

On the synthesis of some bifunctional reactive triazine dyes

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Abstract

The synthesis of two bifunctional reactive monochloro triazine azo dyes was investigated. As basic chromophore one yellow triazine dye, applied in the practice was chosen. Two different reaction schemes for synthesis were studied. Quantitative thin-layer chromatography (Tlc) was applied to monitor the process. Cotton fibres were dyed and the colourimetric characteristics of the dyed fabrics were measured. The dyes were copolymerized with acrylamide and acrylonitrile giving polymers with intense colour that is stable to solvents extraction. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Reactive dyes are well known and applied for dyeing of different materials [1]. Among them triazine derivatives have an important place. Nevertheless their good properties investigations on new and/or modified derivatives is of importance [2–7]. The combination of two different functional (reactive) groups in the dye's molecule improves their dyeing ability and possibility for applications. The 1,3,5-triazine molecules affords an opportunity for this. We have previously reported the synthesis of different unsaturated triazine derivatives—dyes [8–10], fluorescent whitening agents [11] and stabilizers [12,13]. They were capable of copolymeriza-

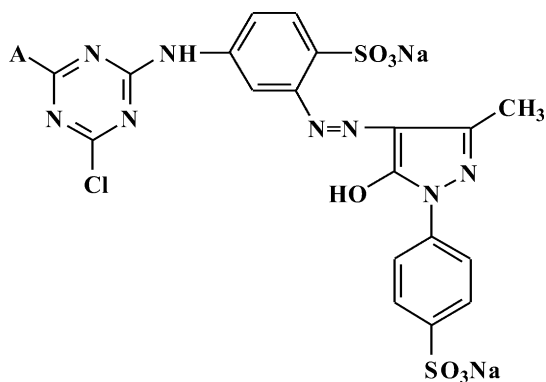
tion with different monomers, thus inherently coloured, bleached and/or stabilized polymers were obtained. Based on our experience, it was of interest to synthesize some bifunctional triazine dyes and to study their properties.

2. Results and discussion

2.1. Synthesis of dyes

An azo monochlorotriazine dye with formula **1a** (Yellow CI 18972) as a model chromophore was used. Our idea was to replace a methanilic acid in the triazine ring with an unsaturated allylic residue, thus a structure with two functional groups to be obtained. The dyes object of the present study can be presented by following general formula (I):

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where A = -Cl No **1**
 A = -NHC₆H₄SO₃H (3) No **1^a**
 A = -NHCH₂CH = CH₂ **1^b**
 A = -OCH₂CH = CH₂ **1^c**

The synthesis of the dyes under investigation can be achieved by two methods:

(a) Firstly 1,3-phenyldiamine-4 sulfonic (m-PDA) acid reacted with cyanuric chloride and the resulting compound after diazotation following traditional procedure [1] and reaction with *N*-(4'-sulfo)phenyl-3-methyl-5-pyrazolone (SP) as a coupling component, was converted to a dye. Using this dye as a basic chromophore derivative, **1a–c** were synthesized.

Dye **1a** was obtained after reaction of dye **1** with methanilic acid (MA—aniline-3-sulfonic acid). The reaction was carried out at 40 °C and pH = 7.5.

The process was monitored by a quantitative Tlc (eluent system *n*-propanol–ammonia 1/1, v/v on silica gel). After 2 h the dye **1a** was isolated and characterised by Tlc (R_f = 0.79), and vis spectra (λ_{\max}). Data are presented in the Experimental section.

Based on our earlier studies [14], the synthesis of dye **1b** was achieved by reaction of the dye **1** with allylamine at 40 °C, monitoring the process by a quantitative Tlc, using the above eluent system. Product **1b** was isolated with 65% yield and was characterized by Tlc (R_f = 0.81), ¹H-NMR, IR and vis spectra. Detailed data are given in the Experimental section.

Our previous investigations [15] showed that the replacement of the second chlorine atom in the

triazine molecule with allylic alcohol took place over a temperature of 60–80 °C. Under this conditions some hydrolysis of chlorine atoms could take place, that is why Scheme 1 was not suitable for the synthesis of this dye.

(b) Another route for the synthesis of the dyes with formula 1 is shown in Scheme 2.

According to Scheme 2, firstly cyanuric chloride reacted with methanilic acid (MA), allylamine (AAm) or allylic alcohol (AA), respectively.

The reaction with MA was performed in a water–acetone media at 0–5 °C and pH = 7, controlled by pH and Tlc (eluent system *n*-propanol–ammonia—3/1, v/v) and was completed after 1 h.

