SYNTHESIS OF SOME NEW BIS(CHLOROTRIAZINE) REACTIVE DYES AND THEIR APPLICATION ON COTTON FABRIC

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ABSTRACT

Four new bis(chlorotriazine) reactive dyes have been synthesized. Two of them are bis(dichlorotriazine) and two are bis(monochlorotriazine) dyes, containing a residue of the stabilizer 4-amino-2,2,6,6-tetramethylpiperidine. They were evaluated for dyeing of cotton fabric. The colour coordinates of the resulting textile samples using the CIE Lab colour space were examined. The degree of exhaustion, fixation and total fixation was determined. The resistance of dyed samples to dry and wet treatments and lights was tested. The photostability of the dyes in water solution and the photostability of the dyed cotton samples have been determined. As a result of the studies carried out it was found that all synthesized dyes are appropriate for dyeing of cotton, as better results for exhaustion and fixation are obtained with the bis(dichlorotriazine) dyes, and the bis(monochlorotriazine) dyes gave better light fastness. The introduction of a 4-amino-2,2,6,6-tetramethylpiperidine fragment in the dye molecule increases the photostability in solution with about 30 % and gives a possibility to obtain colored samples with high stability of light.

Keywords: reactive bis(chlorotriazine) dyes, fastness properties, photostability.

INTRODUCTION

Reactive dyes are synthetic dyes applied for dyeing of different kind of fibers, because they have easy synthesis and application, give materials with colours covering the entire colour gamut, and the dyed materials have good fastness properties [1 - 14]. These dyes form covalent bonds with the fibers during the dyeing, and this is the reason for their good fastness properties. It is known that the mono- and dichlorotriazine reactive dyes hydrolyse easily [15] and to solve this problem, several bi-, tri- and polyfunctional reactive dyes have been synthesized worldwide [16 - 23]. The first homobifunctional and homopolyfunctional reactive dyes were obtained at reaction of dichloro-s-triazinyl dyes with different diamines [19 - 23]. The heterobifunctional dyes containing a chlorotriazine and sulfatoethylsulfonic group or other reactive groups appeared later [7, 8, 24 - 27]. The polyfunctional reactive dyes were displayed high reactivity and excellent degree of exhaustion and fixation [20, 21, 28 - 41]. In addition, the introduction of UV absorbers or antioxidants in the molecule of the reactive dyes can deliver better light properties (UV protective and antioxidant properties) to dyes and materials [3, 14, 42 - 53].

4-Amino-2,2,6,6-tetramethylpiperidine is a representative of the group of HALS (hindered amine light stabilizers). Although it absorbs UV light and can be classified as a UV absorber, its main function is as a hindered amine and antioxidant, which traps free radicals to stop degradation. With oxygen radicals from the atmosphere, it forms nitroxyl radicals, which react very readily with alkoxy radicals and gives non-radical products. The advantage of HALS is the cyclic "regenerability" of the active nitroxyl radical and its possibility to interfere with the oxidation of materials. In addition, a conversion of radical particles into non-radical products occurs [54, 55].

Given the above mentioned, the purpose of the present work was the synthesis of bis(dichlorotriazine) and bis(monochlorotriazine) reactive dyes shown in Fig. 1, where R is a chlorine atom (dyes RD1 and RD3) or a residue of 4-amino-2,2,6,6-tetramethylpiperidine (dyes RD2 and RD4). It is expected that the degree of exhaustion and fixation will increase with the introduction of four chlorine atoms, and the introduction of two stabilizing fragments into the one molecule would lead to an increase in the light stability of both the dye itself and the materials dyed with it.

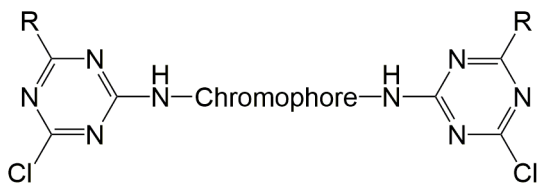
EXPERIMENTAL

Materials and methods

8-Amino-1-naphthol-3,6-disulfonic acid (H acid) (> 95 %), 6-amino-1-naphthol-3-sulfonic acid (I acid), 1,3-phenylenediamine-4-sulfonic acid (PhDS acid), 4-amino-2,2,6,6-tetramethylpiperidine (ATMP) (98 %) (Sigma-Aldrich Co. St. Louis, MO, USA) were used. The solvents (Sigma-Aldrich Co., Ltd., St. Louis, MO, USA and Fisher Scientific, Waltham, MA, USA) were pure or analytical grade. 2-[4-(2,2,6,6-tetrapiperidinyl) amino]-4,6-dichloro-1,3,5-triazine, 2-[N-(3-amino-4-sulpho)phenylamino]-4,6-dichloro-1,3,5-triazine ($\mathbf{a}_1$), 2-[3-(6-sulpho-8-hydroxy)naphthylamino]-4,6-dichloro-1,3,5-triazine ($\mathbf{b}_1$) and 2-[1-(3,6-disulpho-8-hydroxy)naphthylamino]-4,6-dichloro-1,3,5-triazine ($\mathbf{c}_1$) were products synthesized before [51 - 53].

IR spectra were recorded on a Varian 660 instrument (Varian, Inc., Cary, USA). Absorption spectra of the dyes were recorded on a DLAB SP-UV1100 spectrophotometer (DLAB Scientific Co., Ltd., Beijing, China) in a water solution (1×10^{-6} g mL^{-1}). ^1H NMR spectra were recorded on a Bruker AV-600 spectrometer (BRUKER AVANCE II + 600 MHz, Bruker, Billerica, MA, USA). Thin-layer chromatography (TLC) measurements were performed on silica gel plates (Merck, 60 F 254, 20 × 20 cm, 0.2 mm thickness).

