

The Synthesis of Some Mono- and Dichloro- Triazinic Reactive Dyes

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The present paper describes the synthesis and the physico-chemical and tinctorial characterization of some mono- and dichloro- triazinic reactive dyes which have solubilizing molecules attached to the chromophore and linking groups. An example of monotriazinic dye is the one that results from the diazotization of 4-chloro-2-methoxy-5-methylaniline, followed by the coupling of the resulted diazonium salt to acid H, the acylation of the resulted dye with s-2,4,6-trichlorotriazine and, finally the condensation with methanylic acid. The same succession of reactions, without the last mentioned stage, leads to a dichlorotriazinic dye. The structure of the resulted compounds was established by elemental analysis (C, H, N) and by IR and UV-Vis spectra. The main tinctorial qualities of dyeing on cotton were determined and the proposed structured confirmed the analogy with those existing in the literature.

Keywords: reactive dye, 4-chlorine-2,5-dimethoxyaniline, FT-IR and UV-Vis spectra.

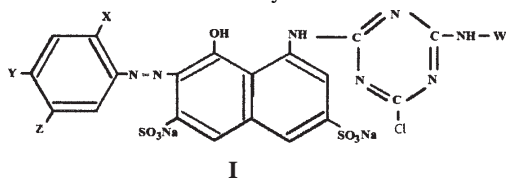
The reactive dyes are a class of products whose main characteristic is that they get fixed to the textile fibre (cellulose, wool, natural silk, polyamidic fibres) through the aminic and amidic covalent groups. The coloured macromolecules which are obtained have a high fastness to wet treatments.

In 1989, it was published a chronologically ordered list of all the groups of reactive dyes [1] which had been mentioned in the literature [2-7,8].

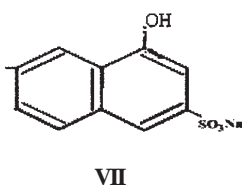
The reactive dyes are applied mostly on cellulose fibres and less on proteic and synthetic polyamidic ones (which have low fastness properties and a reduced dyeing uniformity due to some problems which appear in the fixation process).

The reactive dyes can be of different types depending on the reactive group in the molecule which is responsible for the mechanism of the dyeing process: dyes which have groups with whose fibre they interact with (the dyes described in this paper) or dyes whose reactive system contains a strongly polarized olefinic link which participates at nucleophilic addition with the support they interact with.

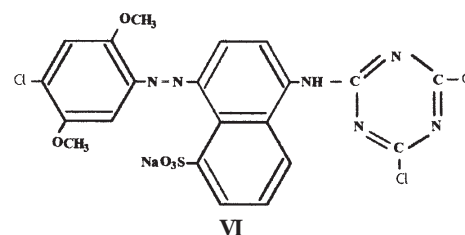
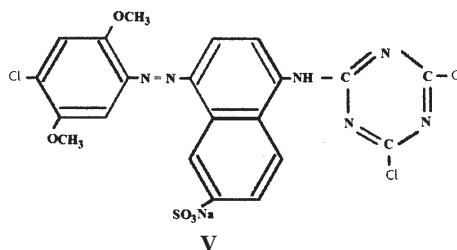
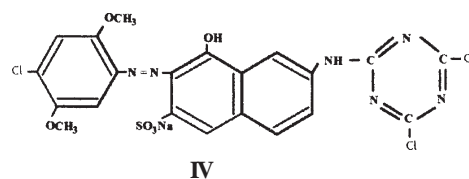
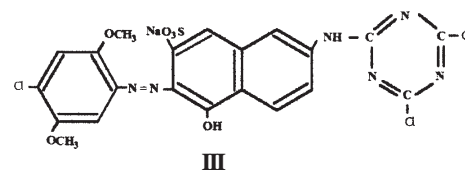
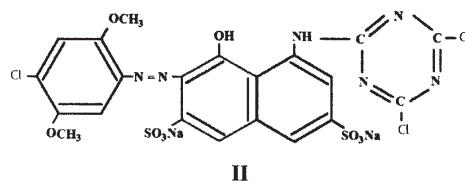
The synthesis and applications of some disazo monochlorotriazinic dyes are described in the literature. These dyes, when applied on cotton, have good and very good tinctorial qualities [8, 9]. This paper presents the next steps of this research and it refers to the synthesis of some mono- and dichlorotriazinic dyes with formulae I-VI:



where: I_a : X=Y=Z=H and W = VII



- I_b: X = OCH₃ ; Y = H; Z = CH₃; W = H
 I_c: X = OCH₃ ; Y = H; Z = CH₃; W = C₆H₅ - SO₃Na
 I_d: X = OCH₃ ; Y = H; Z = CH₃; W = VII
 I_e: X = OCH₃ ; Y = Cl; Z = CH₃; W = H
 I_f: X = OCH₃ ; Y = Cl; Z = CH₃; W = C₆H₅ - SO₃Na
 I_g: X = OCH₃ ; Y = Cl; Z = CH₃; W = VII



