Disazo Dyes, Derivatives of 4, 4 – diaminostilbene – 2,2 – disulfonic Acid

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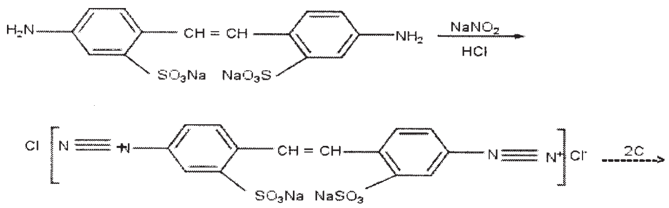
The paper presents a class of disazo dyes, derivatives of 4,4- diaminostilbene – 2,2 – disulfonic acid. These dyes were obtained by the azo coupling reaction of 4,4- diaminostilbene – 2,2 – disulfonic acid diazonium salt with some coupling components as: 1 – phenyl-3- methyl-5- pyrazolone, salicylic acid, acid1-hidroxi-6-benzensulfonic, acetoacetanilide, 2-amino-8-naphthol-6-sulfonic acid, 2-amino-5-naphthol-7-sulfonic acid, 2-naphthol-3,6-disulfonic acid sodium salt, 2-naphthol-6-sulfonic acid sodium salt, 1-amino-8-naphthol-3,6-disulfonic acid, 1-hydroxy-8-naphthol-3,6-disulfonic acid. IR and UV-VIS spectra, chromatography on silica gel characterized the structure of synthesized compounds.

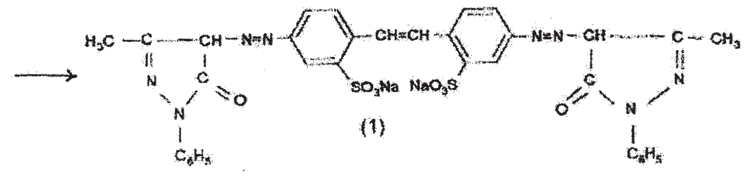
Keywords: azodyes, 4,4- diaminostilbene - 2,2 – disulfonic acid, azo coupling reaction.

The stilbene dyes have various destinations in dyeing of cotton, polyamide fibres, paper and leather.

Such a dye which colors the polyamide in yellow shades has been obtained through the coupling of the diazonium salt of the 4,4- diaminostilbene-2,2-disulfonic acid with *ortho*cresol in a basic medium [1,2]. These dyes applied on the cellulosic fibres have good tinctorial properties and resistances especially to the light. Resistances may be increased through metallic salts treatment, such as copper and chrome[3]. Dying with stilbene dyes features has resistance suitable for humid treatments, as it presents a deaerating tendency of the dye from the fiber, until the solution equilibrium is obtained[4].

This paper presents the synthesis and the physico–chemical and tinctorial characterization of some acid azodyes obtained through the coupling of the 4,4-diaminostilbene-2,2-disulfonic acid diazonium salt with various coupling components as: 1-phenyl-3-methil-5-pyrazolone, salicylic acid, phenol-2-sulfonic acid, acetoacetanilide, 2-amino-8-naphthol-6-sulfonic acid, 2-amino-5-naphtol-7-sulfonic acid, 2-naphthol-3,6-disulfonic acid sodiu salt, 2-naphthol-6-sulfonic acid sodiu salt, 1-amino-8-naphthol-3,6-disulfonic acid,1,8-dihidroxi-naftalin-6-sulfonic acid ilustrated in the foolowing reactions:





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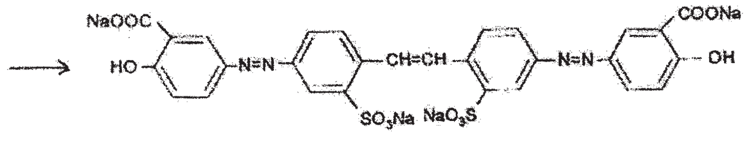