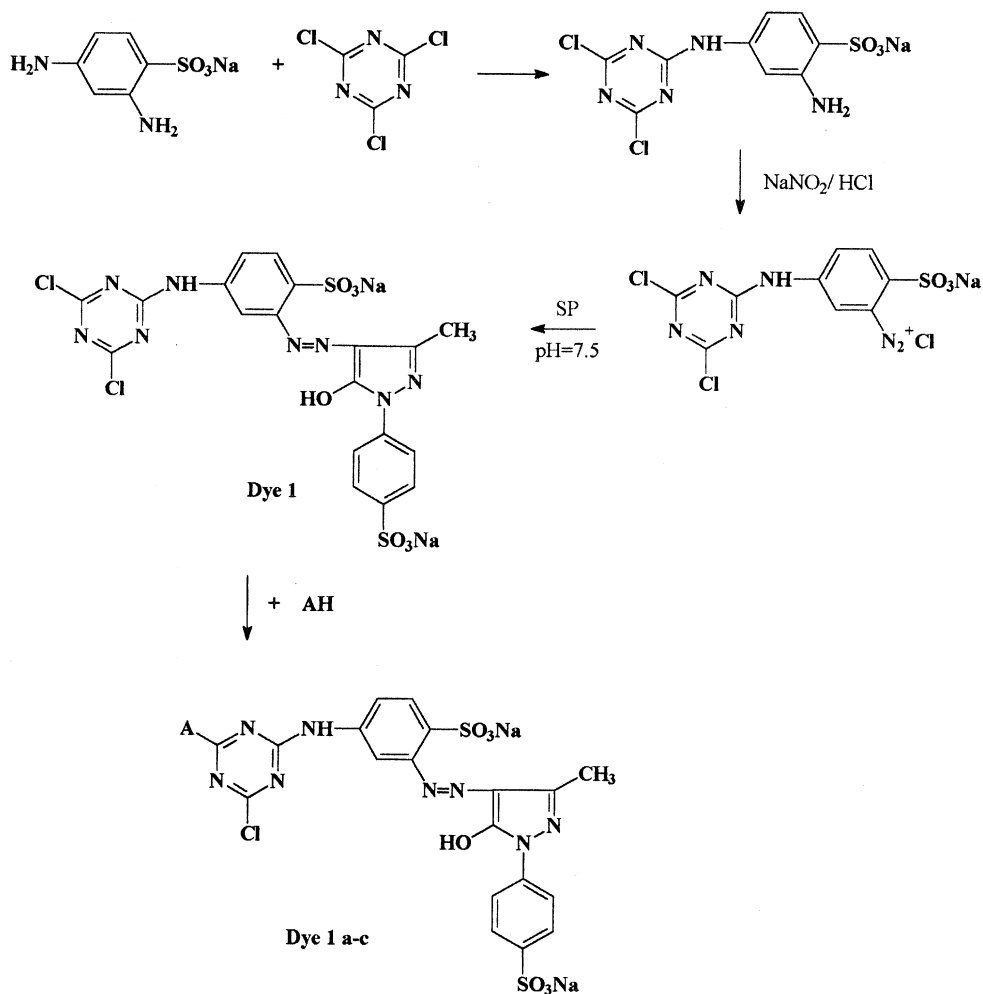
The similar reaction of CC with AAm was undertaken according to the method described in our earlier papers [14] at 10 °C in toluene solution for 3 h. 2-Allyloxy-4,6-dichloro-1,3,5-triazine was also obtained according to a method previously described [11] under the phase-transfer catalysis conditions (PTC) at 0–5 °C for 1 h.

The subsequent step of the synthesis according to Scheme 2, i.e. the reaction of the products 2-(3'-sulfo)anilino-4,6-dichloro triazine or 2-allylamino-4,6-dichloro-1,3,5-triazine, respectively with 1,3-phenyldiamino-4 sulfonic acid, was performed in water–acetone media at 15–20 °C and pH = 7.5. Tlc control showed over 90% conversion after 1 h. The reaction of 2-allyloxy-4,6-dichloro-1,3,5-triazine with m-PDSA was carried out at 0–5 °C and pH = 6 for 3 h.

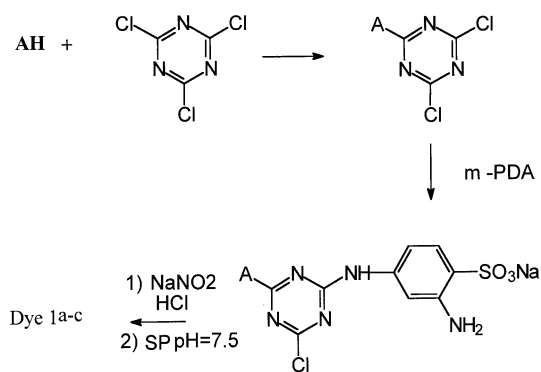
The respective intermediates were characterized by R_f , IR and vis spectra.

