

Monochlorotetrazinyl Reactive Dyes: Synthesis and Characterization

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In present studies, the synthesis and characterization of monochloro-tetrazinyl reactive dyes are reported. Triaminoguanidine monohydrochloride was prepared by reacting guanidine hydrochloride with hydrazine monohydrate and then, converted to 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine by adding 2,4-pentanedione. 3,6-Dihydrazino-1,2,4,5-tetrazine was obtained by the reaction between 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine and hydrazine monohydrate. 3,6-Dichloro-1,2,4,5-tetrazine was formed by passing chlorine through 3,6-dihydrazino-1,2,4,5-tetrazine. The structures of products were confirmed by melting points, HPLC, FT-IR, ¹³C or ¹H NMR and mass spectral data. The chromophore groups of three different dyestuffs known (Reactive blue 4, orange 1 and red 2) were prepared and characterized by ¹H NMR. By reacting trichlorotriazinyl and dichlorotetrazinyl groups with them, dichlorotriazinyl and monochlorotetrazinyl dyes were obtained and their dyeing efficiencies on cotton were tried to be determined in subsequent studies.

Key Words: Reactive dyes, Reactive blue 4, Reactive orange 1, Reactive red 2, Triazine, Tetrazine.

INTRODUCTION

Cellulosic fibers can be dyed with reactive, direct, vat and sulphur dyes. The requirements are fully met by reactive dyes¹. Specific functional groups in structures of these dyes react with some groups present in textile fibers².

The first industrially important reactive dye systems were developed for wool. Vinyl sulfonyl- and 2-sulfooxyethanesulfonyl groups were found to be applicable to both wool and cellulose. Some of these dyes were patented in the 1940s³. The dyes introduced in 1956 by ICI and in subsequent years by ICI and Ciba contained the reactive di- and mono-chlorotriazinyl groups respectively. These dyes based on triazine and the remazol dyes bearing vinyl sulphonyl reactive group are still widely used⁴.

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These two categories are of greatest importance on the world market⁵⁻¹¹. However, many different kinds of reactive systems have been studied and the dyeing efficiency has been tried to be increased.

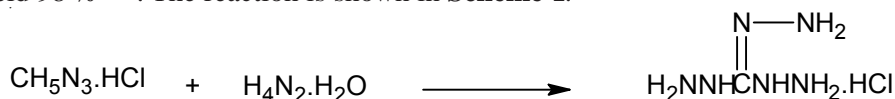
Most mono-anchor dyes are derivatives of 2,4,6-trichloro-1,3,5-triazine. The mono- and di-chlorotriazinyl dyes are commonly used for batch dyeing of cotton¹². In the present study, it was aimed to examine a new reactive group for reactive dyes. Dichlorotetrazinyl reactive group was synthesized and its reactivity was tried to compare with one of another group whose reactivity is thought as close to that of tetrazinyl group. For this purpose, dichlorotetrazinyl and trichlorotriazinyl reactive groups were separately reacted with three different chromogens and their dyeing efficiencies were tried to be determined in subsequent studies.

EXPERIMENTAL

Melting points were determined with a Gallenkamp capillary melting apparatus. FTIR spectra were recorded on a Mattson 1000 using KBr pellets. ¹H NMR and ¹³C NMR spectra were taken in CDCl₃ on a Bruker-Spectrospin DPX 300 Ultra Shield spectrometer. Mass spectra were recorded on a Thermo Finigan apparatus. Elemental analyses were performed in the TÜBITAK (The Scientific and Technological Research Council of Turkey) ATAL analysis center. HPLC results were obtained by using Shimadzu HPLC in which the column contained Hicrom Nucleosil 100-7C18. All of reagents were commercial products of analytical grade quality and used as received¹³.

