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SYNTHESIS AND EVALUATION OF PERFORMANCE PROPERTIES OF DICHLORO AND MONOCHLORO-S-TRIAZINYL REACTIVE DYES DERIVED FROM CYANURATED H-ACID ON WOOL AND COTTON FABRICS

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ABSTRACT

Dichloro-s-triazinyl reactive dyes were synthesized by diazotization and coupling reaction of substituted anilines with cyanuarated H-acid. The dichloro reactive dyes obtained were condensed with heterocylic amine (2-amino-4-trifluorobenzothiazole) to get monochloro-reactive dyes. The dyes were characterized using IR spectroscopic method and then applied by exhaustion dyeing method on wool and cotton fabrics. Percentage exhaustion and fixation of the dyes were evaluated and usage properties of the dyes also examined. The dyes showed very good exhaustion and fixation on wool and cotton fabrics. They also showed good wash and light fastness properties on both substrates.

Keywords: Cyanurated H-acid, Reactive dyes, Exhaustion, Fixation, fastness properties.

I.INTRODUCTION

Reactive dyes are colorants used mainly on cotton to achieve high washfastness on leisurewear. The basis for their good washfastness is the formation of a covalent bond to cellulose chains during the fixation step. Unfortunately, dye fixation is always accompanied by alkali-induced dye hydrolysis, leading to dye molecules that cannot undergo fixation with cellulose. After the dyeing step, effective wash off of unreacted dye is required to obtain excellent fastness properties. Dyeing using reactive dyes have recently led to increased demands on the quality of the dyeing and profitability of the dyeing process. There is compliant still of a demand for novel reactive dyes which have improved properties, especially in respect of application [1]. Reactive dyes that have a sufficient substantivity and at the same time a good ease of washing out of the non fixed portions are required for dyeing. They should furthermore have a good tinctorial yield and high reactivity and dyeing having high degrees of fixing in particular should be produced [2]. Reactive dyes are now a major group of dyes, though a late entry into the family of synthetic dyes, very soon attained a commercial status. There is no slackening of activity in this field as seen from the large number of patent specifications and several ranges which continue to appear in the market [3, 4].

It can also be easily understood that dyes with two reactive groups give a higher fixation yield than dyes with one reactive group for if one of the two dye-fibre bonds is hydrolyzed, one is still left for fixation [5, 6]. The possibility of forming covalent bond between dyes and fibres had long been attractive to dye chemists since attachment by physical adsorption and by mechanical obstruction had the disadvantage of either low wash fastness or high cost [7, 8]. It was anticipated that the covalent attachment of the dye molecules to the fibre would produce very high fastness because covalent bonds were the strongest known binding forces between molecules [9, 10]. It is well known that reactive dyes having low substantivity exhibit low percent fixation but good wash off properties in the hydrolyzed form. On the other hand, reactive dyes having high substantivity show high fixation but poor wash off properties in the hydrolyzed form. Since many of the more modern and environmentally friendly reactive dyes fall into the latter category, it was deemed of interest to design new dyes that not only give high fixation levels but also reactively low substantivity in the hydrolyzed form. As a consequence, the wash off process would be easier to complete. The present study involved lowering the substantivity of the hydrolyzed dye by reducing coplanarity that is usually required between dyes and cellulose for high substantivity. The synthesized dyes were applied to cotton and wool using the exhaustion dyeing process and evaluation of colourfastness properties of the dyes examined.

II.MATERIALS AND METHODS

2.1 General Information

All the chemicals used in the synthesis of the dyes were of commercial grade and were further purified by recrystallisation and distillation. All solvents used were of spectroscopic grade.Melting points were determined by the open capillary method. The visible absorption spectra were measured using HEXIOSY Uv-Visible spectrophotometer for solutions in water and ethanol. IR spectra were recorded on a NICOLET FTIR-100 THEMOELECTRON Spectrophotometer. Wash and light fastness tests were carried out according to the standard methods.

