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SYNTHESIS AND INVESTIGATION OF SOME BIS(DICHLOROTRIAZINE) REACTIVE DYES CONTAINING STABILIZER FRAGMENT

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ABSTRACT

Three bis(dichlorotriazine)reactive dyes containing a residue of 4,4'-diaminostilbene-2,2'-disulfonic acid as bridging group between two identical chromophores were synthesized. The dyes were evaluated on cotton and compared to commercial dichlorotriazine dye C.I. Reactive dye 1. The degrees of exhaustion and fixation were assessed. The optical properties - L, a*, b*, C*, and h* from the CIE Lab colour space of the resulting textile samples have been examined. The photostability of the dyes and dyed samples was investigated. As a result of the studies carried out it was found out that with all reactive dyes, textile samples with uniform colouring and similar colour shades were obtained. The introduction of stabilizer fragment in dye molecule increases the photostability with 20 - 25 %.*

Keywords: bis(dichlorotriazine)reactive dyes, exhaustion and fixation, photostability.

INTRODUCTION

Ecological problems resulting from the coloration of textile materials arise at three different stages: during the dyeing of the respective material (losing a part of the dye in dye bath and pollution of the wastewater), during the use of the coloured material (as a result of tearing the connection material-dye, the last one migrates and could fall on the human skin and cause allergic or toxic reactions) and at the moment of washing and cleaning (a part of the dye releases in the washing water).

One rather successful decision to solve the ecological problems mentioned above is the synthesis of the reactive dyes. These dyes are widely used in the textile industries for dyeing of natural and synthetic fibers and polymers and combination of them [1 - 15]. This is due to their wide shade gamut and the excellent fastness properties achieved with them.

A characteristic structural feature of reactive dyes is the reactive group attached to the chromogenic system. The reactive group, generally based on halogen heterocycle is capable to form a covalent bond with the fibers under alkaline conditions. The most famous dyes containing halogen heterocycle are mono- and dichlorotriazine reactive dyes. The main disadvantage of monochlorotriazine dyes is the easy hydrolysis of the dye during dyeing of textile fibers [16]. The presence of two halogen atoms reduces the degree of hydrolysis, but there is a spatial obstacle and therefore the dyeing is more difficult. In order to achieve a hider degree of exhaustion and fixation and lower water pollution the world investigation have been focused on developing reactive dyes with two and more reactive groups, situated in different part of the dye molecule [3, 17 - 21].

In the world increasing attention has been paid to protective properties of textiles against UV radiation originating from sunlight. The preparation of UV-absorber derivatives of s-triazine and dyes with UV-protection properties based on 4,4'-diaminostilbene-2,2'-disulphonic acid was earlier reported [22 - 27].

Taking into account the above mentioned the purpose of the present work was to synthesize bis(dichlorotriazine) reactive triazine dyes, containing fragment of 4,4'-diaminostilbene-2,2'-disulphonic acid as spacer between two chromophores and examine their dyeing ability, colour and UV protective properties of the dyed cotton and papers.

EXPERIMENTAL

Materials and methods

Cyanuric chloride (98 %), 8-amino-1-naphthol-3,6-disulfonic acid (H acid) (> 95 %), 6-amino-1-naphthol-3-sulfonic acid (I acid) (> 95 %) and 7-amino-1-naphthol-3-sulfonic acid (Gamma acid) (> 95 %) were Sigma-Aldrich (Merck) products; 4,4'-diaminostilbene-2,2'-disulfonic acid (95 %) was product of Alfa Aesar. All solvents are of p.a. or analytical grade (Fluka).

Infrared (IR) spectrum was recorded on a Specord 71 IR Spectrophotometer (Carl Zeiss, Germany) using potassium bromide (KBr) pellets and ^{1}H-NMR spectra - on DRX-250-Brucker equipment. Ultraviolet-visible (UV/Vis) absorption spectra were recorded on a Hewlett Packard 8452A UV/Vis spectrophotometer (Germany) in a water solution (5×10^{-5} mol L^{-1}) at scanning range 190 - 820 nm. The thin layer chromatography (TLC) measurements were performed on ready-to-use plates (20×20 mm) pre-coated with 0.2 mm silica gel oxide 60F254.