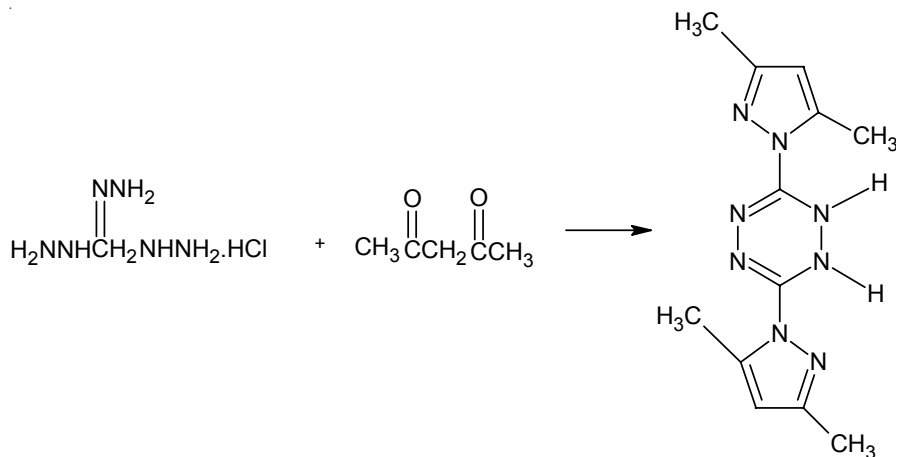
Synthesis of new reactive group

Preparation of triaminoguanidine monohydrochloride (1): Hydrazine monohydrate (34.1 g, 0.68 mol) was added to a well-stirred slurry of guanidine hydrochloride (19.1 g, 0.20 mol) in 1,4-dioxane (100 mL). The reaction mixture was refluxed for 2 h, it was cooled to ambient temperature. The white product was collected by filtration, washed with 1,4-dioxane and dried to give 27.7 g, m.p. 230 °C, yield 98 %^{14,15}. The reaction is shown in **Scheme-I**.



Scheme-I: Synthesis of triaminoguanidine monohydrochloride

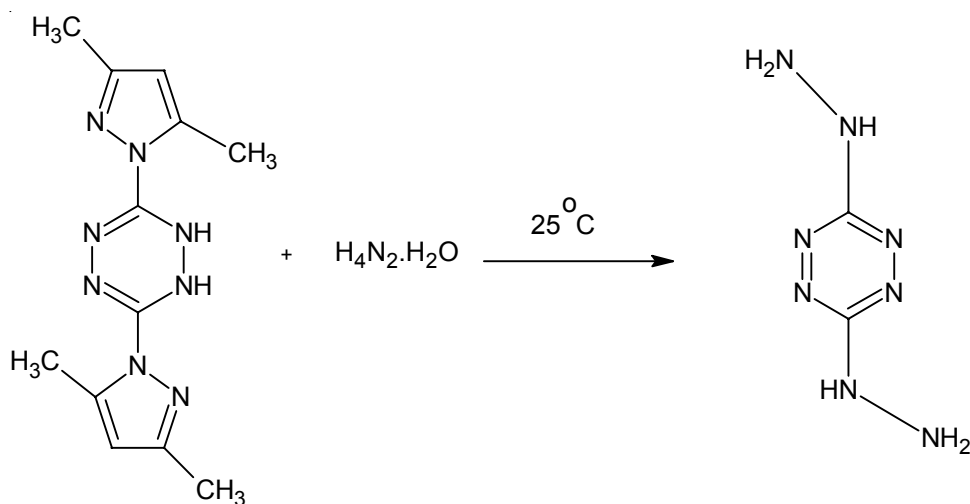
Preparation of 3,6-bis(3,5-dimethylpyrazol-1-yl) -1,2-dihydro-1,2,4,5-tetrazine (2): To a solution of compound (1) (7.03 g, 0.05 mol) in water (50 mL), 2,4-pentanedione was added dropwise with stirring at 25 °C. This mixture was stirred at 25 °C for further 0.5 h. The temperature was then set and maintained at 70 °C for 4 h. The yellow solid precipitated from the cooled mixture was filtered, washed with water and dried to yield 85 %, 5.77 g^{14,15}. ¹H NMR, FT-IR and mass spectra recorded were agreed with the structure of product¹⁵. The reaction route is given in **Scheme-II**.