TLC-MS analysis was performed using a CAMAG TLC-MS Interface 2 (Muttenz, Switzerland) connected to a Waters SQ Detector 2 single quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source operating in positive ion mode. The interface was supplied with elution solvent via an isocratic HPLC pump (model: positive) at a constant flow rate of 0.2 mL min^{-1}. The Waters SQ Detector 2 mass spectrometer and isocratic HPLC pump were obtained from Waters Corporation (Milford, MA,



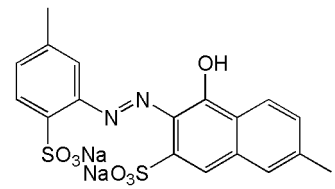
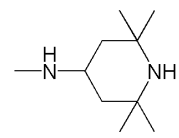
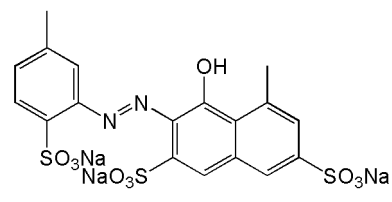
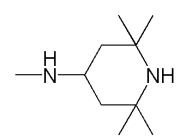
Dye	Chromophore	R
RD1		-Cl
RD2		
RD3		-Cl
RD4		

Fig. 1. Structure of the synthesized dyes RD1-RD4 and their substituents.

USA). Analyte zones were scraped from silica gel TLC plates (at maximum 20 × 20 cm, 0.2 μm layer thickness) and eluted using the TLC-MS Interface 2 in elution mode with a round elution head (4 mm diameter). The TLC plate was placed on the positioning stage and aligned manually using the integrated laser crosshairs. Upon lowering the piston, the elution head established a seal around the zone of interest. Elution was performed for exact 2 min. The mobile phase consisted of acetonitrile : water : acetic acid (50 : 50 : 0.1, v/v/v). The eluted analytes were transferred through stainless steel capillaries and a 0.2 μm inline frit to the mass spectrometer. Mass spectrometric detection was carried out using ESI in positive ion mode, with parameters optimized via IntelliStart. The operating conditions were as follows: Capillary voltage: 3.0 kV, Cone voltage: 30 V, Source temperature: 150°C, Desolvation temperature: 350°C, Desolvation gas flow: 600 L h^{-1}, Cone gas flow: 50 L h^{-1}, Scan range: 100 - 800 m/z. Data acquisition and processing were performed using MassLynx software (version 4.1). After each elution, the system was cleaned by switching the valve to bypass mode and activating the cleaning function three times for 3 s each. Compressed nitrogen (4 - 5 bar) was used to purge the lines and the elution head, ensuring minimal carryover between samples.

Photostability of the dyes in water solution (concentration 5×10^{-5} g mL^{-1}) was studied by a Suntest CPS equipment (Heraeus, Hanau, Germany) supplied with a Xenon lamp (Hanau, Germany, 1.1 kW, 765 W m^{-2}, wavelength λ_{max} = 290 nm).

Photostability of the dyed cotton samples was studied by exposure with a xenon light source on a test camera Q-SUN Xe-1 (Q-Lab corporation, Westlake, OH, USA) according with BDS EN ISO 4892-2.

The color characteristics of the dyed cotton were recorded using ColorTest (ElektroPhysik, Köln, Germany).

The dyed samples were tested, after washing-off using 0.5 g L^{-1} non-ionic detergent at 40°C for 20 min, according to ISO standard methods. The specific tests were: ISO 105-X12 (2004) - colour fastness to rubbing; ISO 105-C06/A1S (2010) - colour fastness to washing; ISO 105-E04 (2013) - colour fastness to perspiration and ISO 105/ B02 - colour fastness to light.

The percentage of the dye exhaustion from the dyeing bath (% E), fixation (% F) and total dye fixation (% T) were calculated using equations Eq. (1) - (3), where C_1, C_2 and C_3 are the concentrations of the dye before and after dyeing, and after washing, respectively [13].

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

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

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

Synthetic procedure for obtaining of the dyes RD1-RD4

Synthesis of the intermediate compounds a_1-c_1

The intermediate compounds $\mathbf{a_1}$-$\mathbf{c_1}$ were synthesized before, using Scheme 1, where R is a chlorine atom [51 - 53]. The data corresponds with the one given in the literature.

Synthesis of the intermediate compounds a_2-c_2

The intermediate compounds $\mathbf{a_2}$-$\mathbf{c_2}$ were synthesized using Scheme 1, where R is a residue from 4-amino-2,2,6,6-tetramethylpiperidine.

0.005 mol (1.52 g) of 2-[4-(2,2,6,6-tetramethyl piperidinyl)amino]-4,6-dichloro-1,3,5-triazine was dissolved in 30 ml acetone. To this, a solution of 0.005 mol of the corresponding compound (PhDS acid, I acid or H acid) in 20 mL water was added. The temperature was maintained at 40 - 45°C and pH 7 - 7.5 (kept with 20 % water solution of sodium carbonate). After 2 h when the synthesis was completed, the products $\mathbf{a_2}$-$\mathbf{c_2}$ were isolated by salting out with 15 % sodium chloride.

Compound 2-[4-(2,2,6,6-tetrapiperidinyl)amino]-4-[N-(3-amino-4-sulpho)phenyl-amino]-6-chloro-1,3,5-triazine ($\mathbf{a_2}$): Yield 1.020 g; Rf (TLC - silica gel plates and eluent system i-propanol : ammonia (3/1/, v/v) - 0.66; λmax (dimethylformamide) = 292 nm; IR spectra, cm^{-1}: 3369 (ν -OH); 3281 (ν -NH); 3005 (ν -CH= from ArH); 2946 (ν -CH_2); 2855 and 2792 (ν -CH_3); 1619 (ν -CH-); 1581 (ν -N=N-); 1534 (δ -NH); 1502 (ν -CH= from ArH); 1432 (δ -CH_2); 1382 (ν -SO_3-); 1257 (ν -C-N); 1179 (ν -SO_3-); 1016 (δ -OH); 799 (ν -C-Cl).