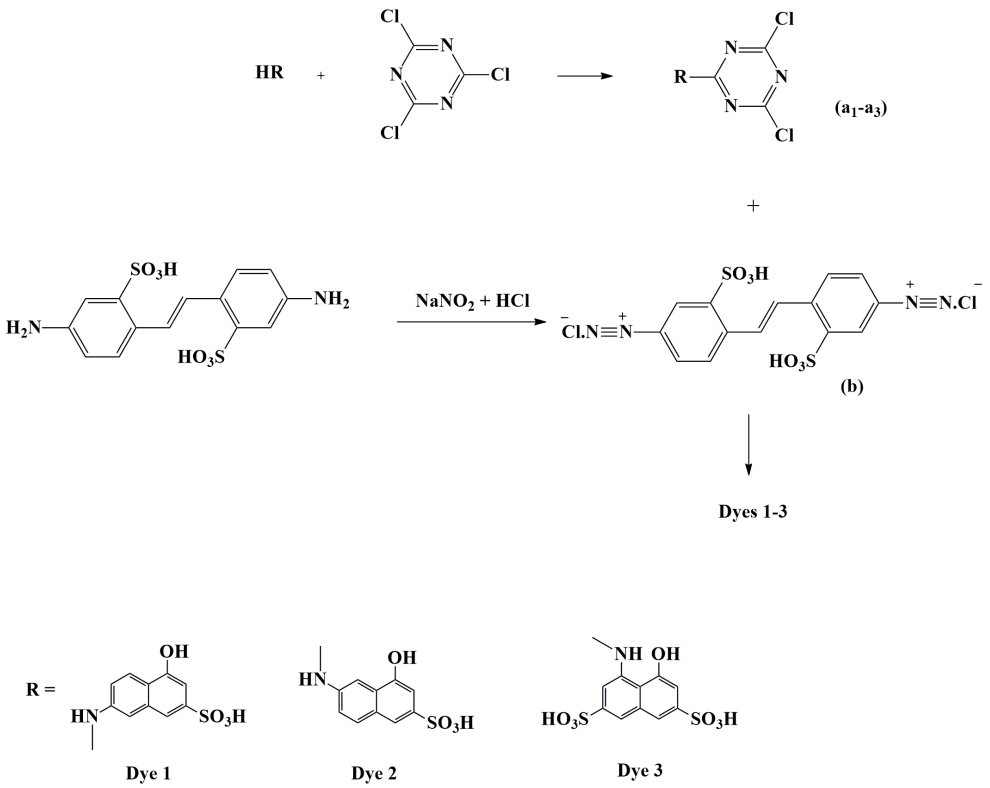
Photostability of the dyes in water solution (concentration $1.5x10^{-4}$ g mL^{-1}) was studied by a Suntest CPS equipment (Heraeus) supplied with a Xenon lamp (Hanau, 1.1 kW, 765 W m^{-2}, wavelength λmax = 290 nm).

Dyeing of 100 % cotton with synthesized reactive dyes (Exhaust at 80°C) was according to standard procedure described in [28]. Using the Konica Minolta Spectrophotometer CM-3630 from Frank - PTI technique and associated software, according to ISO 5631-2:2008, the colour characteristics of the dyed material were recorded.

Synthesis of dyes 1 - 3

The dyes were obtained, using Scheme 1.