Scheme-II: Synthesis of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine

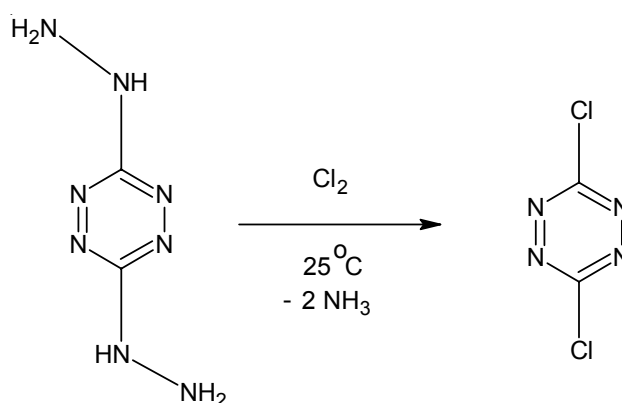
M.p. 150 °C; $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 8.145 (bs, 1H), 6.089 (s, 1H), 2.276 (s, 3H), 2.258 (s, 3H); FT IR (KBr, ν_{max} , cm^{-1}): 3275 (NH), 2970 (C-H), 1660 (C=N); MS: $m/z = 272.21$.

Preparation of 3,6-dihydrazino-1,2,4,5-tetrazine (3): 15 g (55 mmol) of compound (2) was dissolved in 90 mL acetonitrile and to this, 5.5 mL (115.5 mmol, 2.1 eq) hydrazine hydrate was added. The reaction mixture was stirred in an open flask at 25 °C for 48 h. The precipitated red solid was filtered in small portions and washed with acetonitrile (**Scheme-III**). The product was dried over P_2O_5 , yield 7.1 g (91 %), m.p. 192 °C.



Scheme-III: Synthesis of 3,6-dihydrazino-1,2,4,5-tetrazine

Preparation of 3,6-dichloro-1,2,4,5-tetrazine (4): 7.1 g (50 mmol) of compound (3) was suspended in 120 mL acetonitrile and dry chlorine gas was bubbled through it at 25 °C. After 25 to 30 min, the resulting orange solution was filtered through a celite pad and the acetonitrile was evaporated in vacuum. The orange product (5.4 g, 35.7 mmol, yield 72 %) was purified by sublimation (**Scheme-IV**). ¹³C NMR, FT-IR and mass spectra were recorded. The results were in conformity with expected ones. M.p. 148 °C, ¹³C NMR (CDCl₃, δ, ppm) 168.09 (C atom in tetrazine core), FT-IR (KBr, ν_{max}, cm⁻¹): 1650 (C=N), 1260 (N=N), 800 (C-Cl).