Compound 2-[4-(2,2,6,6-tetrapiperidinyl)amino]-4-[3-(6-sulpho-8-hydroxy)naphthylamino]-6-chloro-1,3,5-triazine ($\mathbf{b_2}$): Yield 1.018 g; Rf (TLC - silica gel plates and eluent system n-butanol : acetic acid : H_2O (4/1/5,

v/v/v) - 0.51; λmax (dimethylformamide) = 296 nm; IR spectra, cm^{-1}: 3399 (ν -OH); 3296 (ν -NH); 3016 (ν -CH= from ArH); 2947 (ν $-CH_2$); 2855 and 2782 (ν $-CH_3$); 1619 (ν -CH-); 1580 (ν -N=N-); 1541 (δ -NH); 1511 (ν -CH= from ArH); 1429 (δ $-CH_2$); 1390 (ν $-SO_3$-); 1222 (ν -C-N); 1179 (ν $-SO_3$-); 1041 (δ -OH); 798 (ν -C-Cl).

Compound 2-[4-(2,2,6,6-tetrapiperidinyl)amino]-4-[1-(3,6-disulpho-8-hydroxy)naphthylamino]-6-chloro-1,3,5-triazine (**c_2**): Yield 1.247 g; Rf (TLC - silica gel plates and eluent system i-propanol : ammonia (3/1/, v/v) - 0.44; λmax (dimethylformamide) = 298 nm; IR spectra, cm^{-1}: 3430 (ν -OH); 3247 (ν -NH); 3011 (ν -CH= from ArH); 2944 (ν $-CH_2$); 2824 and 2754 (ν $-CH_3$); 1619 (ν -CH-); 1587 (ν -N=N-); 1540 (δ -NH); 1501 (ν -CH= from ArH); 1421 (δ $-CH_2$); 1390 (ν $-SO_3$-); 1227 (ν -C-N); 1177 (ν $-SO_3$-); 1038 (δ -OH); 797 (ν -C-Cl).

Synthesis of dyes RD1 and RD3

*Diazotation of compound **a_1**:* It was accomplished using traditional recipe [52]. The product obtained **d_1** without isolation was coupled with compound **b_1** or **c_1**.

*Coupling with compound **b_1** or **c_1**:* 0.005 mol of compound **d_1** was added to 10 ml water solution of 0.005 mol (1.94 g) of compound **b_1** or 2.34 g (0.005 mol) of compound **c_1**. The reactions carried out for 2 h at 15-20°C and pH 7-7.5 (kept with 20 % water solution of sodium carbonate). The processes were monitored by TLC (system i-propanol : ammonia = 2:1 on silica gel). The bis(dichlorotriazine) dyes RD1 and RD3 were isolated by 15 % sodium chloride, filtered and dried.

RD1: Yield 3.37 g; TLC (system i-propanol : ammonia = 1 : 1 on silica gel) - Rf = 0.72. UV-vis spectra - λmax (water) = 488 nm, ε = 11 467 L mol^{-1} cm^{-1}. IR spectra (KBr), cm^{-1}: 3430 (a broad band overlapping valent oscillations of -OH and -NH); 1662 (ν -C=N); 1635 (ν -CH-); 1570 (ν -N=N-); 1489 (δ -CH= from ArH); 1430 (δ -OH); 1372 (ν $-SO_3$-); 1216 and 1089 (ν -C-N); 1193 (ν $-SO_3$-); 1045 (ν -N=N-); 1018 (δ -CH= from ArH); 794 (ν -C-Cl). ^{1}H NMR (dimethyl sulfoxide, δ/ppm): 8.24 (bs, 1H, -OH), 8.12 (s, 1H, ArH), 8.06-8.04 (d, 1H, ArH, J = 12Hz), 7.99 (bs, 1H, -OH), 7.95-7.92 (bs, 1H, -OH), 7.84-7.83 (d, 1H, ArH, J = 6Hz), 7.74-7.72 (bs, 1H, -NH), 7.69-7.67 (d, 1H, ArH, J = 12Hz), 7.61-7.59 (d, 1H, ArH, J = 12Hz), 7.54 (s, 1H, ArH), 7.15 (bs, 1H, -NH), 7.09 (s, 1H, ArH). MS: Mm_{exact} [g/mol] calcul. for $C_{22}H_{12}Cl_4N_{10}O_7S_2$ - 734.34, observed 734.94.

RD3: Yield 3.96 g; TLC (system i-propanol : ammonia = 2 : 1 on silica gel) - Rf = 0.44. UV-vis spectra - λmax (water) = 514 nm, ε = 11 735 L mol^{-1} cm^{-1}. IR spectra (KBr), cm^{-1}: 3434 (a broad band overlapping valent oscillations of -OH and -NH); 1662 (ν -C=N); 1557 (ν -N=N-); 1496 (δ -CH= from ArH); 1395 (ν $-SO_3$-); 1193 (ν $-SO_3$-); 1043 (ν -N=N-); 798 (ν -C-Cl). ^{1}H NMR (dimethyl sulfoxide, δ/ppm): 8.17 (bs, 1H, -OH), 8.06 (s, 1H, -OH), 8.04 (s, 1H, ArH), 7.86-7.85 (d, 1H, ArH, J = 6Hz), 7.73 (bs, 1H, -OH), 7.67 (s, 1H, -OH), 7.65 (s, 1H, ArH), 7.60-7.59 (m, 2H, ArH), 7.30 (s, 1H, -NH), 7.22 (s, 1H, ArH), 7.18 (s, 1H, -NH). MS: Mm_{exact} [g/mol] calcul. for $C_{22}H_{12}Cl_4N_{10}O_{10}S_3$ - 814.4, observed 814.86; $[M+H]^+$ observed 815.70; $[M+H]^-$ observed 814.62.