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Experimental part

In order to obtain dyes with formulae I-VI we used diazotizing components substituted in benzene nucleus with methoxy groups and with chlorine, which play an important part in increasing the colouring speed. Similarly, condensations with methanolic acid or 2-hydroxynaphthalenesulphonic acid were performed, in order to increase the solubility of water before application and the molecular mass.

The synthesis of triazinic reactive dyes with general formula I went through the following stages:

- diazotization of aniline [13], cresidine [14] and chlorocresidine [14] which proceeded according to data in the literature;
- coupling of diazonium benzene chloride with acid H [13].

A solution of diazonium salt is prepared from 46.5 g (0.5 moles) of aniline in a similar way to the data in the literature [13]. An amount of 170.6 g (0.5 moles) of acid H monosodium salt is dissolved into 500 mL water in order to obtain a solution with $pH = 6.5 - 7$. It is then cooled at 0° . 35 g (0.33 moles) Na_2CO_3 and ice are added to it. The diazoderivative solution is slowly added in the next 20 minutes, while stirring the mixture.

The reaction mass should be permanently weakly alkaline and it is continuously stirred at $3-5^{\circ}$ for 2 h. Then it is heated at 60° , salified with 200 g NaCl cooled at room temperature and filtered. The precipitate will be dried at $60-70^{\circ}$. The coupling of acid H with cresidine and 6-chlorine-cresidine as diazonium salt proceeds in a similar manner;

- the condensation of monoazoanilic acid H successively with s-2,4,6-trichlorotriazine [13] and ammonia.

An amount of 45.4 g (0.1 moles) of dye is introduced into 1500 mL water which contains 0.5 g surface emulsifying agent (Dispersil OA). The solution is cooled at $0-2^{\circ}$. Then, 21.2 g (0.14 moles) of s-2,4,6-trichlorotriazine are added upon vigorous stirring at the same time with the Na_2CO_3 solution to adjust the pH to 5.5.

The reaction mass is further stirred at $3-4^{\circ}$. While the pH value is continuously checked, small amounts of Na_2CO_3 are introduced to finally adjust the pH to 7. The solution is filtered after 0.5 h of stirring, in order to eliminate insoluble impurities. The filtered liquid is salified with 300 g NaCl at $3-4^{\circ}$. The precipitate is filtered and then mixed with 9 g urea to be stabilized. It is dried in vacuum at 70° .

39.5 g (0.06 moles) of previously prepared dye is dissolved into 200 mL water at 40° and then 20 mL 25 % NH_3 are poured upon vigorous stirring. The mixture is heated at this temperature for 120 min, then it is filtered at 110° . The filtered liquid is later salified with 150 g NaCl.

After 4 h of continuous stirring, the precipitate is filtered and dried at $55 - 60^{\circ}$. The condensation with ammonia, methanolic acid, Schaeffer acid and dyes derived from cresidine proceeds in a similar manner.

The synthesis of dichlorotriazinic dyes with formulae II-VI diazotization of 4-chlorine-2,5- dimethoxyaniline and coupling with acid H in alkaline medium was performed according to the data from the literature [15]. The coupling of 4-chlorine-2,5- dimethoxyaniline with acid I and γ is done in a similar manner. The coupling of Cleve acid 1,6 and Cleve 1,7 requires an acid medium and $pH = 5$.

The condensation of the resulted monoazodyes with s-2,4,6-trichlorotriazine is similar to the procedure which was previously mentioned for dyes I.

Dyes I-VI was purified via dissolving into water and acidification with HCl solution 32-36%, to precipitate the dye as free acid.

It was filtered and washed on a filter with diluted HCl solution 2-3% in order to allow salts to return to the filtered liquid. The salified precipitate was then dried in vacuum to eliminate the remains of HCl, the dye resulting from it as free acid.

These procedures were repeated several times with a view to obtain a pure dye.

The purity of dyes I-VI was tested via thin layer chromatography with silicagel prop and N,N-dimethylformamide as eluent [16]. The UV-VIS spectra were recorded with a VSV-2-Carl Zeiss (Jena).