Scheme-IV: Synthesis of dichloro-1,2,4,5-tetrazine

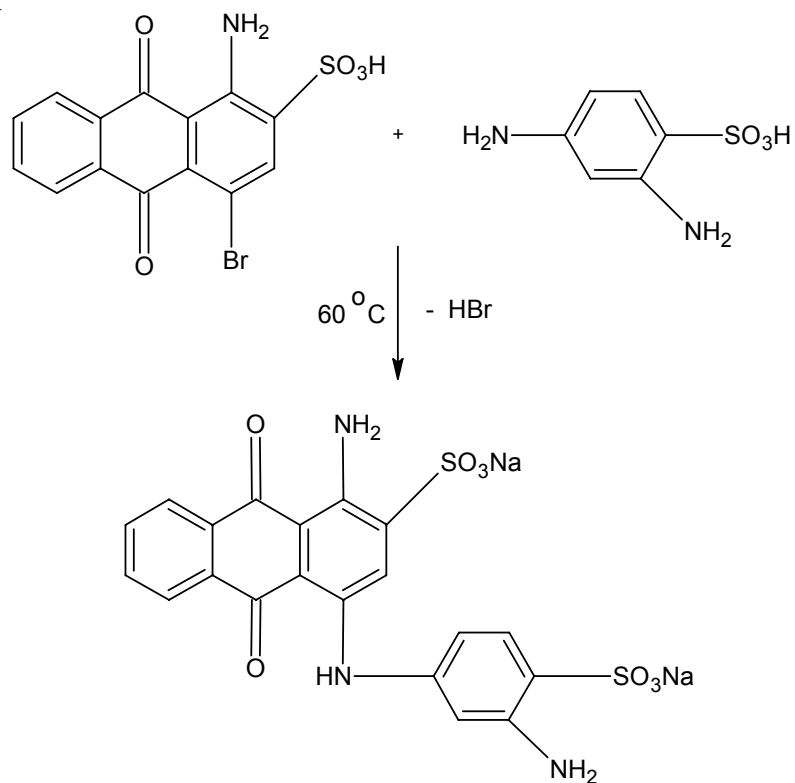
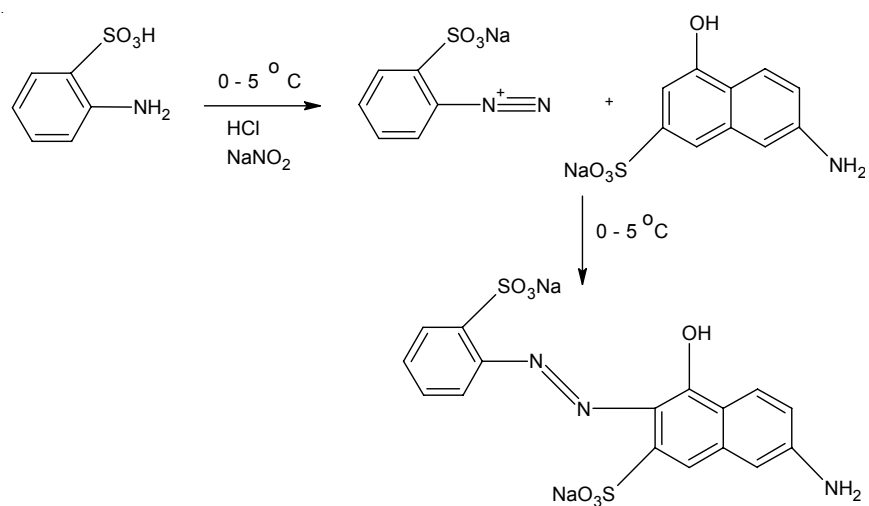
Preparation of chromophore groups (5, 6 and 7): Blue (5), orange (6) and red (7) chromogens were prepared with known methods¹⁶⁻¹⁹. They were purified with column chromatography²⁰ and characterized by ¹H NMR. Reaction routes are outlined in **Schemes V-VII**. ¹H NMR (D₂O, δ, ppm) 6.9, 7.5, 7.8 (blue), ¹H NMR (D₂O, δ, ppm) 6.85, 7.05, 7.35, 7.50, 7.85, 8.40 (orange), ¹H NMR (D₂O, δ, ppm) 7.1, 7.25, 7.45 (red).

Preparation of reactive dyestuffs

Triazinyl dyes: By separately reacting 2,4,6-trichloro-1,3,5-triazine with the chromogens (5, 6 and 7); reactive blue 4 (8), reactive orange 1 (9) and reactive red 2 (10) dyes were obtained with methods as given in preparation of chromophore groups. Their structures are shown in Figs. 1-3, respectively.

Tetrazinyl dyes

Testing reaction of compound (4) with aniline: Dichloro tetrazine (4) reacts with ammonia as a substitution of chloride and amine groups (**Scheme-VIII**)²¹. It is also known that triazinyl groups easily react with aniline even at 0 °C^{22,23}. According to this, a similar reaction may be expected between aniline and tetrazinyl group. In order to test this, two different mixtures of aniline and dichlorotetrazine (4) (1:1 and 2:1 molar ratios) were prepared and the experiments were separately carried out at temperatures of 0 and 25 °C. Methanol was used as a solvent. The product