Without isolation of the above products, after their diazotation and reaction with *N*-(4'-sulfo)phenyl-3-methyl-5-pyrazolone (SP) as a coupling component, the dyes **1a–c** were isolated with good yield (75, 84 and 92%, respectively) and characterised by R_f , ¹H-NMR, IR and vis spectra. The advantages of this method were that the time of the reaction procedure was shorter, the target dyes with better yield were isolated, some of the steps at lower temperature were performed and finally the semi-products (2,4-disubstituted-6-chloro triazine derivatives) could be easily isolated and purified before the next steps of the reaction.

Comparing the results obtained, bearing in mind both their advantages and disadvantages, we



Scheme 1. Synthesis of the compounds by method a.



Scheme 2. Synthesis of the compounds by method b.

concluded that the second method (Scheme 2) was the better one.

2.2. Colour assessment

Cotton fabrics were dyed with dyes **1a–c** at 3% depth o.w.f. according to a standard procedure. Materials with an intense yellow colour were obtained. Using the Data Color technique and associated software, the colour characteristics of the dyes were recorded; results are given in Tables 1 and 2. It is apparent from these data that CIE coordinates of the dyes showed some movement to

Table 1
Colour data of dyes **1a**, **1b** and **1c** on cotton

| Dye No. | WL ^a | Y ^b (%) | x ^c | y ^c |
|---------------|-----------------|--------------------|----------------|----------------|
| Achromatic PT | | | 0.3137 | 0.3308 |
| 1a | 572 | 77.68 | 0.4561 | 0.4645 |
| 1b | 572 | 74.41 | 0.4479 | 0.4610 |
| 1c | 573 | 73.78 | 0.4497 | 0.4571 |

^a WL, complimentary wavelengths.

^b Y, luminance.

^c x and y, chromaticity.

Table 2
Colour data and CIE coordinates of the dyes **1a–1c** on cotton

| Dye No. | L* | a* | b* | C* | H |
|-----------|-------|------|-------|-------|-------|
| 1a | 80.70 | 4.86 | 76.40 | 76.56 | 86.36 |
| 1b | 81.99 | 3.43 | 72.92 | 73.00 | 87.30 |
| 1c | 80.80 | 5.16 | 70.98 | 71.17 | 85.84 |

the blue-greenish colour for **1b** and the blue-redish colour for **1c** in comparison to the basic dye **1a**, but the conclusion was that replacement of methanilic acid residue in the dye molecule with allylamino- or allyloxy ones did not affect significantly the colour characteristics of the dyes.

The percentage of exhaustion of the dyes and wash fastness were performed using the standard procedure in a specialized laboratory [16,17]. The results are given in Table 3.

One can see from these data that the presence of an allylamino or allyloxy group in the dye molecule did not affect the colouristic properties of the monochlorotriazine dye.

2.3. Copolymerization

Having in mind the possibility for application of the above dyes we studied their ability for copolymerization with two monomers acrylamide (ACA) and acrylonitrile (AN).

Table 3
Exhaustion, fixation and wash fastness of dyes **1a–1c** on cotton

| Dye No. | Exhaustion (%) | Fixation (%) | Wash fastness |
|-----------|----------------|--------------|---------------|
| 1a | 79 | 98 | 5/5/5 |
| 1b | 71 | 98 | 5/5/5 |
| 1c | 78 | 99 | 5/5/5 |

2.3.1. Copolymerization with ACA

Polyacrylamide (PACA) is a water-soluble polymer, widely applied in agriculture, food cosmetics and medicine as an ecologically very suitable material. The polymeric modification of organic compounds represents a very promising possibility for their environmental more tolerant application in cosmetics, food and packaging materials [18]. Having in mind this we studied the ability of dyes **1b** and **1c** to copolymer with ACA. The copolymerization was performed in a water solution at 45 °C in the presence of 1 wt.% of the corresponding dye and 3% of potassium persulfate as an initiator. After 3 h intensively yellow coloured polymers were isolated and subjected to reprecipitation to remove the unreacted monomers. After three-fold precipitation and extraction with hot methanol, until colourless filtrates the polymers retained their colour. They were dried under vacuum at 40 °C until constant weight, and subsequently analysed.