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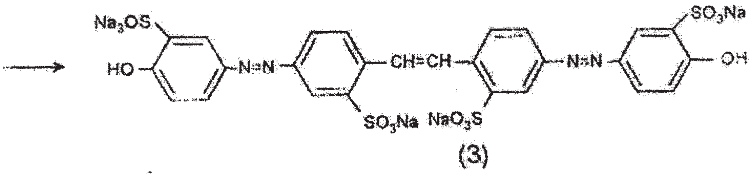

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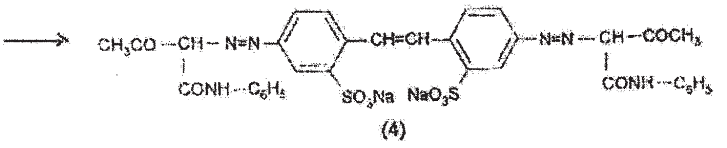

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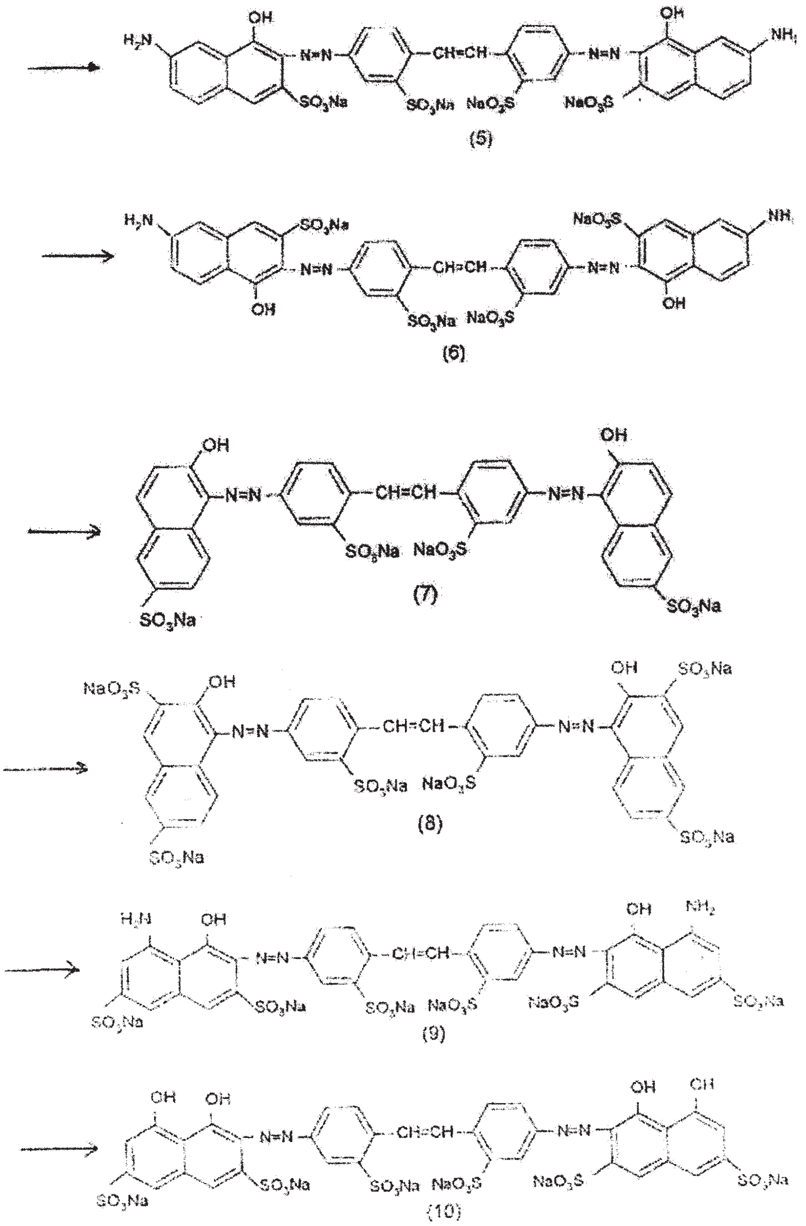