Results and discussion

Formula I dyes were synthesized by the diazotization of aniline, 2-methoxy-4- methylaniline followed by the coupling of their diazonium salts with 1-amino-8-naphthol-3,6-disulphonic acid, the condensation of the resulted monoazodyes with s-2,4,6-trichlorotriazine and finally, condensation with ammonia, methanolic acid or 2-amino-8-naphthol-6-sulphonic acid.

Dyes II-VI were prepared via diazotization of 2-chlorine-2,5-dimethoxyaniline, the coupling of the diazonium salt with one of the following acids: 1-amino-8-naphthol-3,6-disulphonic, 2-amino-6-naphthol-7-sulphonic or 1-amino-naphthalenesulphonic.

In the final stage, the resulted dyes were condensed with s-2,4,6-trichlorotriazine. The diazotization of amines involved in the synthesis as fundamental procedure comes after direct diazotization with 4-chlorine-methoxy-5-methylaniline and 4-chlorine-2,5-dimethoxyaniline.

These amines are partially soluble in aqueous solutions of the hydrochloric acid. The coupling of diazonium salts with the previously mentioned naphthalenesulphonic acids continues with good results (55%) either in alkaline medium, or in acid one, depending on their structure.

The condensation of the amino-monoazodyes with s-2,4,6-trichlorotriazine has good yields (90%). It appears at $3-4^{\circ}$, at $pH = 5.5$, by tamponing the solution with a Na_2CO_3 solution 30%. The dichlorotriazinic dyes are easily hydrolysable when they are precipitated after the reactions. They can be stabilized by mixing them with urea and drying them in vacuum at normal temperatures [10]. In order to obtain monochlorotriazinic dyes with a lower speed in drying than the dichlorotriazinic ones, but with a better stability, they will be condensed with ammonia, methanolic acid or acid γ at temperatures of $80-90^{\circ}$.

The purification of dyes I-VI was performed via dissolving into water and acidification with HCl solution 32-36%, thus the dye having the possibility of precipitating as free acid. After being filtered and washed on a filter with a diluted HCl solution 2-3%, the salified precipitate is dried in vacuum to eliminate the HCl traces, the dye being a free acid. In order to obtain a pure dye, the procedures were repeated several times.

The thin layer chromatography on silicagel prop using N,N - dimethylformamide as eluent was the method which was used to test the purity of dyes I-VI.

The C, H, N elemental analysis (table 1) and the IR and UV-Vis spectra (tables 2 and 3) confirm the structures proposed for dyes I-VI [5, 11, 12].

Table 2 illustrates the values of the main bands of absorption of dyes I-VI in the IR spectra, while table 3 presents the maximums of absorption in the UV-Vis spectra and the corresponding colours.

These dyes were applied on cotton, linen, then on cotton + linen. The dyeing had a high fastness to washing with water at 40 , 60° and even 90° (the values were illustrated in tables 4 and 5) [18].

Table 1
THE ELEMENTAL ANALYSES OF DYES I-VI

Dye	Formula	M	C% calc.	C% found	H% calc.	H% found	N% calc.	N% found
I _a	C ₂₉ H ₂₀ N ₇ O ₁₁ S ₃ Cl	773.5	44.99	45.02	2.58	2.56	12.66	12.63
I _b	C ₂₁ H ₁₈ N ₇ O ₈ S ₂ Cl	467.5	53.90	53.92	3.85	3.81	20.96	20.94
I _c	C ₂₇ H ₂₂ N ₇ O ₁₁ S ₃ Cl	715.5	45.28	45.32	3.07	3.11	13.69	13.67
I _d	C ₃₁ H ₂₄ N ₇ O ₁₂ S ₃ Cl	757.5	49.10	49.08	3.16	3.13	12.93	12.90
I _e	C ₂₁ H ₁₇ N ₇ O ₈ S ₂ Cl ₂	630	40.00	40.02	2.69	2.66	15.55	15.53
I _f	C ₂₇ H ₂₁ N ₇ O ₈ S ₂ Cl ₂	786	41.22	41.17	2.67	2.69	12.46	12.42
I _g	C ₃₁ H ₂₃ N ₇ O ₁₂ S ₃ Cl ₂	792	46.96	46.93	2.90	2.91	12.37	12.33
II	C ₂₁ H ₁₅ N ₆ O ₉ S ₂ Cl ₃	665.5	37.86	37.83	2.25	2.21	12.62	12.65
III	C ₂₁ H ₁₅ N ₆ O ₆ S ₃ Cl ₃	585.5	43.04	43.06	2.56	2.53	14.34	14.31
IV	C ₂₁ H ₁₅ N ₆ O ₆ S ₃ Cl ₃	585.5	43.04	43.05	2.56	2.53	14.34	14.32
V	C ₂₁ H ₁₅ N ₆ O ₅ S ₃ Cl ₃	569.5	44.24	44.21	2.63	2.66	14.74	14.72
VI	C ₂₁ H ₁₅ N ₆ O ₅ S ₃ Cl ₃	569.5	44.24	44.21	2.63	2.65	14.74	14.72