2.3.2. Copolymerization with AN

Polymers and copolymers of AN are widely applied in industry. It was of interest to investigate the possibility of obtaining copolymers of AN with the aforementioned dyes. Polymerization was performed in DMF solution, following the procedure previously described [19]. After 6 h intensively coloured polymers were obtained. They were purified from unreacted monomers by several-fold precipitation and extraction with hot water until the colourless filtrates were observed, dried under vacuum at 50 °C to constant weight.

2.3.3. Analysis of polymers

UV/vis spectra of both type of polymers thus obtained were recorded and compared to the absorption spectra of the monomeric dyes. There was neither a bathochromic nor hypsochromic shift in their spectra observed. Polymers showed the same λ_{max} as the parent dyes, an indication that the basic chromophore did not change either during the polymerization or as a result of its incorporation in the polymer chain. Therefore, by the method of the standard curve, the percentage of the chemically bound dye was calculated. The data obtained were: for dye **1b**: 31% in PACA and

80% in PAN; for **1c**: 30% in PACA and 70% in PAN. Obviously we need additional investigations for optimization of the copolymerization with ACA in order to improve these results. The basic conclusion from these experiments was that the dyes are able to copolymerize with this monomer.

3. Experimental

3.1. Materials, equipment and analyses

Cyanuric chloride (CC) (98%,) was Fluka (Swiss) product; *N*-(4-sulfo)phenyl-3-methyl-5-pyrazolone (SP) and 1,3-phenyldiamine-4 sulfonic acid (m-PDA) are Bayer (Germany) products; 2-allylamino-4,6-dichloro-1,3,5-triazine (AAmT), synthesized by us— $R_f = 0.48$ (silica gel, eluent system *n*-heptane–diethylether 1/1, v/v, λ_{\max} (acetone) = 328 nm; 2-allyoxy-4,6-dichloro-1,3,5-triazine (AOT), synthesized by us— $R_f = 0.68$ (silica gel, eluent system *n*-heptane–diethylether 3/1, v/v, λ_{\max} (acetone) = 330 nm; methanilic acid (MA) (97%, Aldrich, Germany) solvents are of p.a or analytical grade (Fluka). Tlc analyses were made on silica gel plates (Fluka, F60₂₅₄, 5×10 cm, 0.2 mm thickness, ready-to-use) using a Camag (Swiss) Tlc equipment, comprising a Linomat IV device for sample application, a Scanner II and an SP429 Integrator. pH values were monitored using a 704 pH-meter (Metrohm, Swiss). Electronic spectra were recorded on a Hewlett Packard 8452A UV/vis spectrophotometer; IR- on “Specol” (DDR); ¹H-NMR spectra on DRX-250-Brucker equipment; dyeing and colour assessment measurements were performed in a specialized laboratory on a “Data Color” equipment under illuminant D₆₅.

3.2. Synthesis of the compounds

3.2.1. Dye **1a**

A water solution of 7.6 g of MA is added to 100 ml water-suspension of 7.2 g CC. Temperature was maintained 0–5 °C and pH = 7.5, by adding 20% Na₂CO₃. The process was monitored by Tlc on silica gel plates and eluent system *n*-propanol–ammonia—3/1, v/v. After 1 h, at the same temperature and pH, a water solution of 12.2 g of m-PDA was added. When the process was completed

(1 h, Tlc control) the product was diazotized by adding 12 ml HCl and 3 g NaNO₂. The diazo compound thus obtained was added to a solution of 11 g SP at temperature 0–5 °C and pH = 7.5. The process was monitored by Tlc with system *n*-propanol–ammonia—1/1, v/v. After 2 h the dye was isolated using 15% NaCl, filtered off and dried at 35 °C under vacuum. Yield 72%, $R_f = 0.79$, λ_{\max} (H₂O) = 392 nm.

3.2.2. Synthesis of dye **1b**

AAmT (4.1 g) dissolved in 60 of acetone were added to 60 ml ice-water. To this suspension a water solution of 4 g of m-PDA was added, while the temperature was keeping 15–20 °C and pH = 7.5. After 3.5 h (Tlc control, silica gel and system *n*-propanol–ammonia—1/1, v/v, the product with $R_f = 0.77$ was obtained. Diazotation and subsequent reaction with SP were performed as it was described for dye **1a**. Dye **1b** was isolated, filtered off and dried under vacuum at 35 °C. Yield 84%, $R_f = 0.81$, λ_{\max} (H₂O) = 388 nm. IR spectra data (KBr): $\nu_{\text{CH}=\text{CH}_2} = 890 \text{ cm}^{-1}$; ¹H-NMR spectra (D₂O, 250 MHz) δ ppm: 3.6–3.9 (*d*, 2H, CH₂=); 4.9–5.2 (*d*, 2H, –NCH₂–); 5.6–5.9 (*m*, 1H, CH=).