Synthesis of dyes RD2 and RD4

*Diazotation of compound **a_2**:* It was accomplished using traditional recipe [52]. The product obtained **d_2** without isolation was coupled with compound **b_2** or **c_2**.

*Coupling with compound **b_2** or **c_2**:* 0.005 mol of compound **d_2** was added to 20 ml water solution of 0.005 mol (2.53 g) of compound **b_2** or 2.93 g (0.005 mol) of compound **c_2.** The reactions carried out for 2 h at 15-20°C and pH 7-7.5 (kept with 20 % water solution of sodium carbonate). The processes were monitored by TLC (system i-propanol:ammonia = 3:1 on silica gel). The bis(monochlorotriazine) dyes RD2 and RD4 were isolated by 15 % sodium chloride, filtered and dried.

RD2: Yield 4.63 g; TLC (system i-propanol : ammonia = 3 : 1 on silica gel) - Rf = 0.62. UV-vis spectra - λmax (water) = 486 nm, ε = 15 480 L mol^{-1} cm^{-1}. IR spectra (KBr), cm^{-1}: 3487 and 3405 (ν -OH); 3272 (ν -NH); 3078 (ν -CH= from ArH); 2971 (ν $-CH_2$); 2842 (ν $-CH_3$); 1619 (ν -CH-); 1565 (ν -N=N-); 1377 (ν $-SO_3$-); 1234 (ν -C-N); 1184 (ν $-SO_3$-); 1051 (δ -OH); 803 (ν -C-Cl). ^{1}H NMR (dimethyl sulfoxide, δ/ppm): 10.15 (s,1H, -OH), 9.79 (s,1H, -OH), 9.63 (s,1H, -OH), 8.43 (bs, 1H, -NH), 8.31 (bs, 1H, -NH), 7.99 (m, 1H, ArH), 7.62-7.58 (bs, 2H, 2 x -NH), 7.48 (s, 1H, ArH), 7.43-7.41 (d, 1H, ArH, J = 12Hz), 7.31-7.30 (bs, 1H, -NH), 7.28-7.27 (d, 1H, ArH, J = 6Hz), 7.17-7.15 (d, 1H, ArH, J = 12Hz), 7.14 (bs, 1H, -NH),7.07 (s, 1H, ArH), 6.96-6.94 (d, 1H, ArH, J = 12Hz), 4.34 (m, 2H, 2 x -CH- from ATMP), 2.00-1.91 (d, 4H, 2 x $-CH_2$ from ATMP, J = 48Hz), 1.72-1.59 (m, 4H, 2 x $-CH_2$ from ATMP), 1.51-1.44 (bs, 24H, 8 x $-CH_3$ from ATMP). MS: Mm_{exact} [g/mol] calcul. for $C_{40}H_{50}Cl_2N_{14}O_7S_2$ - 973.95, observed 974.68; $[M+H]^+$

observed 975.58; $[M+H]^-$ observed 974.38 and 973.88.

RD4: Yield 4.97 g; TLC (system i-propanol : ammonia = 3 : 1 on silica gel) - Rf = 0.62. UV-vis spectra - λmax (water) = 516 nm, ε = 15102 L mol^{-1} cm^{-1}. IR spectra (KBr), cm^{-1}: 3484 and 3410 (ν -OH); 3266 (ν -NH); 3077 (ν -CH= from ArH); 2982 (ν -CH_2); 2842 (ν -CH_3); 1619 (ν -CH-); 1565 (δ ν-N=N-); 1377 (ν -SO_3-); 1231 (ν -C-N); 1185 (ν -SO_3-); 802 (ν -C-Cl). ^{1}H NMR (dimethyl sulfoxide, δ/ppm): 8.23 (s, 1H,-OH), 8.08 (s, 1H, -OH), 7.84 (s, 1H,-OH), 7.99 (s, 1H, -OH), 7.76 (s, 1H, -NH), 7.66 (s, 1H,-NH), 7.61 (s, 1H, ArH), 7.43-7.42 (d, 2H, ArH, J = 6Hz), 7.29 (s, 1H, -NH), 7.24 (s, 1H, ArH), 7.13 (s, 1H, ArH), 7.11 (s, 1H, -NH), 6.96-6.95 (ds, 1H, ArH), 4.31-4.19 (m, 2H,2 x -CH- from ATMP), 1.97-1.90 (m, 4H, 2 × -CH_2 from ATMP), 1.68-1.59 (m, 4H, 2 x -CH_2 from ATMP), 1.51-1.47 (ds, 24H, 8 x -CH_3 from ATMP) (crystallization of the dye with 4 molecules of ATMP was observed). MS: Mm_{exact} [g/mol] calcul. for $C_{40}H_{50}Cl_2N_{14}O_{10}S_3$ - 1054.01, observed 1054.39; $[M+H]^+$ observed 1055.5 and 1055.89; $[M+H]^-$ observed 1053.59.

Photostability of the compounds

The water solutions of the dyes were radiated with UV light for 2 h. Their concentration during radiation was recorded by spectrophotometer every 15 min.

Dyeing of cotton fabric and related investigations

Dyeing (Exhaust at 90°C) with synthesized dyes RD1-RD4 was performed on 100 % cotton (20 x 20 cm) according to procedure described before [13].