2.2 Cyanuration of H-acid

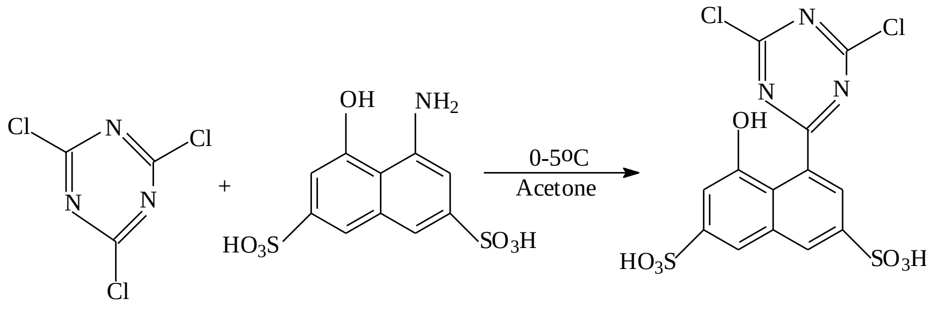
Cyanuric chloride (1.85 g, 0.01 mol) was stirred in acetone (25 ml) at a temperature 0-**5** ^{o}C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01 mol) in aqueous sodium carbonate solution (10 % w/v) was then added in small lots in about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1 % w/v). The reaction mass was then stirred at 0-5 ^{o}C for further four hours. The clear solution of cyanurated H-acid was used for subsequent coupling reaction (Scheme 1).

2.3 General Method of Diazotization of Substituted Anilines

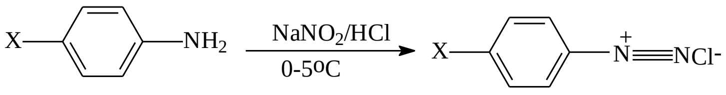
A solution of sodium nitrite (0.01 mol) in water (40 ml) was added slowly to a mixture of aniline (0.01 mol) in water (40 ml) and hydrochloric acid (36 %, 28 ml). After 30 min of stirring at 0-5 ^{o}C and pH less than 2, excess nitrous acid was destroyed by adding suphamic acid.

2.4 Diazotization of 2-Amino-4-Trifluorobenzothiazole

Nitrosylsulphuric acid was used for diazotization. It was prepared by adding sodium nitrite (0.83 g, 0.01mol) to concentrated sulphuric acid (98 %, 11.76 g) at 30 ^{o}C and heating and stirring the mixture to 60-65 ^{o}C over 15 min and maintaining the temperature for 30 minutes to ensure complete dissolution of sodium nitrite. The reaction mixture was cooled to 5 °C, and then concentrated acetic acid (5 ml) was added and stirring continued for 10 mins. The temperature was then reduced to below 5 °C; the 2-amino-4-trifluoro-benzothiazole (0.01mol) was added over 30 min and the whole reaction mixture stirred at the same temperature for 2 hrs. The completion of diazotization was checked by using starch iodide paper for the presence of excess nitrous acid.



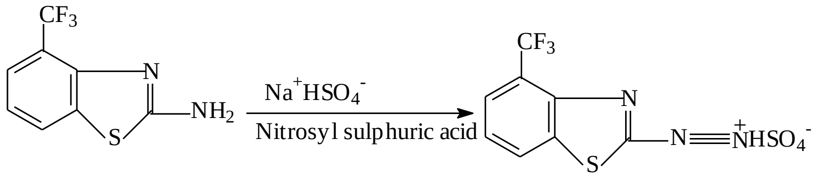
Scheme 1: Preparation of cyanurated H-acid



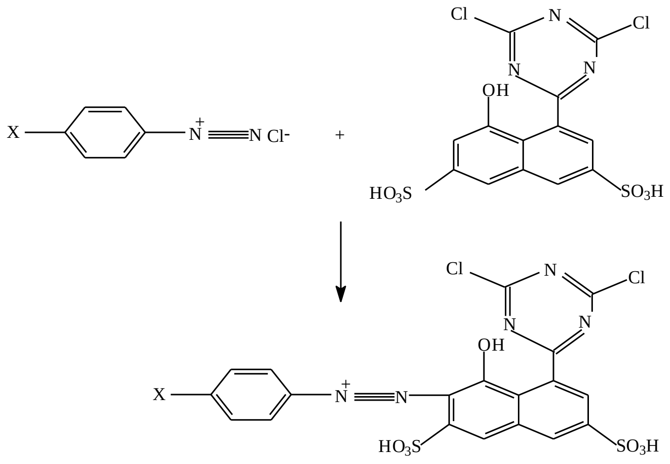
(2)

