($\text{C}_{5'}$), 119.76($\text{C}_{6'}$), 166.59($\text{C}_{7'}$), 139.76($\text{C}_{8'}$), 130.70($\text{C}_{10'}$); 126.72($\text{C}_{11'}$); 123.27($\text{C}_{12'}$); HPLC (C18, 83% aqueous MeOH, isocratic elution; flow rate:0.9mL/min) (λ/nm ; t_R/min : 462; 1.43)

Dye II: TLC (silicagel plates 60F-254, *iso*-propanol:methyl-ethyl ketone:ammonia 25%=4:3:6 (v:v:v)) (R_f : 0.75); VIS (50% aqueous MeOH) ($\lambda_{\text{max}}/\text{nm}$, ($\lg\epsilon_{\text{max}}$: 468; 4.62); IR (KBr) (ν/cm^{-1} : 3414, 1332 (OH), 1632, 1545, 1228, 680 (CONH), 1185, 1071 (SO_3H)); ^{13}C -NMR (100MHz, $(\text{CD}_3)_2\text{SO}$) δ/ppm): 125.29(C_1), 137.76(C_2), 128.09(C_3), 123.34(C_4), 150.66(C_5), 121.93(C_6), 138.76(C_7), 146.55($\text{C}_{1'}$), 126.37 ($\text{C}_{2'}$), 117.20($\text{C}_{3'}$), 158.22($\text{C}_{4'}$), 119.00($\text{C}_{5'}$), 119.53($\text{C}_{6'}$), 166.44($\text{C}_{7'}$), 133.64($\text{C}_{8'}$), 122,70($\text{C}_{9'}$); 128.69($\text{C}_{10'}$); 129.22($\text{C}_{11'}$); HPLC (C18, 83% aqueous MeOH, isocratic elution; flow rate:0.9mL/min) (λ/nm ; t_R/min : 468; 1.44)

The perception of colour is subjective in nature and can be effected by outside factors such as lighting environment and an object's material. The definition of colour is visual perception by which the spectral aspects of a visual stimulus are integrated with its illuminating and viewing environment.

There are different color models that can represent color in a quantitative way. A colour space is a three-dimensional representation of the colors, that can be described using a certain color model. Some common color space are RGB, XYZ, CIELAB, CIELUV, and HCL. The CIELAB & CIELUV color spaces are perceptually uniform meaning that equal color differences in the color

space represent equal color differences that we detect as humans. CIELAB (CIELab) is the most common used color space and is ideal for visual color matching system because it represents color the same way humans perceive color⁶⁻⁸

This system quantifies color with three values : L^* , a^* , and b^* . a^* represents how red or green the object looks, positive a^* values representing red and negative a^* values representing green. b^* represents how yellow or blue an object looks, positive b^* representing yellow and negative b^* representing blue.

Colour is most intuitively described in a three-dimensional color space representing hue, chroma and lightness (h^* , C^* , L^*). Hue (h^*) describes the overall colour of an object such as how red, green, blue or yellow. Chroma (C^*) represents the colour departure from gray. Lightness (L^*) is described on a scale from black to white with gray in the middle.

It is well known that colour differences are always calculated as sample-standard values. In time new colour differences formula were developed⁹. ΔE_{ab^*} is based on L^* , a^* , b^* colour difference and was intended to be a single number metric for pass/fail decision. ΔE_{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, F2 illuminants and 10° observer

Illuminant		W Stand.	W ₁ 2%dye	W ₂ 5%dye	W ₃ 8%dye	W ₄ 15%dye
D65	L^*	95.20	79.62	74.68	71.59	66.03
	a^*	0.12	16.64	21.35	23.39	26.40
	b^*	4.02	21.18	28.61	33.22	36.47
	C^*	4.02	26.93	35.70	40.63	45.03
	h°	1.54	0.90	0.93	0.96	0,94
	$\Delta E_{ab^*}/\Delta E_{CMC}$		28.47/27.90	38.43/37.84	44.18/43.41	50,94/48.72
A	L^*	95.50	82.36	78.58	76.01	71.16
	a^*	1.23	18.51	23.12	25.82	29.10
	b^*	4.03	27.00	35.48	40.67	44,73
	C^*	4.21	32.74	42.35	48.18	53.36
	h°	1.28	0.97	0.99	1.01	0.99
	$\Delta E_{ab^*}/\Delta E_{CMC}$		31.61/32.66	41.89/43.43	48.25/49.99	55.01/56.00
F2	L^*	95.42	81.60	77.36	74.64	68.95
	a^*	0.13	11.15	14.36	15.46	17.70
	b^*	4.27	25.04	33.50	38.21	41.72
	C^*	4.27	27.41	36.45	41.21	45.32
	h°	1.54	1.15	1.17	1.19	1.17
	$\Delta E_{ab^*}/\Delta E_{CMC}$		27.27/26.83	37.19/36.96	42.64/42.30	49.10/47.19

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°), indicate a redder colour for the dye I (obtained using 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 3-bromosalicylanilide as coupling component) compared to dye II (obtained using 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 4-

bromosalicylanilide as coupling component). Regarding the dye **I**, increased values of the chroma (C^*) 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). The colour differences (ΔE_{ab^*}) and (ΔE_{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, F2 illuminants and 10° observer

Illuminant		W Stand	W ₁ 2%dye	W ₂ 5%dye	W ₃ 8%dye	W ₄ 15%dye
D65	L*	95.20	78.92	75.31	72.47	66.77
	a*	0.12	16.61	20.72	23.15	24.54
	b*	4.02	22.56	28.63	32.23	33.40
	C*	4.02	28.02	35.34	39.68	41.44
	h°	1.54	0.94	0.94	0.95	0.94
	$\Delta E_{ab^*}/\Delta E_{CMC}$		29.68/29.03	37.76/37.36	42.93/42.34	47.62/44.73
A	L*	95.50	82.23	79.08	76.82	71.40
	a*	1.23	18.65	23.01	25.34	27.01
	b*	4.03	28.05	35.27	39.41	40.93
	C*	4.21	33.68	42.11	46.86	49.04
	h°	1.28	0.98	0.99	1.00	0.99
	$\Delta E_{ab^*}/\Delta E_{CMC}$		32.51/33.67	41.48/43.15	46.72/48.50	51.07/51.22
F2	L*	95.42	81.36	77.96	75.21	69.56
	a*	0.13	11.31	14.17	15.68	16.63
	b*	4.27	26.51	33.42	37.27	38.42
	C*	4.27	28.82	36.30	40.43	41.86
	h°	1.54	1.17	1.17	1.17	1.16
	$\Delta E_{ab^*}/\Delta E_{CMC}$		28.59/28.35	36.76/36.75	41.70/41.44	45.90/43.39

Materials and Methods

The chemicals employed in this study as *p.a.* commercial products were provided by Acrōs 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⁻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, 3.38 g of 95% coupling components (3-bromosalicylanilide and 4-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 8.5 by periodic addition of 10% Na₂CO₃ aqueous solution. The temperature did not exceed 8°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 2.5 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 N, N-dimethylformamide and 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'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_{ab}^* and ΔE_{CMC}) 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 3-bromosalicylanilide and 4-bromosalicylanilide 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}^* and ΔE_{CMC}) calculated against one standard reveal a good colouring power of the dyes **I** and **II** in the white pigment mixture.

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