3.2.3. Synthesis of **1c**

AOT (4.2 g) was dissolved in 60 ml acetone and added to 60 ml of water. To this suspension a solution of 4 g of m-PDSA was added. The mixture was stirred at 0–5 °C and pH = 6 for 3 h. The reaction was monitored by Tlc (silica gel and *n*-propanol–ammonia—1/1, v/v.). The product without isolation was subjected to diazotation and reaction with SP as it was described for dye **1a**. The dye **1c** was isolated with yield 94% and characterized by $R_f = 0.82$ and λ_{\max} (H₂O) = 392 nm. IR spectra data (KBr): $\nu_{\text{CH}=\text{CH}_2} = 900 \text{ cm}^{-1}$. ¹H-NMR spectra (D₂O, 250 MHz) δ ppm: 3.6–3.8 (*d*, 2H, CH₂=); 5.0–5.4 (*d*, 2H, –OCH₂–); 5.5–6.0 (*m*, 1H, CH=).

3.3. Dyeing

Cotton fabrics (100%) were dyed according to standard procedure [17] (official Bulgarian standard) in a specialized laboratory at 3% depth o.w.f. Colourimetric investigations using standard calibration curve were performed with solutions of

the dyes in water (concentration 2.5×10^{-4} g/ml) and for the polymers (2.5×10^{-2} g/ml).

3.4. Polymerization with ACA

ACA (5 g), 0.15 g of potassium persulfate and 0.05 g of the corresponding dye were dissolved in 40 ml water. The solution was stirred at 45 °C for 3 h. After cooling to the ambient temperature the polymers thus obtained were dissolved in 70 ml of water. These solutions were precipitated by methanol, which is a good solvent for the dyes, but not for PACA. After 3-folds precipitation, until the colourless filtrates were observed, an indication that the unreacted dye was removed, the polymers retained their colour. The precipitated polymers were dried at 35–40 °C under vacuum till constant weight and analyzed.

3.5. Polymerization with AN

Polymerization of 2.5 g of AN, 0.0125 g dye, 0.025 g ABIN in 10 ml of DMF was performed according to method previously described [19]. Purification of PAN was performed by 4-fold precipitation with hot water. Polymers were dried at 50 °C until constant weight.

References

- [1] Warnig D, Hallas G, editors. The chemistry and application of dyes. London: Plenum, 1990.
- [2] Lewis DM, Parton B, Tapley K. International Conference on New Development in Dyeing Theory, Harrogate, UK, March 1992.
- [3] Burkinshaw S, Willmott N. *Dyes and Pigments* 1994; 26:129.
- [4] Burkinshaw S, Katsarelias D. *Dyes and Pigments* 1995; 29(21):39.
- [5] Lewis DM, Ho Y. *Dyes and Pigments* 1995;28(4):237.
- [6] Lewis DM, Renfrew A, Soddique A. *Dyes and Pigments* 2000;47:151.
- [7] Blackburn R, Burkinshaw S, Gandhi K. *Advances in Colour Science & Technology* 1999;2:109.
- [8] Konstantinova T, Draganov A. *Die Angew Makrom Chemie* 1975;43:29.
- [9] Konstantinova T. *Dyes and Pigments* 1989;10(10):63.
- [10] Konstantinova T, Meallier P, Konstantinov Hr, Staneva D. *Polymer Degradation and Stability* 1995; 48(11):61.
- [11] Konstantinova T, Konstantinov Hr, Betcheva R. *Dyes and Pigments* 1999;43:197.
- [12] Konstantinova T, Bogdanova A, Stanimirov S, Konstantinov Hr. *Polymer Degradation and Stability* 1994; 43:187.
- [13] Bojinov VI, Konstantinova T. *Polymer Degradation and Stability* 2000;68:265.
- [14] Konstantinova T, Tzaneva G, Toneva G, Milanova S. *Bulg Chem Comm* 1995;28:187.
- [15] Konstantinova T, Bojinov VI. In: Pelicer N, editor. *Chemical industry and environment*, vol. III. Girona, 1993. p. 293.
- [16] Modi B, Desai N, Mistry B, Desai K. *J Indian Chem Soc* 1994;72:697.
- [17] Bulgarian Standard (ISO 105 CO6).
- [18] Walford J, editor. *Development in food colors*. London: Appl Sci, 1990. p. 95.
- [19] Guthrie GT, Konstantinova T, Ginova E. *Dyes and Pigments* 1997;34(4):287.