**Scheme-V:** Preparation of blue anthraquinone chromophore**Scheme-VI:** Preparation of orange azo chromophore

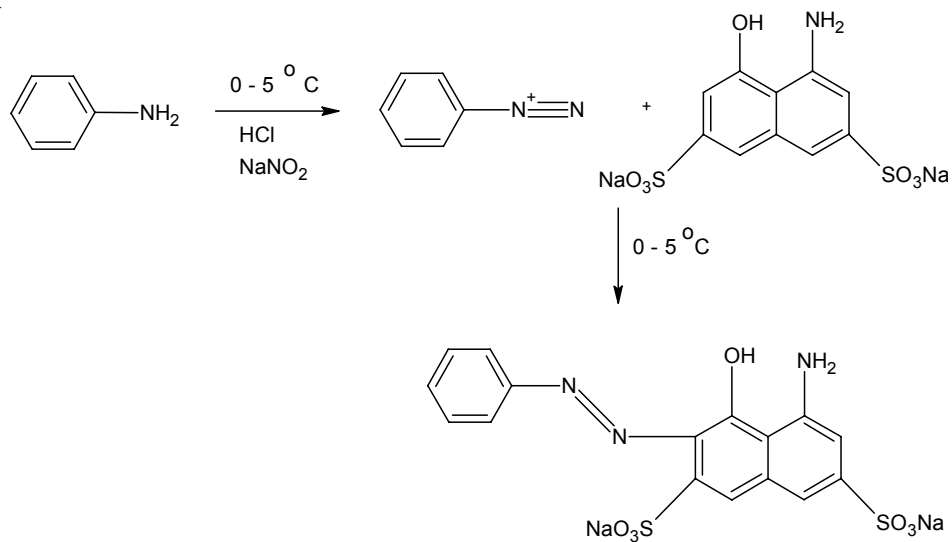
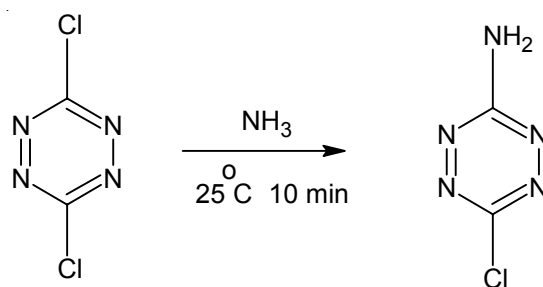
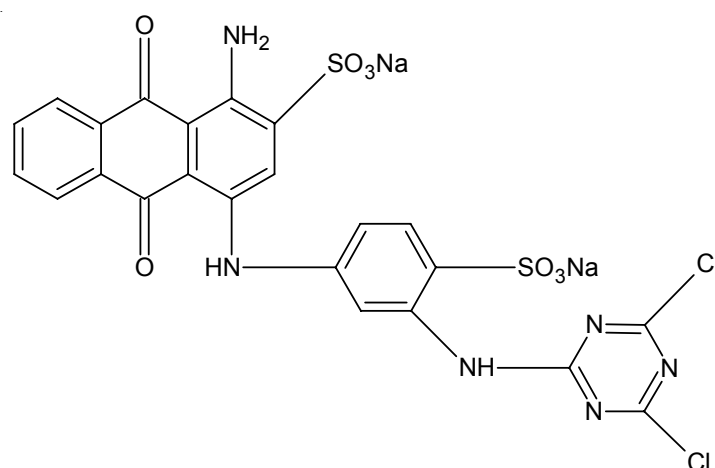
**Scheme-VII:** Preparation of azo red chromophore**Scheme-VIII:** Reaction of 3,6-dichloro-1,2,4,5-tetrazine with ammonia