Experimental part

The diazotation of the 4,4-diaminostilbene-2,2-disulfonic acid is performed in accordance with literature dates [5,6]. A quantity of 18.5 g (0.01 moles) of 4,4-diaminostilbene-2,2-disulfonic acid is dissolved in 50 ml of water at 40 °C with Na_2CO_3 add-on to obtain a neutral solution, then 2 ml (1.09 mol) HCl, a quantity of 5 g of ice is introduced in order to cool the solution and a quantity of 3.3 g (2.1moles) of $NaNO_2$, 30% solution is added to obtain an acid reaction mass (positive reaction with Congo red paper) containing nitrous acid (test with iodine - amidonated paper). After an hour of stirring, the reaction is completed. The exces of nitrous acid (0.05 mol)is distroyed with urea (2g).

The diazonium salt /tetrazonium salt coupling with C coupling components. The amount of coupling components (table 1) is dissolved in solution prepared from 4g (0.1 moles) of NaOH and 150 mL of water heated at 80°C, then 100 g of ice is introduced for cooling at 10°C and the diazonium suspension is added. The reaction mass is further on stirred until tetrazonium salt is consumed (test with H acid solution, in the aureole of a salified sample on filter paper). It has to be permanently an excess of coupling component (detected with aqueous solution of diazonium salt of 4-nitro aniline in aureola). After stirring it for a determined time (table 1), the reaction mass is filtered and the precipitate is washed with water until neutral *p*H and dried at 80°C. The reaction work conditions are represented in table 1.

The affinity of synthesized dyes on textiles

In the dying bath, together with the material to be dyed, it was introduced a textile made of different categories of fibers: mercerized cotton, cellulose, polyamide, cellulose acetate, polyester in order to determine the affinity of synthesized dyes for these fibers. It was ascertained that in the conditions in which the dying took place through the exhaustion in neutral medium procedure, the synthesized dyes colour or not the respective fibers. Thus, the fibers of cellulose triacetate, polyester acetate cellulose and polyester are colored with these dyes.

The aplication of cotton dyes has been realized through the exhaustion dying procedure in neutral medium. The wet treatments to which the dyes have been subject are to determine:fastness to water, washing (40°C), perspiration (*p*H = 5.5). The above mentioned treatments to which the dyes have been subject are to determine: dry and wet friction fastness.

The water fastness has been determined in accordance with ISO-SR-EN. It has been subject to test tube trial, made of one test tube for textile dying and two test tubes for bleached undyed materials and bleached materials (cotton and wool). The color change produced after a trial in respect of dyed test tube not subject to testing is taken into consideration. The color contrast between two dyed test samples is estimated in accordance with ISO-SR-EN and with the aid of grey scale for evaluating the colour change.

The washing resistance (40°C), has been determined in accordance with ISO-SR-EN. A test tube made of textile material and dye is mechanically stirred for 30 min, at 40°C in a soap solution, and after that it is rinsed and dried. The material colour intensity before and after washing is estimated on a grey scale.

Perspiration resistance (*p*H = 5.5) has been determined in accordance with ISO-SR-EN. A test sample made of dyed textile material is tested together with a bleached cotton texture. After the test the contrast between the bleached texture and the identical test sample not subject to test is ascertained. The resuls obtained from these treatments are presented in table 2.

The rezulted dyes were purified by a crystallization, in order to be characterized. Dyes 1-10 recrystallized from ethyl acetate where as dyes 1-10 recrystallized from chloroform. Their purity was evaluated on a thin-layer chromatography, using sillicagel prop and ethyl alcohol as element. Electronic spectra of the synthesized dyes were performed for the purified samples.

Their purity was checked by determining melting point on a Boetius apparatus.