X = (a) = H
(b) = Cl
(c) = NO_2
(d) = COOH
(e) = CH_3

Scheme 2: Diazotization of substituted aniline

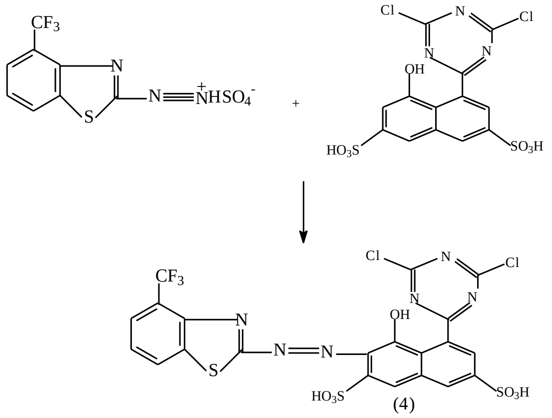


Scheme 3: Diazotization of 2-amino-4-trifluorobenzothiazole



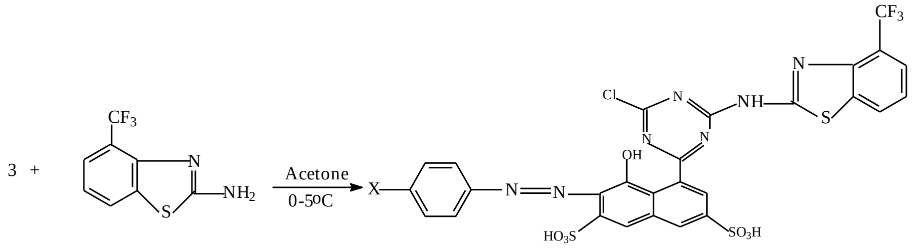
(3) dichrolo-s-triazinyl dyes

Scheme 4: Coupling of diazonium salts of substituted amines with cyanurated H-acid



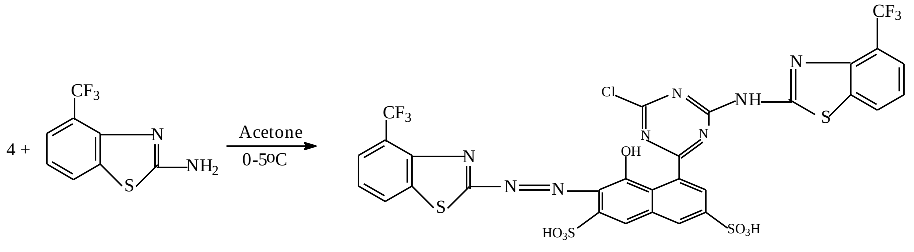
(4)

Scheme 5: Coupling of diazonium salt of 2-amino-4-trifluorobenzothiazole to cyanurated H-acid



(5) Mono-chloro-s-triazinyl dyes

Scheme 6: Synthesis of mono-chloro reactive dyes from substituted anilines



Scheme 7: Synthesis of mono-chloro reactive dye (6)

2.5 Coupling of Diazotized Amines with Cyanurated H-Acid to obtain Dichloro Reactive Dyes (Dyes 3)

Freshly prepared diazonium salt (0.01 mol) was added dropwise to well-stirred solution of cyanurated H-acid (0.01 mol). The solution was maintained at pH 9 by adding 20 % (w/v) Na_2CO_3 and the coupling step was continued for 4 hr at 0-5 ^oC. The dye was isolated by salting out of solution using NaCl (12 g). The pH was adjusted to 7 using HCl (5 %) w/v) and stirring were continued for 2 hr. The dye was collected by filtration and washed with 5 % (w/v) NaCl. Salt was removed by stirring the crude dyes with dimethylformamide (DMF), followed by the dye precipitation by adding EtOAc to the filtrate. The dye was collected, washed with EtOAc and dried at 45 ^oC for 12 hr.

2.6 Preparation of Mono-Chloro-Reactive Dyes (Dyes 5)

Each of the dichloro reactive dye was condensed with 2-amino-4-trifluoro-benzothiazole to yield the corresponding mono-chloro reactive dye. 2-Amino-4-trifloro-benzothiazole (4.66 g, 0.05 mol) was added slowly to the equal mole of dicloro reactive dye prepared above in distilled water (100 ml), and the temperature was raised to 30-40 ^oC with stirring at pH 5-6, for 2 hrs. When the reaction was complete, the solution was allowed to stand for 30 min, and the resulting precipitated product was collected by filtration and purified by dissolving in distilled water (100 ml) and re-precipitated by the slow addition of ethanol (200 ml).