The concentration of the dye in dye bath and in the wash waters were measured at λmax of the corresponding dye. The percentage of the dye exhaustion (% E), fixation (% F) and total dye fixation (% T) on cotton was calculated and the colour characteristics of the dyed material were recorded. The dyed samples after washing-off were tested according to ISO standard methods: washing at 40°C (BDS EN ISO 105-C06); acid and alkaline perspiration (BDS EN ISO 105-E04); dry and wet rubbing BDS EN ISO 105-X12).

The dyed samples were radiated with UV light for 8 h. The colour characteristics of the dyed material were recorded every hour during the radiation.

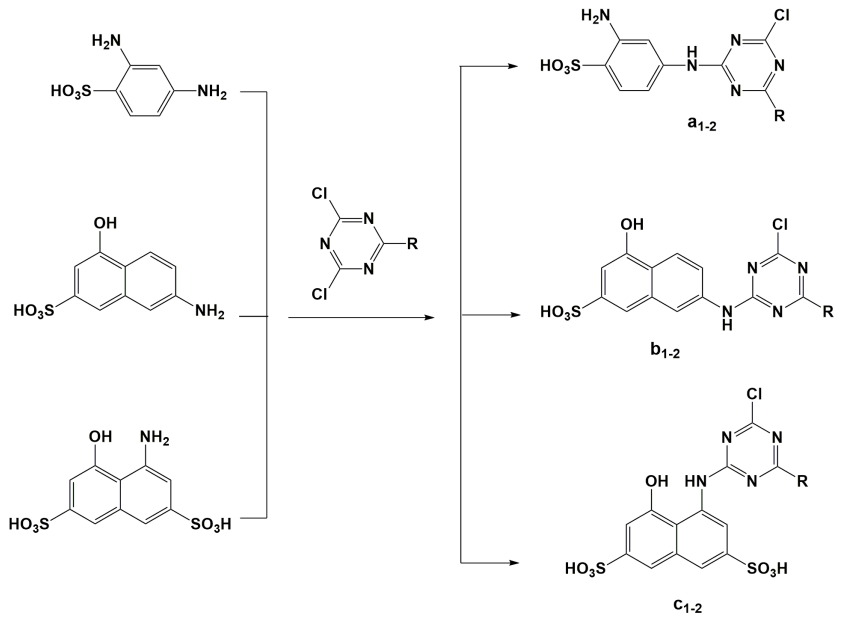
RESULTS AND DISCUSSION

Synthesis of dyes RD1-RD4

The intermediate compounds $\mathbf{a_1}$-$\mathbf{c_1}$ were synthesized before using Scheme 1, where R is a chlorine atom [51-53]. The products were isolated by salting out with 15 % sodium chloride and characterized. The data corresponds with that, given in the literature.

The intermediate compounds $\mathbf{a_2}$-$\mathbf{c_2}$ were obtained, using Scheme 1, where R is a residue of ATMP. The products were isolated by salting with 15 % sodium chloride and characterized.

The dyes RD1-RD4 were obtained, using Scheme 2,



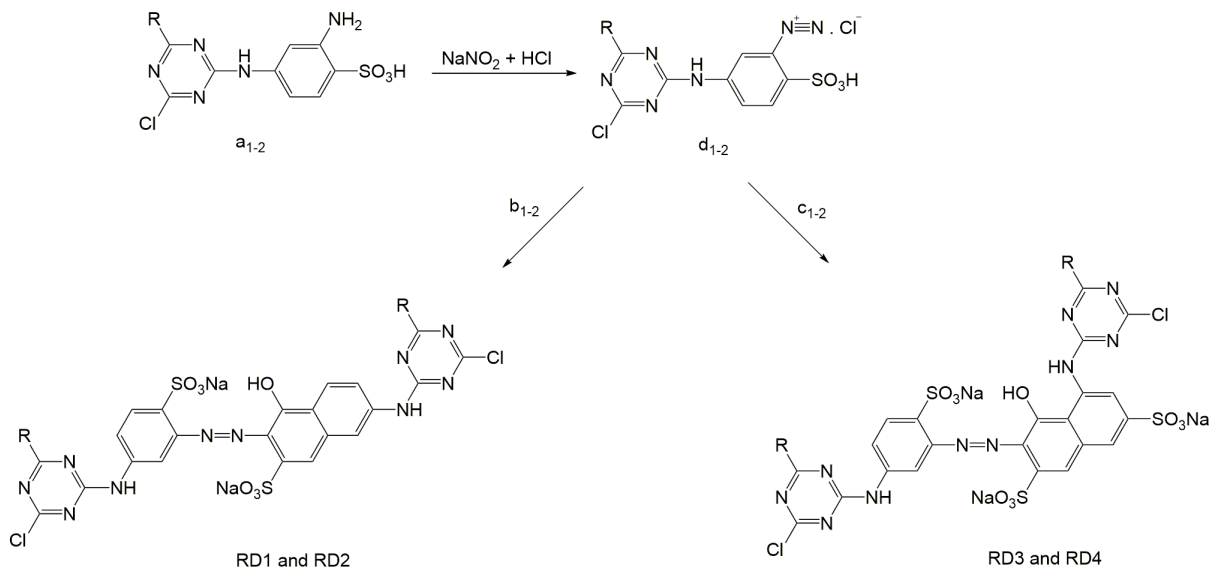
Scheme 1. Synthesis of the intermediate compounds $\mathbf{a_{1-2}}$-$\mathbf{c_{1-2}}$, where R is chlorine atom ($\mathbf{a_1}$-$\mathbf{c_1}$) or a residue of ATMP ($\mathbf{a_2}$-$\mathbf{c_2}$).

where R is chlorine atom (for dyes RD1 and RD3) or a residue of ATMP (for dyes RD2 and RD4). The products were isolated by salting out with 15 % sodium chloride and characterized by UV-Vis spectra (Fig. 2), ^{1}H NMR and MS spectra.