Electric conductibility was determined with a Phillips P.R. 9500 device in DMFA($10^{-3}\mu$). The IR spectra [7] were recorded on an PERKIN-ELEMFR device in K Br (p.Q) MERK. The electric spectra [7] were recorded with a VSV- 2 CARL ZEISS (Yena) device.

Results and discussions

By using the tetrazonium salt of 4,4-diaminostilbene-2,2-disulfonic acid as disazo component and various coupling components, disazo dyes have been obtained in accordance with the previously ilustrated reactions. The synthesis of azo compounds 1-10 was performed without any special problems, in accordance with the curent methods described in the literature with reaction yields situated in 90-95% domain (table 1).

Purifying the disazo dyes

With the dyes obtained as sodium salts dissolve in water and sodium solution of the obtained dyes washed in HCl, 2 % solution and filtering the salts, and after that they are

Table 1

THE WORK CONDITIONS TO OBTAIN 1-BISAZODYES

Dye	DASD Quantity (g/moles)	Coupling Component quantity (g/moles)	Reaction time (hours)	Yield %	Poweder	Rez values
1	18.5/0.05	18.8/0.1	8	96	Orange	0.45
2	18.5/0.05	19.9/0.11	24	95	Yellow	0.51
3	18.5/0.05	19.1/0.17	24	90	Yellow	0.62
4	18.5/0.05	23.9/0.11	25	95.2	Yellow	0.61
5	18.5/0.05	23.9/0.11	15	91.8	Bleu	0.74
6	18.5/0.05	25.8/0.11	20	93.9	Bleu-violet	0.73
7	18.5/0.05	36/0.10	8	92.8	Violet	0.51
8	18.5/0.05	35.8/0.10	11	97	Blue	0.71
9	18.5/0.05	38.22/0.105	10	96.9	Blue	0.71
10	18.5/0.05	38.7/0.105	8	92.5	Blue	0.74

Table 2

MECHANICAL WET TREATMENTS

Dye Nr.	Water			Washing at 40			Perspiration pH=5.5			Friction	
	Color change	Cotton ceding	Wool ceding	Color change	Cotton ceding	Wool ceding	Color change	Cotton ceding	Wool ceding	Dry	Wet
1	4-5	4	5	4	3	5	4-5	3-4	5	4-5	3
2	4	2	4	3-4	4-5	5	3-4	2	4	5	4
3	3	2-3	5	3	5	5	3-4	2-3	5	5	4
4	5	4	5	5	4-5	5	5	4	5	5	4
5	4	2	4	4	3	5	4	2	4-5	5	3
6	4-5	2-3	3-4	4	3	5	4-5	2-3	3-4	5	3-4
7	4	2	4	3-4	4	5	4	2-3	4-5	5	3
8	4-5	3	4-5	4	4-5	5	4-5	3	4-5	5	4
9	4	2	2-3	4	5	5	4	2	3	5	5
10	4	2	3	4	4-5	5	4	1-2	3	5	3

filtered once again. A dilute NaOH solution is added to form again the sodium salt of the dye which isolates through filtering. In order to verify purity to press cake of the compounds there were performed chromatograms on thin layer with station phase aluminum silicate, and silica gel on alumina as mobile phase, Rf values are presented in table 1.

In the infrared spectra recorded on spectrometer there were identified the bands characteristic for hydroxyl groups – OH (~ 3.500 cm^{-1}) and – NH (2 bands situated around 3.474 cm^{-1}), the vibration values of the azo group (asymmetrical at 1490-1.570 cm and symmetrical at 1.340 cm^{-1}), of $-SO_3Na$ group (1.004 – 1.053 cm^{-1} and 1.180 – 1.190 cm^{-1}), as well as the deformation bands of naphthalene nuclei (650 – 970 cm) and the harmonics of these vibration in region 1.620 – 1.637 cm^{-1} [7].