Fig. 1. Reactive blue 4 dye

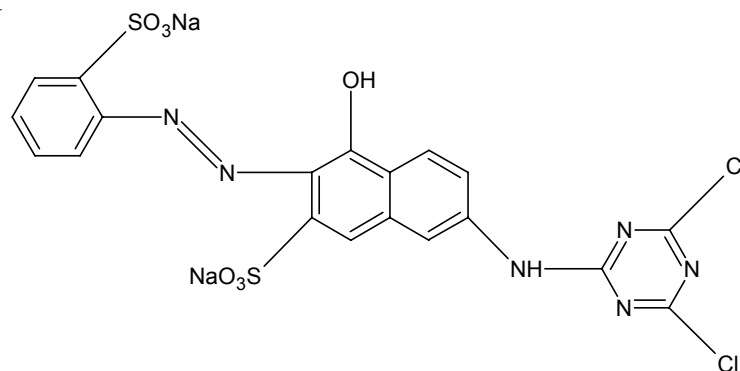


Fig. 2. Reactive orange 1 dye

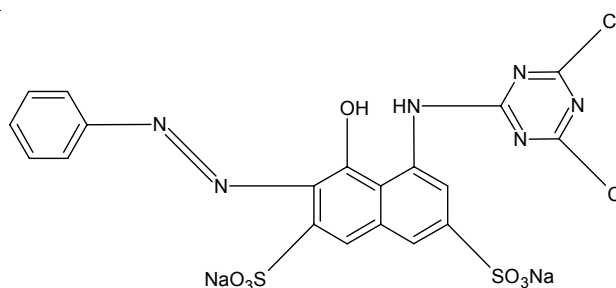


Fig. 3. Reactive red 2 dye

(6-chloro-N-phenyl-1,2,4,5-tetrazin-3-amine) (**11**) was crystallized from ethanol and its elemental analysis was performed (Table-1). In addition to this, ^1H NMR, FT-IR and mass spectra were taken. All of these results revealed that a substitution reaction between aniline and dichlorotetrazine has been carried out as given in **Scheme-IX**. ^1H NMR (CDCl_3 , δ , ppm) 7.23 (m, 1H), 7.45 (m, 2H), 7.65 (m, 2H), 7.75 (bs, 1H); FT-IR (KBr, ν_{max} , cm^{-1}): 3346 (NH), MS: $m/z = 208$.

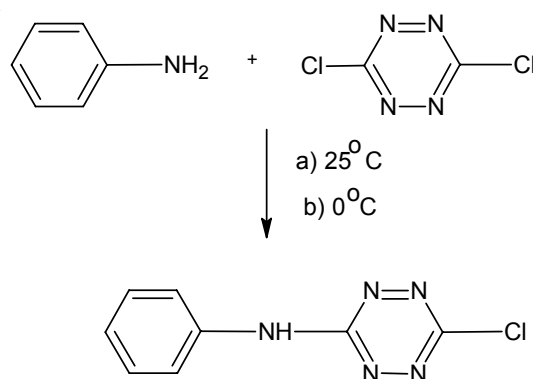
**Scheme-IX:** Reaction of 3,6-dichloro-1,2,4,5-tetrazine with aniline

TABLE-1
RESULTS OF ELEMENTAL ANALYSIS FOR
6-CHLORO-N-PHENYL-1,2,4,5-TETRAZIN-3-AMINE

	Molar ratio	C %	H %	N %
Theoretical values		46.28	2.91	33.73
Experimental values at 25 °C	1:1	46.51	3.05	33.22
	2:1	45.45	3.33	32.10
Experimental values at 0 °C	1:1	46.52	2.44	33.35
	2:1	46.90	2.44	33.64

Reaction of compound (4) with chromophore groups (5, 6 and 7): It was thought that a reaction between compound (4) and chromophore groups (5, 6 and 7) used in this study may be carried out as similar to the reactions of tetrazine with aniline and also of triazine with the chromophore groups. A similar procedure was adopted and the experiments were performed with the methods given for triazinyl dyes. Differently from there, the equivalent quantity of compound (4) instead of triazine was used in experiments. Details of methods are as follows.

Reaction of compound (4) with blue chromogen (5): Bromamine acid (3.02 g, 0.01 mol), 2,4-diaminobenzene sulfonic acid (2.2 g, 0.0115 mol), copper sulfate (2.2 g) and sodium carbonate (3.0 g) in water (100 mL) was stirred and refluxed at 60 °C for 4 h. The reaction mixture was cooled to 0-5 °C and then compound (4) (1.68 g, 0.011 mol) in acetone (10 mL) was added into the vigorously stirred mixture. During the reaction of 5 h, the pH was maintained at 7.0-7.5 by adding dilute sodium carbonate solution as required. Finally, the sodium chloride (20 % w/v) was added, the product (12) was precipitated by stirring at 0-5 °C for 0.5 h. It was filtered, washed with diethylether and dried²⁴. Although the structure expected could not be spectrometrically confirmed because of impurities and ionic groups (SO₃Na⁺), a different compound formed by this reaction was observed in HPLC analyses (Table-2). A possible structure may be proposed as that in Fig. 4.