Photostability of the dyes RD1-RD4

The solutions of synthesized dyes RD1-RD4 in water were subjected to radiation with UV light for 2 h. The concentration of the corresponding compound in the solution during the radiation was recorded spectrophotometrically every 15 min using the method of the standard calibration curve. The data obtained is given in Fig. 3.

From the studies carried out it is seen that the concertation of the dyes in the end of the second hour is 32 - 35 % for bis(dichlorotriazine) dyes RD1 and RD3 and 63 - 65 % for bis(monochlorotriazine) dyes RD2 and RD4 (Fig. 3). The introduction of residues of ATMP leads to about 30 % enhancement in the photostability.



Scheme 2. Synthesis of the dyes RD1-RD4.

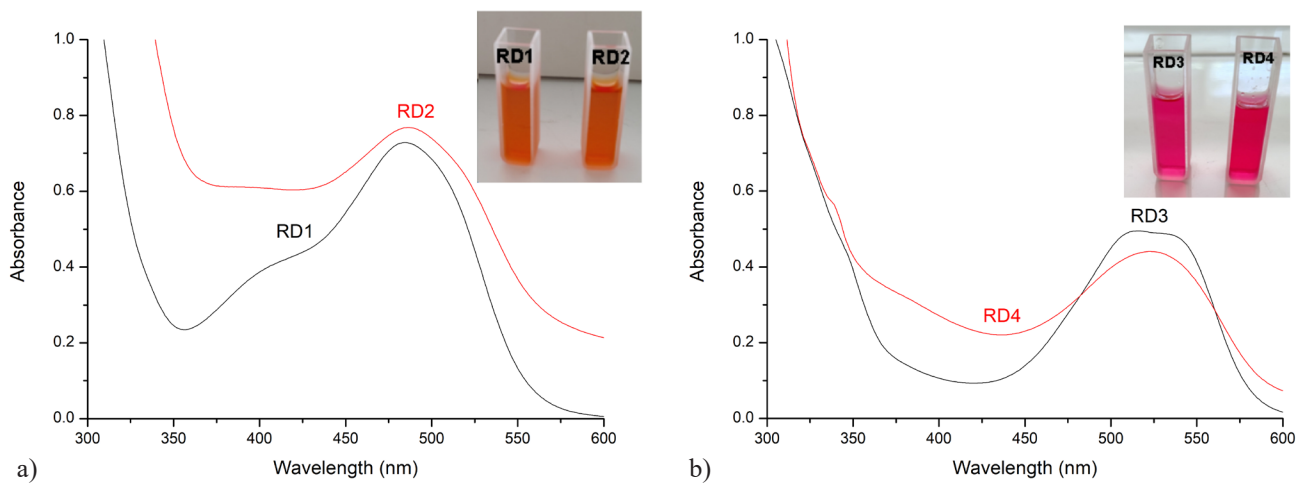


Fig. 2. Absorption spectra of dyes RD1 and RD2 (a) and dyes RD3 and RD4 (b) in water.

Dyeing of cotton fabric

Cotton fabric was dyed with dyes RD1-RD4 at 1 % depth o.w.f. according to traditional procedure [13] and samples with intensive colours were obtained (Fig. 4).

The percents of exhaustion, fixation and total fixation were calculated after a spectrophotometric determination of concentrations of the dye bath before and after dyeing, and after washing using the standard calibration curve of the corresponding dye. The data is given in Fig. 5.

From Fig. 5 the percent of exhaustion for the bis(monochlorotriazine) dyes RD2 and RD4 is 65 - 68 % and for the bis(dichlorotriazine) dyes RD1 and RD3 is 75 - 77 %. The percent of fixation for all dyes is approximately the same (95 - 96 %). The total fixation was 62 - 65 % for the bis(monochlorotriazine) dyes and 72 - 74 % for the bis(dichlorotriazine) dyes. From the dyeing investigation, it can be concluded that the dyes containing four chlorine atoms, regardless of the possible existing steric hindrance, have a 10 % higher degree of exhaustion and total fixation than the bis(monochlorotriazine) dyes. The increase in the exhaustion and fixation values when using bis(dichlorochlorotriazine) dyes, compared to bis(monochlorochlorotriazine) dyes is due to the ability to form twice as many chemical bonds with cotton fibers. Comparing the obtained values for exhaustion and fixation of the bis(dichlorotriazine) dyes RD1 and RD3 with those for dichlorotriazine dyes with similar chromophores [13], it was found that they increase by about 10 - 12 %. The reduction in exhaustion and fixation values by about 15 % for bis(monochlorotriazine) dyes RD2 and RD4 compared to similar dyes, non-contained stabilizer fragments is due to the steric hindrance of the introduced HALS amine [13].

The fastness properties of dyed samples on washing at 40°C, acid and alkaline perspiration, dry and wet rubbing, and light were determined according to ISO standard methods. Data is given in Table 1.

From the results it can be seen that the change in the color of dyed sample and undyed cotton did not observe during the washing. No change in the colour of the dyed samples is observed upon exposure to acidic and alkaline sweat. However, staining of the wool samples is observed both during washing and under the influence of acidic and alkaline sweat. The values of wet and dry rubbing are good to excellent, which corresponds to data reported in the literature for triazine reactive dyes. The light fastness values are excellent for the dyes, containing fragments of stabilizer (RD2 and RD4) and good for dyes RD1 and RD3.

The colour coordinates of dyed samples were determined by CIE Lab colour space coordinate system (Table 2 and Table 3).

From CIE colour coordinates (Tables 2 and 3) the samples dyed with RD1 and RD2 have orange colour and the samples dyed with RD3 and RD4 have magenta colour, which corresponds to the samples given on Fig. 3.