The reaction of cyanuric chloride with H acid, I acid or Gamma acid was performed using traditional recipe [29, 30]. The compounds (a_{1-3}) were obtained. The data corresponds with the one in the literature. The diazotization of 4,4'-diaminostilbene-2,2'-disulfonic acid was performed using traditional recipe [31, 32] and a compound (b) was obtained. For the



Scheme 1. Synthesis of dyes 1 - 3.

synthesis of bis(dichlorotriazine) dyes 1 - 3, 0.01 mol of corresponding compounds (a_1 - a_3) was dissolved in 30 mL of water. A solution of 0.005 mol (2.06 g) of compound (b) was added. The process was carried out at 0 - 5°C and pH 7 - 7.5 (kept with 10 mL 20 % water solution of sodium carbonate) for 3 hours (for dyes 1 and 2) and 4 hours (for dye 3), respectively. Thin-layer chromatography (system *i*-propanol : ammonia = 1 : 1 on silica gel) was applied to monitor the process. The dyes 1 - 3 were isolated by 15 % sodium chloride, filtered and dried under vacuum at 40°C till constant weight. The dyes were characterized and identified by TLC (system i-propanol : ammonia = 1:1 on silica gel) - Rf, UV-vis spectra - λmax (water), IR and ^{1}H NMR spectra.

Dye 1: Yield 95 g, Rf = 0.51, λmax = 526 nm, IR spectra (KBr), cm^{-1}: 3427 (a broad band overlapping valent oscillations of -OH, -NH, and -CH= of aromatic rings); 1661, 1547 и 1486 (ν-CH of aromatic rings); 1403 (δ-CH=CH-); 1186 (νSO_3H); 1048 (ν-N=N-); 781 (ν-C-Cl), ^{1}H NMR (DMSO-d_6, ppm): 10.78 (s, 2H, 2 x –CH= from ArH); 10.37 (s, 2H, 2 x –CH= from ArH); 8.34-8.04 (m, 6H, 6 x –CH= from ArH); 8.20 (bs, 2H, 2 x –OH); 7.88 (bs, 2H, 2 x –OH); 7.79 (bs, 2H, 2 x –OH); 7.64-7.59 (d, 2H, 2 x -CH=CH-); 7.52 (s, 2H, 2 x –CH= from ArH); 7.30 (bs, 1H,–NH-);7.13-7.10 (s, 2H, 2 x –CH= from ArH); 7.04 (bs, 1H,–NH-).

Dye 2: Yield 97 g, Rf = 0.76, λmax = 538 nm, IR spectra (KBr), cm^{-1}: 3442 (a broad band overlapping valent oscillations of -OH, -NH, and -CH= of aromatic rings); 1623, 1565 и 1488 (ν-CH of aromatic rings); 1404 (δ-CH=CH-); 1190 (νSO3H); 1025 (ν-N=N-); 797 (ν-C-Cl). ^{1}H NMR (DMSO-d6, ppm): 10.75 (s, 2H, 2 x –CH= from ArH); 10.42 (s, 2H, 2 x –CH= from ArH); 8.32 - 8.00 (m, 6H, 6 x –CH= from ArH); 8.17 (bs, 2H, 2 x –OH); 7.82 (bs, 2H, 2 x –OH); 7.77 (bs, 2H, 2 x –OH); 7.60-7.54 (d, 2H, 2 x -CH=CH-); 7.52 (s, 2H, 2 x –CH= from ArH); 7.28 (bs, 1H,–NH-);7.13-7.10 (s, 2H, 2 x –CH= from ArH); 7.06 (bs, 1H,–NH-).

Dye 3: Yield 98 g, Rf = 0.74, λmax = 554 nm, IR spectra (KBr), cm^{-1}: 3443 (a broad band overlapping valent oscillations of -OH, -NH, and -CH= of aromatic rings); 1633, 1532 и 1488 (ν-CH of aromatic rings); 1393 (δ-CH=CH-); 1197 (νSO_3H); 1048 (ν-N=N-); 669 (ν-C-Cl). ^{1}H NMR (DMSO-d6, ppm): 10.72 (s, 2H, 2 x –CH= from ArH); 10.46 (s, 2H, 2 x –CH= from ArH); 8.31-8.00 (m, 6H, 6 x –CH= from ArH); 8.14 (bs, 2H, 2 x –OH); 8.09 (bs, 2H, 2 x –OH);7.80 (bs, 2H, 2 x –OH); 7.74 (bs, 2H, 2 x –OH); 7.62-7.55 (d, 2H, 2 x -CH=CH-); 7.51 (s, 2H, 2 x –CH= from ArH); 7.22 (bs, 1H,–NH-);7.14-7.10 (s, 2H, 2 x –CH= from ArH); 7.01 (bs, 1H,–NH-).