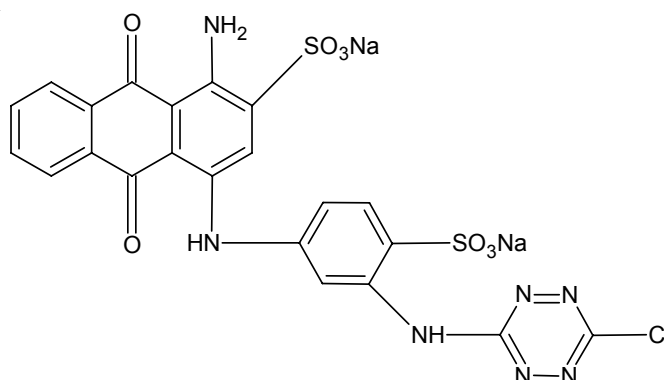


Fig. 4. Possible structure of blue dye with tetrazinyl reactive group

TABLE-2
RESULTS OF HPLC ANALYSIS FOR TETRAZINYL DYES

Dye		Retention time (min)	Maximum wavelength (nm)
Blue	Base	3.74	230, 305, 380, 595, 630
	Triazine	3.74/4.5	210, 236, 290, 378, 595, 630
	Tetrazine	3.74/5.1	230, 305, 380, 595, 630
Orange	Base	3.58	204, 251, 284, 292, 472
	Triazine	3.37/3.79	213, 265, 480
	Tetrazine	3.58	216, 274, 474
Red	Base	3.68	235, 310, 530
	Triazine	3.38	193, 237, 290, 331, 515, 547
	Tetrazine	3.37	194, 234, 507, 550

Reaction of compound (4) with orange chromogen (6): Concentrated hydrochloric acid (30 %, 7.7 mL) was added to a solution of aniline-2-sulfonic acid (1.77 g, 0.01 mol) and sodium nitrite (1.8 g) in water (75 mL) at 0-5 °C and the mixture was stirred for 2 h. Excess of nitrous acid was removed by adding sulfamic acid and the suspension was poured into the coupler solution (J-acid, 2.84 g, 0.106 mol) at 0-5 °C. Sodium acetate (10 g) was added and the reaction mixture was stirred at 0-5 °C for 3 h. A solution of compound (4) (1.68 g, 0.011 mol) in acetone (10 mL) was poured into the vigorously stirred mixture. The pH was maintained at 5-6 by addition of dilute sodium carbonate solution. The reaction mixture was stirred for further 0.5 h to complete the reaction. Sodium carbonate was added as required to raise the pH to 7. Finally, the sodium chloride (20 % w/v) was added and the product (13) was precipitated by stirring at 0-5 °C for 0.5 h. It was filtered, washed with diethylether and dried²⁴. The structure could not be spectrometrically confirmed because of reasons mentioned above. However, a new compound formed was observed in HPLC analyses (Table-2). A possible structure is shown in Fig. 5.

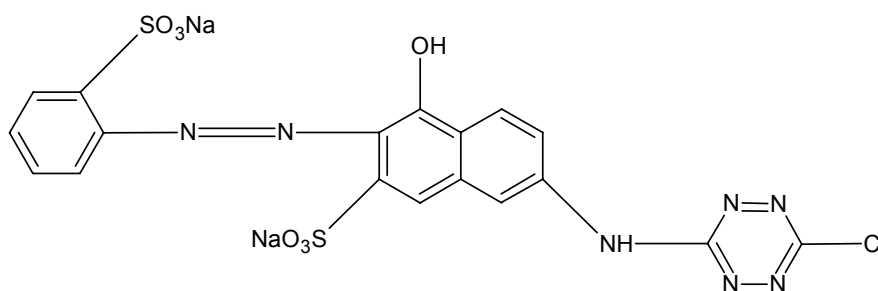


Fig. 5. Possible structure of orange dye with tetrazinyl reactive group

Reaction of compound (4) with red chromogen (7): Concentrated hydrochloric acid (30 %, 7.7 mL) was added to a solution of aniline (9.4 g, 0.01 mol) and sodium nitrite (1.8 g) in water (75 mL) while maintaining the temperature at 0-5 °C and the reaction mixture was stirred for 2 h. Excess of nitrous acid was removed