The photostability of the dyed cotton samples was

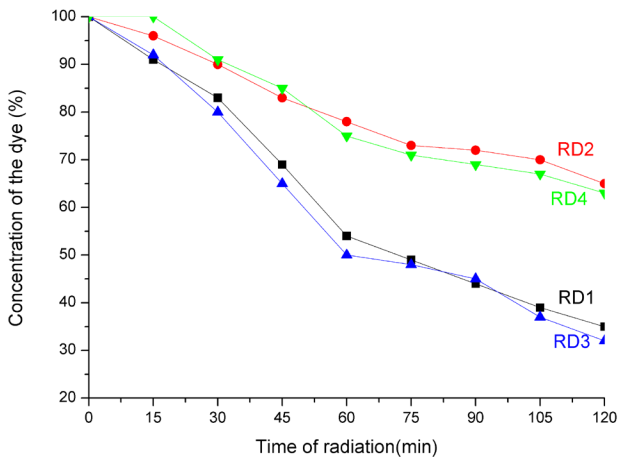


Fig. 3. Dependence of the concentration of the dye in water solution on the time of radiation.

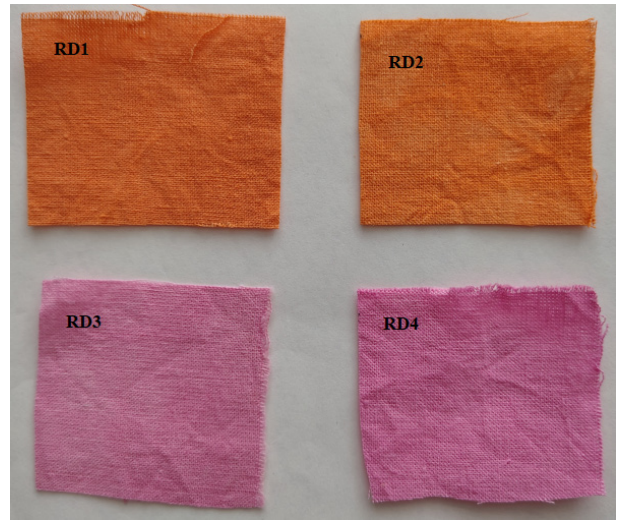


Fig. 4. Cotton fabric dyed with dyes RD1-RD4 at 1 % depth.

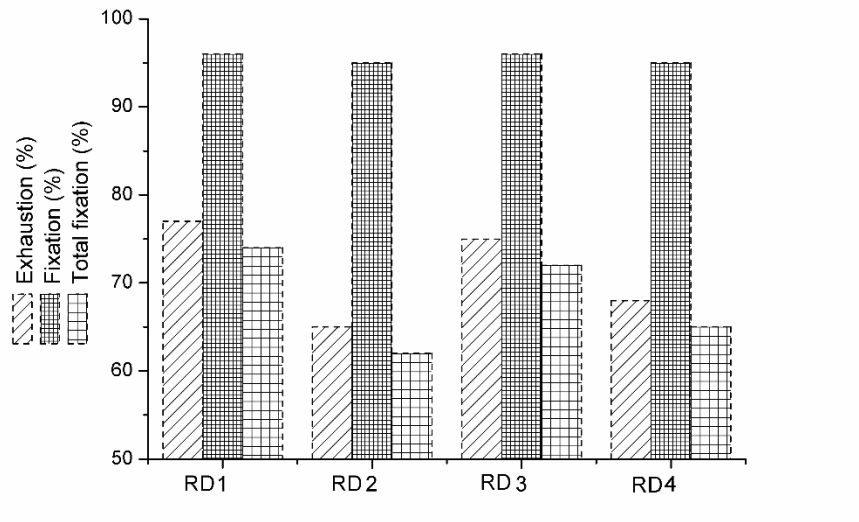


Fig. 5. Exhaustion (% E), fixation (% F) and total fixation (% T) of dyes RD1 - RD4.

Table 1. Fastness properties data of the samples of cotton fabric dyed with dyes RD1 - RD4.

Dye	Washing at 40°C	Perspiration		Rubbing		Light
		Alkaline	Acid	Dry	Wet	
RD1	5/4/5	5/3-4/4	5/4/4-5	5	4	4
RD2	5/4-5/5	5/4/4-5	5/4-5/4-5	5	4	5
RD3	5/4/5	5/4/4	5/3-4/4-5	5	4	4
RD4	5/5/5	5/4-5/5	5/4/4-5	5	4	5

**Data x/y/z indicates: the change in color of dyed sample/ the change in color of undyed wool/the change in color of undyed cotton; Washing & Rubbing fastness: 1 - poor; 2 - fair; 3 - good; 4 - very good; 5 - excellent; Light fastness: 1 - poor; 2 - slight; 3 - moderate; 4 - fair; 5 - good; 6 - very good; 7 - excellent.*

determined by investigation of the change in the colour characteristics during the radiation under UV light for 8 h (Table 2 and Table 3). For each sample, ten measurements were made at different locations on the surface. The experimental results show that light exposure affects the samples dyed with bis(dichlorotriazine) dyes to a greater extent. The observed change in ΔE is in the order of 11-13 units. In contrast, the change in ΔE for the samples dyed with bis(monochlorotriazine) dyes is in the order of 2-5 units. The observed significant difference is due to the presence of the two stabilizing tetramethylpiperidine fragments, providing higher photostability of the dyed samples.

The same pattern is observed in the values for the change in ΔL (L - L_0) (Fig. 6). It is also observed that until the 4 h, the values of L of the samples dyed with the dyes containing I acid (RD1 and RD2) fluctuate. After that, however, an increase in ΔL is observed, which is also characteristic of the other samples.