Photostability of the compounds

The photodegradation of the dyes in water solution was monitored spectrophotometrically using the method of standard calibration curve.

Dyeing of cotton fabrics

Dyeing (Exhaust at 80°C) with synthesized reactive dyes (1 - 3) was performed on 100 % cotton (15 x 25 cm) according to standard procedures described in [28].

Dye exhaustion and fixation

The concentration (g L^{-1}) of the dye bath was measured at λmax of the corresponding dye. The percentage of the dyes' exhaustion on cotton (% E), dye fixation ratio (% F) and the total dye fixation (T) were calculated using equations 1, 2 and 3 [33, 34]. Data is given in Table 1.

$$\%E = \frac{C_1 - C_2}{C_1} \cdot 100 \quad (1)$$

$$\%F = \frac{C_1 - C_2 - C_3}{C_1 - C_2} \cdot 100 \quad (2)$$

$$\%T = \frac{\%E \cdot \%F}{100} \quad (3)$$

where: C_1, C_2 and C_3 - the concentration of the dye before dyeing, after dyeing and after extraction of the unfixed dye, respectively.

Colour characteristics of the dyes

The colour characteristics of the dyed material before and after radiation were recorded. Data is given in Table 2.

RESULTS AND DISCUSSION

The synthesized dyes are presented with formulas 1 - 3 (Fig. 1).

Synthesis of dyes 1 - 3

The dyes were obtained using Scheme 1. According to the scheme the I acid, Gamma acid or H acid, reacts