Table 2
THE MAIN BANDS OF ABSORPTION IN THE IR SPECTRA

/dye	v[cm ⁻¹]	I _a	I _b	I _c	I _d	I _e	I _f	I _g	II	III	IV	V	VI
aromatic cycle	v _{CH}	3020	3021	3019	3020	3022	3018	3020	3021	3020	3019	3020	3020
aromatic cycle	v _{CH}	1805	1805	1807	1805	1805	1806	1807	1805	1805	1806	1806	1807
aromatic cycle	v _{C=C}	1580	1580	1582	1580	1579	1580	1582	1580	1580	1578	1580	1580
aromatic cycle	v _{CH}	1220	1220	1222	1220	1219	1221	1220	1221	1220	1219	1222	1220
CH ₃ -O Carom	v _{CH3 sim}	-	2850	2850	2849	2852	2852	2850	2849	2850	2850	2850	2850
CH ₃ -O Carom	v _{C-O-C as}	-	1250	1252	1250	1250	1251	1250	1252	1250	1249	1250	1250
CH ₃ -O Carom	v _{C-O-C sim}	-	1050	1051	1050	1049	1051	1050	1051	1052	1051	1052	1050
CH ₃ -Carom	v _{CH3 as}	-	2961	2960	2962	2960	2961	2960	-	-	-	-	-
CH ₃ -Carom	v _{CH3 sim}	-	2870	2870	2869	2871	2870	2872	-	-	-	-	-
CH ₃ -Carom	v _{CH3 as}	-	1461	1460	1461	1462	1460	1460	-	-	-	-	-
NH ₂ -Ar	v _{NH2 as}	-	3500	-	-	3500	-	-	-	-	-	-	-
NH ₂ -Ar	v _{NH2 sim}	-	3400	-	-	3400	-	-	-	-	-	-	-
Ar-NH-	v _{NH}	3450	-	3450	3450	-	3450	3450	3449	3451	3450	3452	3450
SO ₃ H	v _{SO2 as}	1350	-	1350	1351	-	1350	1352	1350	1351	1350	1352	1350
SO ₃ H	v _{SO2 sim}	1160	-	1161	1160	-	1160	1160	1160	1162	1160	1162	1160
SO ₃ H	v _{S-O}	700	-	700	702	-	700	701	700	701	700	702	700
OH	v _{OH}	3200	3200	3200	3200	3200	3200	3200	3200	3200	3200	-	-
		-	-	-	-	-	-	-	-	-	-	-	-
		3400	3400	3400	3400	3400	3400	3400	3400	3400	3400	-	-

Table 3
MAXIMUMS OF ABSORPTION IN THE UV-Vis SPECTRA OF DYES I-VI AND THEIR CORRESPONDING COLOURS [17]

/dye	I _a	I _b	I _c	I _d	I _e	I _f	I _g	II	III	IV	V	VI
λ _{max}	290-560	289-565	295-560	297-570	290-563	287-575	298-585	292-561	296-583	289-566	285-563	287-565
colour	garnet-red	light violet	light violet	violet	light violet	violet	dark violet	garnet-red	dark violet	brown-violet	brown	brown