From the studies conducted on the application of synthesized dyes for dyeing cotton, it can be concluded that all synthesized dyes are applicable for dyeing cotton. Of these, bis(chlorotriazine) dyes have a higher degree of exhaustion and fixation, and bis(monochlorotriazine) dyes have a higher photostability.

CONCLUSIONS

Four new bis(chlorotriazine) reactive dyes, two of them containing stabilizer residues in their molecule have been synthesized. Cotton fabric was dyed with the synthesized dyes. The degree of exhaustion, fixation and total fixation was determined, and it was found that they are better for the bis(dichlorotriazine) dyes. The

Table 2. CIE Lab colour coordinates (illuminant D_{65}) of dyed cotton with RD1 and RD2 before (0 h) and after radiation.

Dye	Time of radiation, h	L	a	b	ΔE	X	Y	Z
RD1	0	64.75	39.70	39.52	66.01	43.99	33.50	13.19
	1	66.50	32.89	34.38	57.99	44.83	36.44	17.28
	2	66.30	31.56	33.96	57.11	44.47	36.32	17.32
	3	67.43	30.43	32.54	54.98	44.72	36.83	18.08
	4	67.52	31.07	33.16	55.65	42.64	34.44	15.87
	5	67.65	30.44	31.58	54.71	42.99	34.93	16.68
	6	67.84	30.25	32.01	54.39	43.72	34.37	15.56
	7	67.98	30.34	32.15	54.55	46.02	38.29	19.77
	8	68.44	29.38	30.99	52.90	43.01	34.96	16.09
RD2	0	64.57	34.66	33.96	59.08	49.48	39.55	19.93
	1	64.89	34.75	33.39	59.43	43.08	34.21	16.17
	2	65.31	34.63	33.39	59.11	43.41	34.42	16.11
	3	65.67	34.3	33.36	58.69	44.06	35.05	16.82
	4	65.61	33.82	32.22	57.80	44.99	36.16	17.65
	5	65.76	32.96	31.79	56.39	44.05	35.03	17.37
	6	65.93	33.05	31.41	56.72	44.40	35.83	17.66
	7	66.79	33.28	31.45	56.76	43.46	34.94	17.08
	8	66.94	33.34	32.38	56.84	43.47	35.02	17.36

Table 3. CIE Lab colour coordinates (illuminant D65) of dyed cotton with RD3 and RD4 before (0 h) and after radiation.

Dye	Time of radiation, h	L	a	b	ΔE	X	Y	Z
RD3	0	68.86	33.24	-13.51	47.46	48.88	39.83	55.18
	1	69.45	29.49	-12.72	44.27	48.17	40.86	55.48
	2	70.80	26.92	-11.42	41.26	50.51	43.56	57.75
	3	71.61	24.66	-10.09	38.14	50.04	43.74	57.62
	4	71.87	24.83	-10.03	39.49	51.17	45.01	58.43
	5	72.51	24.18	-9.98	37.16	50.27	44.39	57.73
	6	73.01	22.76	-9.61	36.51	50.91	42.12	57.94
	7	73.42	24.48	-9.80	38.81	51.29	45.13	58.56
	8	73.91	22.90	-9.47	35.91	52.81	46.66	59.99
RD4	0	71.51	21.41	-8.16	36.06	47.6	42.97	39.73
	1	71.68	19.21	-5.24	34.44	47.86	43.48	41.84
	2	71.62	19.41	-4.78	34.54	46.38	42.51	41.55
	3	71.78	17.19	-4.03	33.1	47.75	44.18	44.84
	4	72.46	16.96	-2.67	31.43	48.67	45.16	45.96
	5	72.75	16.83	-2.61	31.95	48.75	45.19	46.27
	6	73.11	16.83	-2.12	30.78	49.4	46.03	47.23
	7	73.34	16.99	-3.19	31.59	49.27	45.96	47.03
	8	73.48	16.45	-2.58	31.13	49.51	45.84	46.05

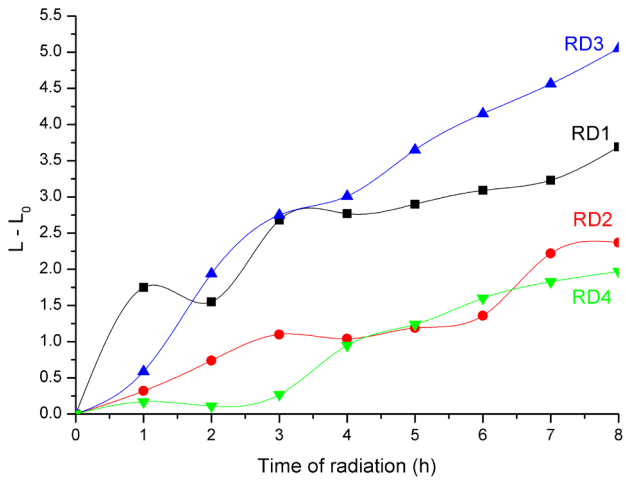


Fig. 6. Dependence of ΔL on the time of radiation.

colour coordinates of the resulting textile samples were examined. The resistance of dyed samples to dry and wet treatments and lights was tested and it was found that all dyes have good fastness properties. The light fastness was better for the bis(monochlorotriazine) dyes, containing a stabilizer fragment. The photostability of the dyes in water solution and dyed cotton samples have been determined. Results obtained lead to the conclusion that the dyes can die cotton fabric with very good percents of exhaustion and fixation and good to excellent values for fastness properties. The introduction of 4-amino-2,2,6,6-tetramethylpiperidine fragment in the dye molecule increases the photostability in solution with about 30 % and gives coloured samples with high stability of light.

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Authors' contributions

P.M.: Data collection and original draft preparation, writing - review and editing.

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