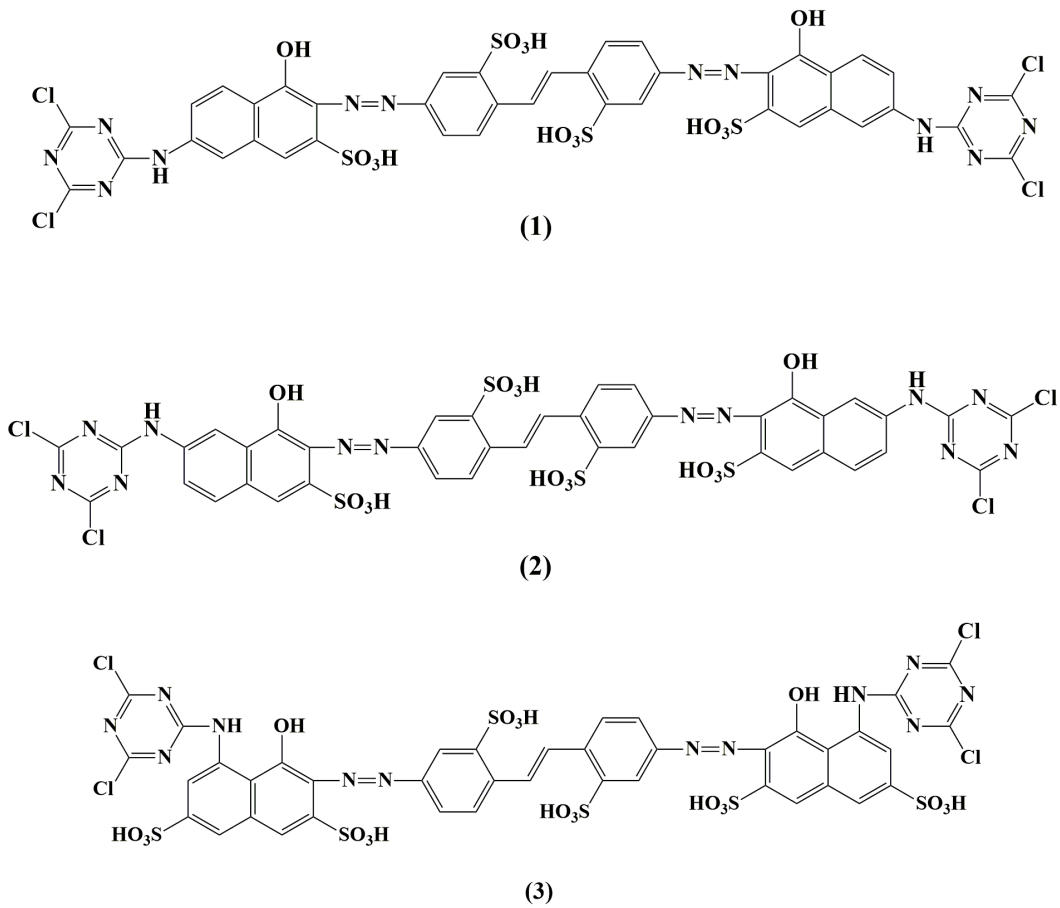


Fig. 1. Structure of dyes 1 - 3.

with cyanuric chloride [29, 30] to give a product (a_1 - a_3). The diazotization of 4,4'-diaminostilbene-2,2'-disulfonic acid (compound b) was performed using a traditional recipe [31, 32].

Bis(dichlorotriazine) dyes 1 - 3 were obtained after coupling compounds (a_1 - a_3) with product (b) in ratio 2:1. The dyes were characterized and identified by TLC (system i-propanol : ammonia = 1 : 1 on silica gel) - Rf, UV-vis spectra - λmax (water), IR and ^{1}H NMR spectra. The absorption spectra of dyes 1 - 3 were recorded in distilled water with concentration 5×10^{-5} mol L^{-1} (Fig. 2).

As can be seen from the presented spectra, the reactive dyes 1 - 3 absorb in range of 450 - 650 nm with λmax = 526 nm (for dye 1), 538 nm (for dye 2) and 554 nm (for dye 3). The broad absorption spectra of dyes are resulted from the absorption bands for the different conjugated systems present in the molecules. That is why the dyes are violet in colour.

Photostability of the compounds

To study the photostability, both the newly synthesized dyes and the commercial dichlorotriazine reactive dye C.I. Reactive red 1 (Fig. 3) were subjected to radiation under UV light in water solution for 2 hours.

The concentration of the dyes in the solution is recorded every 15 min. Just like during the radiation, no change in the absorption maxima (λmax) was registered. The process was followed spectrophotometrically with the method of the standard calibration curve. The dependence of the compound's concentration on the time of radiation is presented in Fig. 4. The initial concentration of the compounds was accepted to be 100 %.

One can see from the Fig. 4 that the introduction of a fragment of 4,4'-diaminostilbene-2,2'-disulphonic acid in the dye molecule (dyes 1 - 3) increases the photostability

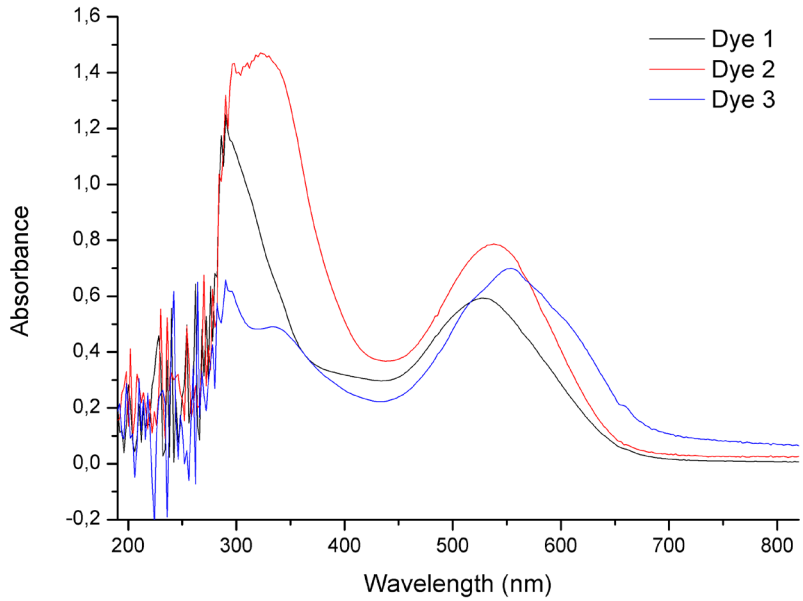


Fig. 2. Absorption spectra of dyes 1 - 3 in distilled water.