2.7 Dyeing and Fastness Tests

Dyeing and fastness tests were carried out according to the standard procedures [11]

III. RESULTS AND DISCUSSION

3.1 Synthesis of Intermediates and Dyes

Cyanurated H-acid was prepared by condensing cyanuric chloride with H-acid in acetone at a temperature 0-5 ^{o}C as shown in Scheme 1. Substituted anilines were diazotized using dilute acid and corresponding amine as shown in Scheme 2 to obtained diazonium salts of the substituted anilines. Scheme 3 shows the diazotization of 2-amino-4-trifluorobenzothiazole using nitrosylsulphuric acid method. The diazonium salts of substituted anilines were coupled to cyanurated H acid to obtain dichloro-s-triazinyl reactive dyes in series (3) as shown in Scheme 4. Similarly the diazonium salt of 2-amino-4-trifluorobenzothiazole was coupled to cyanurated H-acid to obtain dye (4) as shown in Scheme 5. The dichloro-reactive dyes in series (3) were condensed respectively with 2-amino-4-trifluorobenzothiazole to obtain monoazo-s-triazinyl reactive dyes in series (dyes 5) as shown in Scheme 6. Similar condensation of dye (4) in acetone with 2-amino-4-trifluorobenzothiazole gave dye (6) in low yield (Scheme 7). Physical characteristics and spectroscopic properties of the dyes are summarized in **Table 1**.

3.2 Physical and Spectroscopic Properties of the Dyes

The physical and spectroscopic properties of the dyes are summarized in **Table 1**. All the dyes exhibit sharp melting points and moderate molecular weight. The yields are moderate to good apart from dyes (4) and (6) that have low yield. All the dyes were soluble in water. The visible absorption properties of the dyes were measured in water and ethanol and they all showed maximum absorption wavelength in the visible region which established all the compounds as good colourants.

Dye (3a) which was obtained by coupling diazotized aniline with cyanurated H-acid showed maximum absorption wavelength at 505 nm in distilled water and when chlorine was introduced into the para position using p-chloro-aniline as diazonium ion, the dye (3b) obtained also showed maximum absorption wavelength at the same wavelength (505 nm). Similar replacement of chlorine by NO_2, COOH and CH_3 respectively gave dyes (3c), (3d) and (3e) with maximum absorption wavelength at same wavelength (505 nm), which showed that changing the substituent has no effect in the absorption maximum of the dyes in water. However, dye (4) which was obtained by coupling diazotized 2-amino-4-trifluorobenzothiazle with cyanurated H-acid absorbed at 530 nm in water, giving a bathochromic shift of 25 nm when compared with dyes (3). The origin of bathochromic shift when heterocylic diazo-components are used is well known [12].

When the dichloro dyes (3) were converted to mono-chloro dyes (5) by condensation with 2-amino-4-trifluorobenzothiazole, the resulting dyes (5) also showed different maximum absorption wavelengths. For example, dye (5a) absorbed at 510 nm in distilled water, which is bathochromic by 5 nm when compared with dye (3a). Dye (5b) absorbed at 500 nm and is hypsochromic by 5 nm when compared with dye (3a). Dye (5c) gave maximum absorption wavelength at 480 nm in distilled water and is hysochromic by 25 nm when compared with (3c). Dye (5e) gave maximum absorption wavelength at 515 nm and is more bathochromic by 15 nm when compared with dye (3e). Similarly, dye (6) gave λmax at 570 nm and is the most bathochromic of all the dyes which is blue in colour and bathochromic shift of 40 nm compared with dye (4). This is due to the effect of heterocylic character of the diazo component. All the dyes gave very good extinction coefficients and the mono-chloro derivatives showed higher extinction coefficients.

The effects of solvents polarity on the visible absorption spectra are also shown in **Table 1**. Most of the dyes showed positive solvatochromism when the solvent was changed from ethanol to more polar solvent (water) and some showed negative solvatochromism. Solvatochriomism is due to various solute-solvent interactions in both the ground and excited states. The bathochromic shift observed on changing to a more polar solvent suggests that the dye molecule has a more polar excited state than the ground state and this will lower the energy of the transition. Thus the energy difference between the gound and the excited states is reduced leading to a bathochromc shift of the visible band. On the other hand those dyes with negative solvatochromism means that the dye molecules have more polar ground state than the excited state and this will increase the energy different between the ground and the excited states, thus leading to hypochromic shift in the visible absorption region of the spectrum.