Table 4
THE REACTION OF DYES I-VI TO DYEING ON COTTON AND LINEN

dye	dyeing on	reaction to water at 40°	reaction to water at 60°	reaction to water at 90°	alkaline medium	wet treatment	dry treatment
I _a	cotton	5/4/5	5/4/5	5/4/5	5/5/5	5	4
	linen	5/4/5	5/3/5	5/2/5	5/5/5	—	—
I _b	cotton	5/4/5	5/3/5	5/2/5	5/5/5	5	4
	linen	5/3/5	5/2/5	5/2/5	5/5/5	—	—
I _c	cotton	5/3/5	5/2/5	5/1-2/5	5/5/5	5	3
	linen	5/2/5	5/2/5	5/1-2/5	5/5/5	—	—
I _d	cotton	5/3/5	5/3/5	5/2/5	5/5/5	5	4
	linen	5/4/5	5/3/5	5/2/5	5/5/5	—	—
I _e	cotton	5/3/5	5/3/5	5/2/5	5/5/5	5	4
	linen	5/2/5	5/2/5	5/2/5	5/5/5	—	—
I _f	cotton	5/3/5	5/3/5	5/2/5	5/5/5	—	—
	linen	5/3/5	5/3/5	5/2/5	5/5/5	5	3
I _g	cotton	5/4/5	5/3/5	5/2/5	5/5/5	—	—
	linen	5/3/5	5/2/5	5/2/5	5/5/5	5	4
II	cotton	5/4/5	5/2/5	5/2/5	5/5/5	—	—
	linen	5/4/5	5/3/5	5/2/5	5/5/5	5	4
III	cotton	5/3/5	5/3/5	5/2/5	5/5/5	—	—
	linen	5/3/5	5/3/5	5/2/5	5/5/5	5	3
IV	cotton	5/2/5	5/2/5	5/2/5	5/5/5	—	—
	linen	5/3/5	5/3/5	5/2/5	5/5/5	5	4
V	cotton	5/4/5	5/3/5	5/2/5	5/5/5	—	—
	linen	5/4/5	5/3/5	5/2/5	5/5/5	5	4
VI	cotton	5/3/5	5/3/5	5/2/5	5/5/5	—	—
	linen	5/4/5	5/2/5	5/2/5	5/5/5	5	4

Observation (the same for tables 4 and 5):

- 1) the first figure represents the changing of colour in time,
- 2) the second figure represents application on cotton,
- 3) the third figure represents application on linen.

Table 5
THE REACTION OF DYES I-VI TO DYEING ON COTTON AND COTTON + LINEN (THERMOFIXATION) [18]

dye	colouring on	reaction to water at 40°	reaction to water at 60°	reaction to water at 90°	alkaline medium	wet treatment	dry treatment
I _a	cotton	5/5/5	5/4/5	5/4/5	5/5/5	5	4
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	4-5	3
I _b	cotton	5/5/5	5/4/5	5/3/5	5/5/5	5	4
	cotton +linen	5/5/5	5/4-5/5	5/4/5	5/5/5	4-5	4
I _c	cotton	5/5/5	5/4-5/5	5/4/5	5/5/5	5	3
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	5	3
I _d	cotton	5/5/5	5/4/5	5/3/5	5/5/5	4-5	4
	cotton +linen	5/5/5	5/4-5/5	5/4/5	5/5/5	5	4
I _e	cotton	5/5/5	5/4/5	5/4/5	5/5/5	5	3-4
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	4-5	4
I _f	cotton	5/5/5	5/4-5/5	5/4-5/5	5/5/5	5	3-4
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	4-5	4
I _g	cotton	5/5/5	5/4/5	5/4-5/5	5/5/5	5	4
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	5	3
II	cotton	5/5/5	5/4/5	5/4/5	5/5/5	5	3-4
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	4	4
III	cotton	5/5/5	5/4/5	5/4/5	5/5/5	4	4
	cotton +linen	5/5/5	5/4-5/5	5/4/5	5/5/5	5	3-4
IV	cotton	5/5/5	5/4/5	5/3-4/5	5/5/5	5	4
	cotton +linen	5/5/5	5/4/5	5/4/5	5/5/5	5	4
V	cotton	5/5/5	5/4/5	5/4-5/5	5/5/5	4-5	3-4
	cotton +linen	5/4/5	5/4/5	5/4-5/5	5/5/5	5	3
VI	cotton	5/5/5	5/4/5	5/4/5	5/5/5	5	3
	cotton +linen	5/5/5	5/4-5/5	5/4/5	5/5/5	5	3

Conclusions

The synthesis of mono- and dichloro- triazinic dyes I-VI is performed with raw materials which are commonly used in the industry of dyes, in mild reaction conditions.

Additionally, the coupling of the diazonium salts with the naphthalenesulphonic acid has a good yield (55%)

either in an alkaline medium or in an acid one, depending on their structure. The condensation of amino-monoazo dyes with s-2,4,6-trichlorotriazine has a better yield (90%) than in the literature.

Dyes I-VI have bright, intense colours and a very good speed of the reactive fixation reaction. The new dyes were used to dye cellulose fibres of cotton and linen type.

The dyeing process had no difficulties of uniformization and their fastness to wet treatments was very high.

The resulted dyes absorb in UV-Vis at wavelengths ranging from 285 and 585 nm, having red and violet shades.

The investigations which were carried out estimated the degree of purity of these dyes and led to the formulae presented in the paper.

The elemental analysis and the UV-VIS spectra confirmed the structures which had been proposed for dyes I-VI.

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