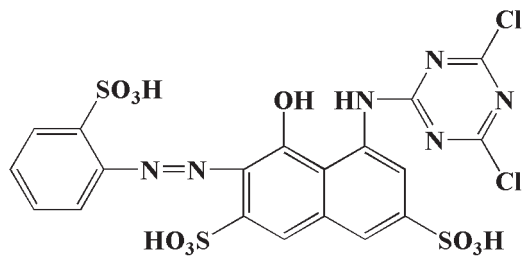


Fig. 3. Structure of the dye C.I. Reactive red 1.

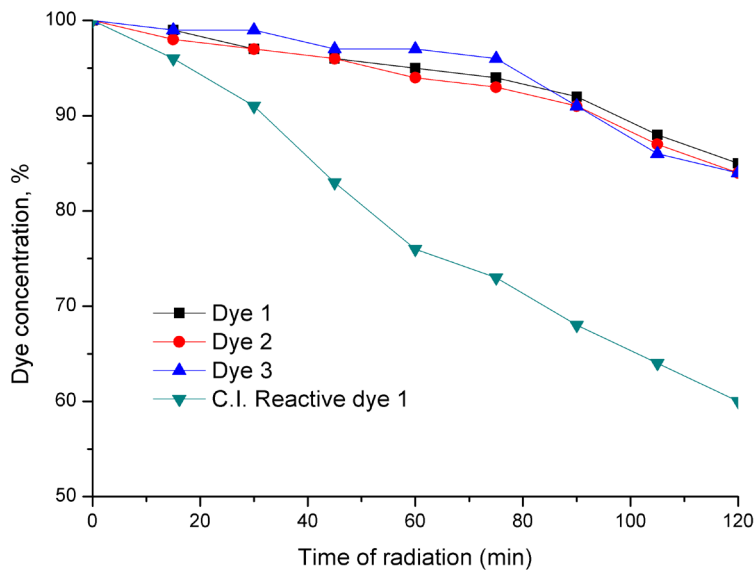


Fig. 4. Dependence of the concentration of the dyes in water (wt. %) on the time of radiation under UV light (min).

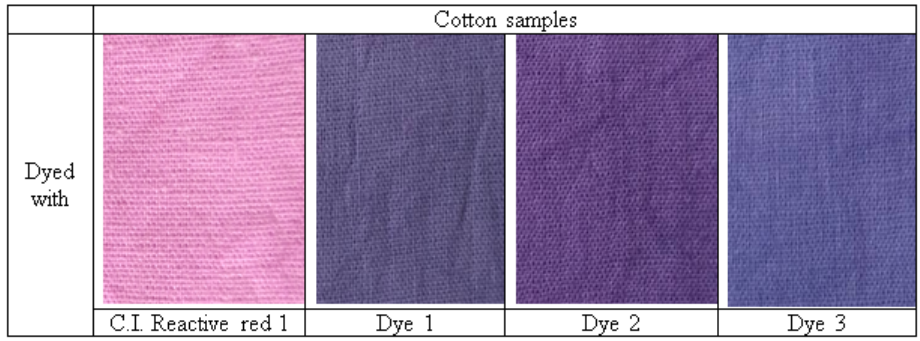


Fig. 5. Cotton fabrics dyed with dyes 1 - 3 at 2 % depth o.w.f.

Table 1. Exhaustion (%), fixation ratio (%F) and total dye fixation (T).

Dye	Dye bath	Absorbance	Concentration, g mL^{-1} x 10^{-4}	% E	% F	% T
C.I. Reactive red 1	before dyeing	3.1831	1.569	74	97	71
	after dyeing	1.1312	0.407			
	after washing	0.1032	0.059			
1	before dyeing	3.0925	1.456	90	99	89
	after dyeing	1.1012	0.151			
	after washing	0.0178	0.0122			
2	before dyeing	3.0737	1.440	85	98	83
	after dyeing	1.1283	0.219			
	after washing	0.0615	0.029			
3	before dyeing	3.0361	1.351	89	99	88
	after dyeing	1.0962	0.153			
	after washing	0.0411	0.014			

with 20 - 25 % in comparison with this of a commercial dichlorotriazine reactive dye C.I. Reactive red 1.