with sulfamic acid and the suspension was poured into the coupler solution (H-acid sodium salt, 3.99 g, 0.106 mol) at 0-5 °C. Sodium acetate (10 g) was added and the reaction mixture was stirred at 0-5 °C for 3 h. A solution of compound (4) (1.68 g, 0.011 mol) in acetone (10 mL) was poured into the vigorously stirred mixture. The pH was maintained at 5-6 by addition of dilute sodium carbonate solution. The reaction mixture was stirred for 0.5 h to complete reaction. Sodium carbonate was added as required to raise the pH to 7. Finally, the sodium chloride (20 % w/v) was added and the product (14) was precipitated by stirring at 0-5 °C for 0.5 h. It was filtered, washed with diethylether and dried²⁴. A structure for new compound observed in HPLC analyses (Table-2), but not confirmed spectrometrically, may be given as that in Fig. 6.

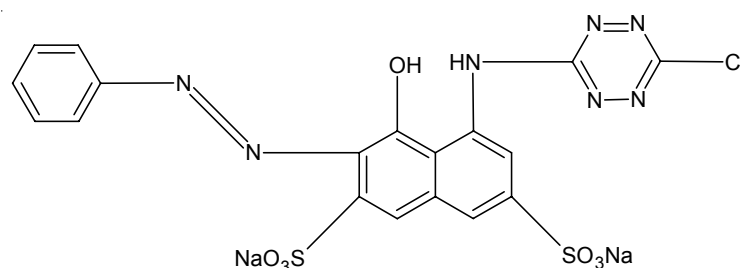


Fig. 6. Possible structure of red dye with tetrazinyl reactive group

RESULTS AND DISCUSSION

It was aimed the synthesis of monochlorotetrazinyl reactive dyes. Firstly, the synthesis of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine was carried out by using the USP study of Coburn and Ott¹⁵. Its structure was confirmed spectrometrically. ¹H NMR, FT-IR and mass spectra recorded were agreed with expected ones.

At the second stage, Prof. Dr. K. Andras of Etvos Lorand University suggested the way and the structure of 3,6-dichloro-1,2,4,5-tetrazine prepared was supported by spectrometric analyses. By basing on the reactions of dichloro tetrazine with ammonia and also triazinyl groups with aniline, this group (3,6-dichloro-1,2,4,5-tetrazine) was reacted with aniline. For this purpose, their two different mixtures (1:1 and 2:1 molar ratios) were prepared and the experiments were separately carried out at temperatures of 0 and 25 °C. The substitution reaction expected between these two compounds was confirmed by spectrometric and elemental analyses (Table-1). The results revealed that the product obtained was 6-chloro-N-phenyl-1,2,4,5-tetrazin-3-amine although it contains impurities.

In last, three different chromogens (blue, orange and red) were prepared and reacted with the triazinyl group by using the known methods. By basing on these reactions in addition to the substitution with aniline, the performing of a reaction

between dichloro tetrazine and these chromogens was expected. Three different tetrazinyl dyes were tried to be obtained by following similar procedure to the previous ones. The structures of these dyes could not be spectrometrically confirmed because of impurities and ionic groups (SO_3Na^+). However, a different compound formed at the end of the reaction was determined by HPLC analyses (Table-2).

As seen from the table, different wavelenghts and retention times observed for orange and red dyes showed the formation of new structures clearly. For blue dye, the wavelengths of base and tetrazinyl ones were same to each other. Although, a second peak observed in the tetrazinyl chromatogram means that a new blue dye in different structure from the base one was formed. According to this, it may also be used in dyeing studies. However, the results obtained for this mixture must be evaluated more cautiously.

Conclusion

Monochlorotetrazinyl dyes containing a new reactive group were synthesized. In the first part of the study where the reactive groups were prepared, the known methods were used and the results were agreed with expected ones. In the second one carried out to prepare dyes, some methods used for triazinyl dyes were modified for tetrazinyl ones. The structure expected for these dyes could not be spectrometrically confirmed because of impurities and ionic groups (SO_3Na^+). However, different compounds formed were determined by HPLC analyses. In subsequent studies, these dyes were applied to cotton fabrics. Their dyeing efficiencies were closed to those of dichlorotriazinyl ones.

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