The absorption spectra in visible have been performed in aqueous solution (10- 10moles/L). The absorption spectra for dye 1 shows the absorption in orange region (480 – 490 nm), absorption that is in accordance with shown colour. Dye 2 and dye 3 have similar structure. The difference consists in the fact that in the case of dye 2 on the benzene nucleus there is grafted a carboxylic group and in the case of dye 3 a sulfonic group. Both spectra show the absorption in the yellow – green domain (400-435 nm), but the relatively small difference of molecular structure has caused a change in the length of the absorbed wavelength. Dye 3 has a hue of yellow lighter than dye 2.

The absorption spectra length for dye 4 shows absorption in the yellow – green region (400-435 nm), which is in accordance with the showed color. Dye 4 has a yellow hue situated between those of dye 2 and dye 3. Dyes 5 and 6 have similar structures, but the difference is due to the molecular structure of the acid and the position of the amino group in the naphthalene nucleus. This has determined a fundamental change of the color. The absorption spectra for dye 6 shows a yellow color situated between dyes 2 and 3. The absorption spectra of dye 6 shows absorption maximum in the violet region (550-580 nm) and the absorption spectra for dye 5 shows absorption maximum in the region (580-595 nm), absorption that are in accordance with the showed color. Dye 8 has a different structure as dye 7 which has one sulfonic group more in the molecule.This has determined a slight change of the color. Dye 7 has a darker violet colour than dye 8. The same thing can be noticed from the values of the absorbed wavelengths, dye 7 absorbing a larger wavelength than dye 8. Vibration spectra for the two dyes show absorption in the purple region (500 – 550 nm), absorption that is in accordance with the showed color. Dye 9 and dye 10 are similar concerns the molecular structure. The differences are: in the case of dye 9, there is an amino group in position 1 of the naphthalene nucleus, and in the case of dye 10 a hydroxyl group. This molecular structure difference causes a change in the length of the absorbed wave. There can be noticed that the values of the wavelength corresponding to dye 9 are batho-chromicaly shifted. The absorption spectra for dyes 9 and 10 indicate absorption in the region 580 – 590 nm, absorption which are confirmed by the showed color. Dyes 5,6,7,9,10 have darker color than dyes 1,2,3,4.

It has been ascertained that in the experimental condition the synthesized dyes color certain fibers [8]. Following their application on cotton, the dyes have been subject to humid and mechanical treatments. As a result of these treatments for each dye there have been determined 3 types of fastness (table 2). It has been ascertained that the best fastness to water is present on dye 2 and 4, as the change of color degree, as well as the fixing degree on fiber and dye 3 shows the weakest fastness. As regards the washing resistance (40°C), the best resistance is presented dye 4, than compounds 8, 9 and 10 and the weakest dye 7. In the case of perspiration the best fastness is presented on dye 4. One can notice that a good fastness is presented on dyes 1,7 but 8 shows a color change degree and the degree of ceding on wool. At friction all of the dyes present good fastness. One can notice that the fastness are weaker in the case of wet friction.

Conclusions

Begining from the idea that using the 4,4-diaminostilbene-2,2-disulfonic acid as diazo component for obtaining ten new direct stilbene dyes and different azo coupling components as: 1 – phenyl-3- methyl-5-pyrazolone, salicylic acid, phenol-2-sulfonic acid, acetoacetanilide, 2-amino-8-naphthol-6-sulfonic acid, 2-amino-5-naphthol-7-sulfonic acid, 2-naphthol-3,6-disulfonic acid sodium salt, 2-naphthol-6-sulfonic acid sodium salt, 1-amino-8-naphthol-3,6-disulfonic acid, 1-hydroxy-8-naphthol-3,6-disulfonic acid for extending the range of such dyes. The purified dyes were characterized by means of VIS and IR spectroscopy and tinctorial analysis. The colorings and the fastness of the obtained dyes presented good values, which make them suitable for cotton dying.

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