Dyeing of cotton fabrics

Cotton fabrics were dyed with dyes 1 - 3 at 2 % depth o.w.f. according to procedure mentioned above. Materials with an intense colour were obtained (Fig. 5).

The dye exhaustion (%) and the dye fixation ratio (%F) was determined spectrophotometrically. The absorbance of each dyebath solution before and after dyeing was measured, using 1 cm quartz cells housed in a visible scanning spectrophotometer, at the λ_{max} and standard calibration curve of each dye (Table 1).

From the data given in Table 1, it can be seen that the total dye fixation is with 10 - 20 % higher for bis(dichlorotriazine) dyes in comparison with dichlorotriazine dye C.I. Reactive red 1.

Photostability of the dyed samples

To study the photostability, both the dyed samples with newly synthesized dyes and the commercial dichlorotriazine reactive dye C.I. Reactive red 1 were subjected to radiation under UV light for 8 hours. The colour characteristics of the dyed simples before and after radiation at CIE Standard Illuminants D65, A and C were recorded (Table 2).

As can be seen from the presented data, no change in the hue of the coloured samples was observed. There

Table 2. Color characteristics of the dyed cotton samples before and after radiation under UV light for 8 hours.

Dye	Sample/Illuminant		L^*	a^*	b^*	C^*	h^*
C.I. Reactive red 1	non-radiated	D_{65}	64.78	26.53	-9.50	28.18	340.3
		A	67.24	25.14	-4.01	25.46	350.9
		C	64.75	29.64	-9.16	31.03	342.8
	radiated	D_{65}	68.45	18.88	-6.72	20.04	340.4
		A	70.18	18.20	-2.93	18.44	350.9
		C	68.42	21.22	-6.54	22.21	342.9
Dye 1	non-radiated	D_{65}	61.90	7.14	-13.22	15.02	298.4
		A	61.77	6.69	-12.97	14.60	297.3
		C	61.43	10.86	-13.96	17.69	307.9
	radiated	D_{65}	70.35	9.02	-4.91	10.27	331.4
		A	71.06	9.38	-3.41	9.98	340.0
		C	70.25	10.91	-5.08	12.04	335.0
Dye 2	non-radiated	D_{65}	39.44	14.75	-10.04	17.84	325.8
		A	40.61	16.53	-7.53	18.16	335.5
		C	39.21	18.88	-10.35	21.53	331.3
	radiated	D_{65}	46.98	17.84	-5.26	18.60	343.6
		A	48.85	19.67	-1.62	19.73	355.3
		C	46.99	20.97	-5.21	21.61	346,1
Dye 3	non-radiated	D_{65}	59.89	9.82	-20.51	22.74	295.6
		A	59.41	7.07	-20.28	21.48	289.2
		C	59.19	14.67	-21.41	25.95	304.4
	radiated	D_{65}	69.41	12.12	-9.77	15.56	321.1
		A	70.11	11.50	-7.91	13.96	325.5
		C	69.16	14.92	-10.01	17.97	326.1

is a change in the brightness of the samples (it increases after irradiation).

CONCLUSIONS

Three new bis(dichlorotriazine) reactive dyes, containing a residue of 4,4'-diaminostilbene-2,2'-disulphonic acid, were synthesized. The dyes were evaluated on cotton and compared with a commercial dichlorotriazine dye C.I. Reactive dye 1. The degrees of exhaustion and fixation were assessed and it was found that the dyes 1 - 3 showed better results. The photostability of the dyes in water solution and the photostability of the dyed cotton samples were studied and it was found out that it increases with 20 - 25 % when the dyes contained fragment of 4,4'-diaminostilbene-2,2'-disulphonic acid.

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