Table 1: Physical Characteristics of the Dyes

Dye No	M.Wt (mol/gm)	M.Pt (^{o}C)	Yield (%)	λ_{max}/nm in Ethanol	λ_{max}/nm in water	Extinction coefficient 10 x lmol^{-1}cm^{-1}
(3a)	594	234	39	400	505	1.48
(3b)	629	240	62	505	505	1.60
(3c)	639	238	68	420	505	1.58
(3d)	638	204	88	525	505	1.61
(3e)	503	219	69	510	505	1.23
(4)	719	215	16	455	530	9.94
(5a)	776	206	28	510	510	6.74
(5b)	813	198	62	505	500	5.12
(5c)	823	214	97	400	480	5.74
(5d)	820	209	42	500	505	8.52
(5e)	685	219	30	550	515	4.73
(6)	901	234	11	450	570	9.64

3.3 Infrared Spectra of the Dyes

The infrared spectra showed absorption peaks due to different functional groups that are predominant in the dyes. Dye (3a) showed NH peak at 1606 cm^{-1}, OH peak at 3433 cm^{-1}, SO_3Na peak at 1040 cm^{-1}and C-Cl peak at 653 cm^{-1}. Dye (3b) showed NH peak at 1615 cm^{-1}, OH at 3401 cm^{-1}, SO_3Na at 819 cm^{-1} and C-Cl at 647 cm^{-1}.Dye (3c) showed NH peak at 1514 cm^{-1}, OH at 3343 cm^{-1}, SO_3Na at 843 cm^{-1}, NO_2 at 1327 and C-Cl at 651 cm^{-1}.Dye (3d) showed NH peak at 1604 cm^{-1}, OH at 3421 cm^{-1}, SO_3Na at 784 cm^{-1}, COOH at 1228 and C-Cl at 644 cm^{-1}. Dye (3e) showed NH peak at 1540 cm^{-1}, OH at 3408 cm^{-1}, SO_3Na at 815 cm^{-1}, CH_3 at 1215 and C-Cl at 658 cm^{-1}.Dye (4) showed NH peak at 1526 cm^{-1}, OH at 3362 cm^{-1}, SO_3Na at 862 cm^{-1}, C-Cl at 767 cm^{-1} and C-F at 1317 cm^{-1}. Dye (5a) showed NH peak at 1626 cm^{-1}, OH at 3283 cm^{-1}, SO_3Na at 761 cm^{-1}, C-Cl at 658 cm^{-1} and C-F at 1317 cm^{-1}. Dye (5b) showed NH peak at 1628 cm^{-1}, OH at 3386 cm^{-1}, SO_3Na at 816 cm^{-1}, C-Cl at 653 cm^{-1} and C-F at 1321 cm^{-1}. Dye (5c) showed NH peak at 1515 cm^{-1}, OH at 3339 cm^{-1}, SO_3Na at 884 cm^{-1}, NO_2 at 1322 cm^{-1}, C-Cl at 651 cm^{-1} and C-F at 1213 cm^{-1}.Dye (5d) showed NH peak at 1612 cm^{-1}, OH at 3411 cm^{-1}, SO_3Na at 832 cm^{-1}, C-Cl at 762 cm^{-1}, C-F at 1157 cm^{-1} and COOH at 1432 cm^{-1}. Dye (5e) showed NH peak at 1540 cm^{-1}, OH at 3433 cm^{-1}, SO_3Na at 1038 cm^{-1}, C-Cl at 660 cm^{-1}, C-F at 1324 cm^{-1} and CH_3 at 812 cm^{-1}. Dye (6) showed NH peak at 1555 cm^{-1}, OH at 3362 cm^{-1}, SO_3Na at 862 cm^{-1}, C-Cl at 656 cm^{-1}, and C-F at 1342cm^{-1}.

3.4 Dye Exhaustion and Fixation of the Dyes on Cotton and Wool

The synthesized dyes were applied to cotton and wool fabrics and the dyeings showed different shades on the fabrics. The dyes showed red, purple, and blue-green on the fabrics. The percentage exhaustion and fixation on wool and cotton fabrics are shown in **Table 2**.

Table 2: Dye Exhaustion and Fixation on Wool and Cotton Fabrics.

Dye No	**Wool**		**Cotton**	
	Exhaustion (%)	Fixation (%)	Exhaustion (%)	Fixation (%)
(3a)	99	72	58	88
(3b)	99	48	58	75
(3c)	99	75	56	50
(3d)	99	60	97	91
(3e)	100	92	62	90
(5a)	95	78	52	72
(5b)	91	98	90	90
(5c)	64	98	67	90
(5e)	100	98	24	70
(6)	100	80	91	33

From the results shown in **Table 2**, dichoro reactive dyes (3a – e) gave 99 to 100% exhaustion on wool fabric and fixation ranges from 48 % to 92 %. Dye (3a) from aniline gave 99 % exhaustion and fixation of 72 %. When chlorine was introduced into para position of dye (3a) giving dye (3b), the percentage exhaustion was the same but fixation was reduced to 48 %. When the chloro group was replaced by nitro group to give dye (3c) the fixation recorded was 75 % which is better than the fixation of dye (3a) when there was no substituent. Replacement of the nitro group by the carboxylic group gave dye (3d) with the same percentage exhaustion but the fixation obtained with dye (3d) was only 60 %. Dye (3e) that was obtained when p-methylaniline was used as diazo-component gave 100 % exhaustion with fixation value of 92 % which is the best dye in this series.

When the dichloro dyes (3) were converted to monochloro derivatives, the dyes (5) also gave very good exhaustion ranging from 64 % to 100 %. For example, dye (5a) from aniline gave 95 % exhaustion and 78 %fixation on wool fabric. Dye (5b) with chloro group as substituent in the para position gave 91 % exhaustion and fixation of 98 %. Dye (5c) with carboxylic group replacing the chloro group in dye (5b) gave 64 %exhaustion and fixation of 98 % also. Dye (5e) with methyl group also gave 100 % exhaustion and percentage fixation of 98 %. Dye (6) from heterocyclic amine as diazo-component also gave 100 % exhaustion and fixation value of 80 % on wool fabric.

The percentage exhaustion of the dyes on cotton is also displayed in the **Table 2** alongside that of the wool. The exhaustion of most of the dyes on cotton is not as good as on wool substrate. For example, dye (3a) gave 58 % exhaustion on cotton compared with 72 % exhaustion of the same dye on wool. However, the percentage fixation is good in most cases but not better than the fixation on wool fabric.

3.5 Fastness Properties of the Dyes

The results of the wash and light fastness properties of the dyes are summarized in **Table 3**.

Table 3: Wash and Light Fastness Rating of the Dyes

Dye No	**Wash fastness Change in shade**		**Light fastness rating**	
	Wool	Cotton	Wool	Cotton
(3a)	5	4-5	5	5
(3b)	4-5	5	7	6
(3c)	5	4-5	5-6	5
(3d)	5	3-4	5	5
(3e)	4-5	3-4	4-5	5
(4)	4	4	4	5
(5a)	4	5	4-5	5
(5b)	4-5	5	5	5-6
(5c)	5	4-5	6	5
(6)	3-4	4	4	6

As can be seen from the results of the wash and light fastness ratings summarized in **Table 3**, all the dyes showed good to excellent wash fastness on both cotton and wool fabrics. Wash fastness rating of 1 shows poor fastness; 2, indicates fair; 3, good; 4, very good and 5, excellent. The light fastness rating is from 1-8, where 7-8 is excellent; 5-6, very good;4-5, good; 3-4, fair; 2-3, poor and 1, is very poor. There are many factors that affect colour fastness properties of dyed fabrics. Some of them are the depth of the colour, the presence of foreign substances and for the light fastness especially, the photostability of the chromophore and the chemical nature of the fibres.

IV.CONCLUSION

Dichloro-s-triazinyl reactive dyes were successfully synthesized with cyanurated H-acid and then converted to mono-chloro-s-triazinyl reactive dyes by condensation with 2-amino-4-trifluorobenzothiazole. Both the dichloro and mono chloro dyes were applied to cotton and wool fabrics. The dyes gave good to excellent exhaustion and fixation efficiency on both fabrics. The fastness properties of the dyes both to washing and light also showed good to very good ratings. The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes to the fabrics. The dyes can be recommended for commercial usage.

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